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POLYNUCLEAR SCHIFF BASE COMPLEXES OF
SOME FIRST ROW TRANSITION METAL IONS

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POLYNUCLEAR SCHIFF BASE COMPLEXES OF
SOME FIRST ROW TRANSITION METAL IONS

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.	ii
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS.	vi
SUMMARY.	vii
Chapter	
I. INTRODUCTION.	1
Review of Structural Aspects of Schiff Base Complexes	
Bidentate Ligands	
Tridentate Ligands	
Tetradentate Ligands	
Petadentate Ligands	
Hexadentate and Heptadentate Ligands	
II. EXPERIMENTAL.	23
Preparations of Complexes	
Sources of Analytical Data	
Determinations of Magnetic Moments	
Crystallographic Data	
III. RESULTS AND DISCUSSION.	78
Complexes of N-(3-hydroxypropylsalicylimine)	
Complexes of N-(2-hydroxypropylsalicylimine)	
Complexes of N-(N-methylaminopropylsalicylimine)	
Mixed Oxidation State Complexes of Salicylidene-glycine	
An Iron(III) Complex of bis{(2-phenylsalicylimine)} disulfide	
IV. CONCLUSIONS	112
LITERATURE CITED	116
VITA	122

LIST OF TABLES

Table	Page
1. Acronyms Used for Schiff Base Ligands	10
2. Analytical Data	28
3. Magnetic Data	33
4. Cell Parameters for Structures.	44
5. Final Refinement Data	45
6. Rigid Refinement Data for Toluene of Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL . .	46
7. Final Positional and Thermal Parameters for Fe(SALPA)Cl . .	47
8. Final Positional and Thermal Parameters for Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL	48
9. Final Positional and Thermal Parameters for $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$	49
10. Final Positional and Thermal Parameters for Fe(SAL ₂ DIAPS)Cl.	51
11. Observed and Calculated Structure Factors for Fe(SALPA)Cl	53
12. Observed and Calculated Structure Factors for Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL.	56
13. Observed and Calculated Structure Factors for $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$	61
14. Observed and Calculated Structure Factors for Fe(SAL ₂ DIAPS)Cl	68
15. Comparison of Bond Distances and Angles for Cu(SALPAH)Cl, Fe(SALPA)Cl, and Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL . . .	85
16. Calculated Best Least-Squares Planes and Distances of Atoms from Planes in Cu(SALPAH)Cl.	87
17. Calculated Best Least-Squares Planes and Distances of Atoms from Planes for Fe(SALPA)Cl and Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL. .	88

Table	Page
18. Bond Distances and Angles [Fe(H ₂ O) ₆][Fe(SALGLY) ₂] ₂ · 2H ₂ O	102
19. Bond Distances and Angles Fe(SAL ₂ DIAPS)Cl	109

LIST OF ILLUSTRATIONS

Figure		Page
1.	Structural Types of Polynuclear Complexes Formed by Schiff Base Ligands	7
2.	Schiff Base Ligand Types Considered	8
3.	A Perspective Drawing of the Structure of Cu(SALPAH)Cl. . .	82
4.	A Perspective Drawing of the Structure of Fe(SALPA)Cl . . .	84
5.	Plot of μ_{eff} vs. temperature for Fe(SALPA)Cl.	91
6.	A Perspective Drawing of the Structure of $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$	100
7.	A Perspective Drawing of the Packing in $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$	101
8.	Schematic Drawings of Ligand SAL_2DIAPS and Idealized Octahedron of Complex $\text{Fe}(\text{SAL}_2\text{DIAPS})\text{Cl}$	107
9.	A Perspective Drawing of the Structure of $\text{Fe}(\text{SAL}_2\text{DIAPS})\text{Cl}$	108

SUMMARY

The purpose of this research project was to synthesize and study the structural and magnetic properties of new examples of polynuclear Schiff base complexes of first row transition metal ions with special attention being given to obtaining complexes which exhibit exchange coupling and serve as model systems for biologically important molecules.

New polynuclear complexes of some first row transition metal ions have been prepared using tridentate Schiff base ligands; the physical properties, the magnetic behavior, and the crystal structures of four iron compounds have been determined. A correlation between the structural features and the magnetic properties of these complexes and comparisons to structurally similar complexes have been made.

The preparations of several transition metal ion complexes with the Schiff base ligand SALPAH_2 (formed by the condensation by salicylaldehyde and 3-aminopropanol) are reported. Structures of the crystals of $\text{Cu}(\text{SALPAH})\text{Cl}$, $\text{Fe}(\text{SALPA})\text{Cl}$, and $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$ were determined by X-ray diffraction; the structure of the latter crystal was determined since only very small crystals of $\text{Fe}(\text{SALPA})\text{Cl}$ could be obtained and, as a result, an incomplete data set was initially collected. The structure of the dimeric complex $\text{Cu}(\text{SALPAH})\text{Cl}$ was determined by a co-worker and the structural features of this complex were compared to those of the dimeric complex in $\text{Fe}(\text{SALPAH})\text{Cl}$ and $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$. The metal ions in both the iron and copper complexes were found to be five-coordinate,

but the stereochemistry of the metal ion in the copper complex is a distorted trigonal bipyramid, whereas in the iron complex the metal ion is square pyramidal with the iron displaced from the base of the pyramid. In $\text{Cu}(\text{SALPAH})\text{Cl}$, the dimer was found to be bridged by the phenolic oxygen of the monoanion ligand, whereas the alcohol oxygen of the dianion ligand acts as the bridging group in $\text{Fe}(\text{SALPA})\text{Cl}$. In both $\text{Cu}(\text{SALPAH})\text{Cl}$ and $\text{Fe}(\text{SALPA})\text{Cl}$ the bridging oxygens are planar and three-coordinate and both complexes have subnormal magnetic moments. Based on these findings, the most effective mechanism for magnetic exchange appears to be a π -type interaction involving the oxygen $p\pi$ orbitals of the bridging group and the $d\pi$ orbitals of the metal ion.

Using the ligand SALGLY (formed by the condensation of salicylaldehyde and glycine), and iron compound of the formulation $[\text{Fe}(\text{H}_2\text{O})_6]$ $[\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$ was prepared. An X-ray structure determination revealed a polynuclear structure consisting of a central iron octahedrally coordinated by six waters; two additional iron ions octahedrally coordinated by two tridentate SALGLY ligands are held to the central complex by hydrogen bonds between the carboxyl oxygens and the waters of the central iron complex. Additional hydrogen bonds hold these units together such that an infinite chain is formed. The compound was found to have a magnetic moment consistent with two iron(III) ions per iron(II). Additional investigations by a co-worker revealed that the analogous manganese compound is isomorphous with the iron complex and that a compound of the same empirical formula was formed by cobalt; the structure of the cobalt compound consists of a trimeric unit rather than an infinite chain.

A unique iron(III) complex was prepared using the ligand $\text{SAL}_2\text{DIAPSH}_2$ (formed by the condensation of salicylaldehyde and 2,2-diaminodiphenyldisulfide) and the structure determined by X-ray diffraction. In $\text{Fe}(\text{SAL}_2\text{DIAPS})\text{Cl}$ the ligand is pentadentate, coordinating to the iron through both oxygens, both azomethine nitrogens, and one sulfur of the disulfide linkage. A chloride completes the octahedral coordination of the iron(III). The temperature independent magnetic moment of 5.90 B.M. is consistent with a high-spin iron(III) complex.

CHAPTER I

INTRODUCTION

Many inorganic compounds of first row transition metal ions are held together by bridging groups into units containing two or more metal ions, which are referred to as polynuclear complexes. In complexes of this type where the metal ions are paramagnetic, magnetic interactions between the metal ions often occur. If the distance between the ions is approximately equal to the sum of the covalent radii, the exchange is attributed to a direct metal-metal interaction, but if the separation is sufficiently large to preclude overlap of orbitals, a phenomenon called superexchange accounts for the interactions between metal ions. Superexchange is the interaction arising from mixing of the orbitals of the bridging group and the d orbitals of the metal ion into a molecular orbital.

In cases where orbitals are available for π bonding on both the bridging groups and the metal ions, superexchange is the interaction through a π -type molecular orbital. However, in cases such as CuO all of the outer orbitals of the bridging oxygen are tied up in σ bonding and the molecular orbital through which superexchange occurs must be a σ type (1). In other cases where both σ and π molecular orbitals are possible it is difficult to decide the relative importance of the σ and π pathway and additional studies are needed.

Interactions between metal ions can result in alignment of spins

in the same direction, i.e., ferromagnetic interaction, and as a result produce susceptibilities greatly in excess of those for normal paramagnetic materials. Alignment of the spins in opposite directions results in antiferromagnetic interaction and, as a result, lowers the susceptibility. In extreme cases (direct metal-metal bonding), such as $\text{Fe}_2(\text{CO})_9$ and $[\text{W}_2\text{Cl}_9]^{3-}$ antiferromagnetic interaction results in complete spin pairing between the metal ions. The factors affecting both type and magnitude of the interactions include the electron configuration of the metal ions, the metal-metal separation, the electronic structures of the anions and associated ligands, and the stereochemistry of the bridging group (2).

Exchange coupling in polynuclear complexes is of particular interest due to the importance of exchange interactions in the theories of chemical bonding and in magnetic materials research (3). In many polynuclear complexes, both intermolecular and intramolecular interactions occur and as a result a theoretical treatment of the magnetic interactions would be difficult. However, in polynuclear complexes containing organic chelates the metal ions are effectively shielded from interactions with other polynuclear units and a theoretical treatment of the exchange phenomenon is possible. Although progress has been made in understanding the relationship between the structure and the magnetic properties, relatively few systems have been adequately treated and further progress is predominately dependent upon the availability of different types of polynuclear complexes with known structures for detailed magnetic studies.

One type of organic chelate that has been found effective in insulating polynuclear complexes is the Schiff base type of ligand. These compounds, which can be made by reacting aldehydes or ketones with primary amines, contain the azomethine group, $>C=N-R$, and can coordinate to metal ions through the electron pair on the nitrogen. However, an additional coordination site (such as a second donor group or an acidic group like an $-OH$) is normally required for the formation of stable transition metal ion complexes. It has been found that Schiff base ligands form a wide variety of polynuclear complexes. Salicylaldehyde complexes (formed from salicylaldehyde and various primary amines) are probably the most thoroughly investigated of the Schiff base complexes.

In addition to the importance polynuclear complexes have in the study of magnetic exchange, they potentially are model systems for the structural features, bio-chemical properties, and the magnetic properties of biologically important molecules which are also polynuclear complexes of transition metal ions. The ferredoxin proteins and several of the copper proteins are examples of this type of complex. Due to the very high molecular weights of the copper proteins no structural studies have been done and model systems would be useful. The ligands in many of these complexes are Schiff bases of pyridoxal. Although an X-ray study of one of the smaller molecules of the ferredoxin proteins (molecular weight $\sim 60,000$) has shown that the basic unit in the system consists of two iron-sulfur cubane units held in the organic framework (4), model systems are still needed for investigations of the functions

of these complexes.

The purpose of this research project was to synthesize and study the structural and magnetic properties of new examples of polynuclear Schiff base complexes of first row transition metal ions with special attention being given to obtaining complexes which exhibit exchange coupling and serve as model systems for biologically important molecules.

Schiff base complexes of iron received the most attention, but complexes of other metal ions were investigated and reported. This thesis reports the preparation of 13 compounds and the X-ray structure determinations for four iron complexes. For one of the copper complexes prepared early in this study, a structure determination has been carried out by co-worker Kelley (5) and a comparison of that structure to the structure determinations performed in this work is included.

This thesis will report on the preparation, structural features, and magnetic properties of these new polynuclear Schiff base complexes. A survey of Schiff base complexes will be given with the specific categorization being the degree of chelation provided by the ligand. The discussion of properties and structural features will include complexes formed from bidentate through heptadentate ligands. The approach in the experimental section of this thesis will be to present the preparations, structures, and magnetic properties separately; this approach is employed with hopes that the features and properties of the complex studied will be more easily compared and that, as a result, the final conclusions will be more evident.

Review of Structural Aspects of Schiff Base Complexes

Because of the vast number of Schiff base complexes synthesized and characterized, the following discussion will be organized in terms of the number of donor groups provided by the ligand and will include bidentates through heptadentate ligands. The major emphasis will be on polynuclear structures, but some references will be made to mononuclear complexes wherever is deemed appropriate. No attempt will be made to review the vast number of papers on preparative work in the area. Several reviews on Schiff base complexes have been published within the past ten years (6,7).

There are three preparative procedures employed in making Schiff base complexes (5).

1. Reaction of a metal ion and a Schiff base in the presence of added base. Normally these reactions are carried out in an alcohol or aqueous-alcohol solution using a base such as acetate or hydroxide.

2. Reaction of primary amines with bis- or tris-(salicylaldehyde) metal ion complex. This procedure was discovered by Schiff and is probably the most important preparative method.

3. Template reactions. Complexes are synthesized by reacting a preformed metal-ammine complex with salicylaldehyde in the presence of pyridine. In the reaction, the metal-ammine complex serves as the template.

Of all Schiff base complexes, those derived from salicylaldehyde have been the most thoroughly investigated. As a result of the ease of synthesis, the preparation of a wide variety of complexes with first row

transition metal ions has been accomplished. The properties of these complexes are often very dependent upon the detailed ligand structure. Tridentate Schiff base ligands differing only by a single methylene group can produce very different stereochemistries with the same metal ion under the same conditions. Thus, a variety of stereochemistries and magnetic properties are possible by varying chain size and type of Schiff base ligand.

Transition metal ion complexes derived from Schiff bases have been known since 1840 when Ettling isolated a dark green crystalline product from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia. This product was almost certainly the bis (salicylaldimino) copper(II) complex (Figure 2, Ligand type I, R=H). In the late 1860's the substituted phenyl and aryl derivatives were isolated by Schiff who established the 1:2 metal-ligand stoichiometry. Additional work performed by Schiff and later by Delépine demonstrated the 1:2 metal-ligand stoichiometry of the complexes which they had prepared. In 1889 Combes isolated the first copper complex of a β -ketoamine Schiff base. There were no studies for a number of years, then Pfeiffer and co-workers became interested in this type of complex. They studied problems of synthesis, metal-exchange, ligand replacement, transamination, stereochemistry, and esterification, utilizing in particular salicylaldimine derivatives of copper(II). These studies provided the basic understanding for much of the presently known chemistry of Schiff base complexes and as a result numerous investigations have followed (6).

Schiff base complexes in general form a wide variety of

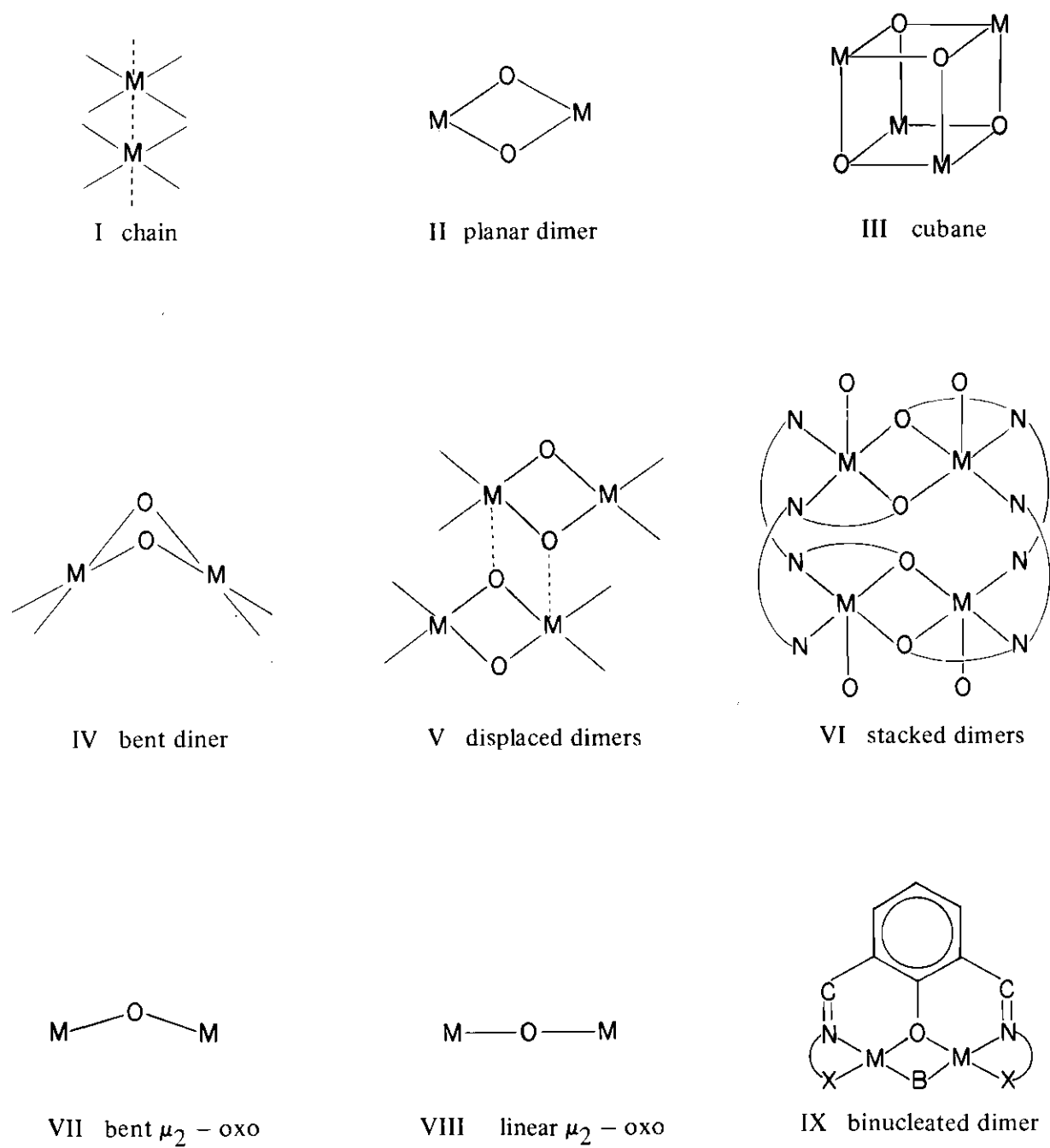


Figure 1. Structural Types of Polynuclear Complexes formed by Schiff Base Ligands

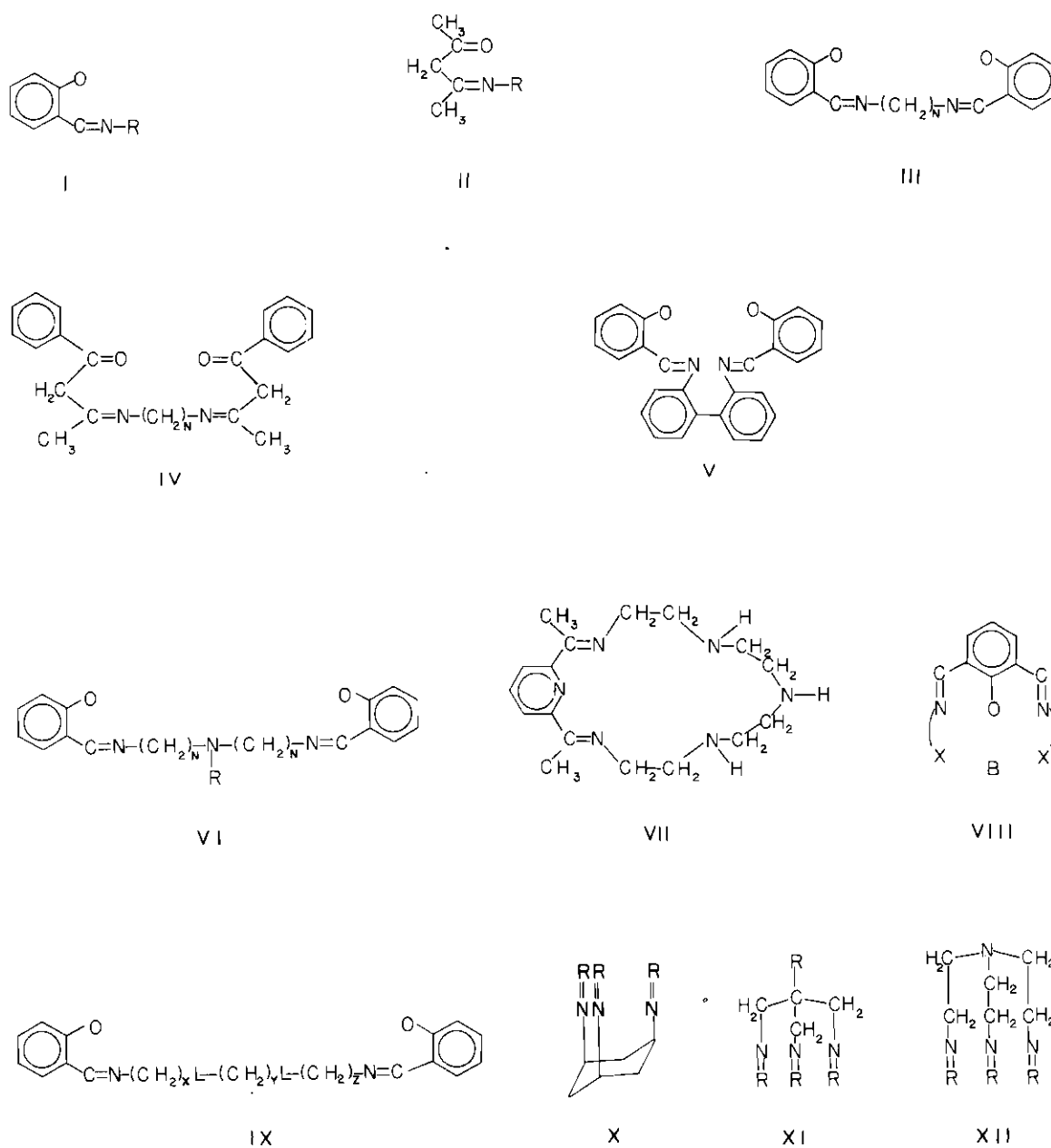


Figure 2. Schiff Base Ligand Types Considered

polynuclear complexes which are structurally represented on page 7.

A general schematic representation for each ligand type considered in the discussion of bidentates through heptadentates ligands and a table of ligand acronyms used throughout the remainder of the thesis are also given.

Bidentate Ligands

For bidentate Schiff base ligands (Ligand type I, R=non-coordinating group) structure determinations indicate that coordination occurs in the normal geometry for a given metal ion; that is, planar for nickel(II), copper(II), palladium(II); tetrahedral for cobalt(II) and zinc(II) (8). The planar complexes of salicylaldimines appear to have a transconfiguration in all cases. However, the stereochemical effect of the R group is such that increasing the bulk of the group may cause marked changes in the structures of many complexes. This effect is readily observed in the bis complexes of ligand I (Figure 2) with nickel(II); if R=CH₃, Ni(SALMA)₂ (β-form), the azomethine carbon is displaced from the plane of the chelate ring. The coordination of the metal ion is square planar and the complex is diamagnetic. Increasing the bulk of the R group to R= i-propyl results in planar chelate rings, but the rings make an angle of 82° with respect to each other. Hence, in Ni(SALIPA)₂ the coordination of the metal ion is approximately tetrahedral and the complex is paramagnetic. There are still certain ambiguities concerning the distortion of the chelate rings even though the major factor is the steric interaction of the R group attached to the nitrogen with the group adjacent to the phenolic oxygen of the other

Table 1. Acronyms Used for Schiff Base Ligands

Acronym	Form	Made From
SALMA	Monoanion	Salicylaldehyde and methylamine
SALIPA	Monoanion	Salicylaldehyde and i-propylamine
SALGLY	Dianion	Salicylaldehyde and glycine
SALETAH	Monoanion	Salicylaldehyde and 2-aminoethanol (alcohol proton present)
EIA	Dianion	2,4-pentanedione and 2-aminoethanol
PIA	Dianion	2,4-pentanedione and 3-aminopropanol
AIA	Dianion	2,4-pentanedione and anil
SALPYA	Monoanion	Salicylaldehyde and 2-aminopropanol
SAL ₂ EN	Dianion	Salicylaldehyde and ethylenediamine
BZAC ₂ EN	Dianion	Benzoylacetone and ethylenediamine
SAL ₂ BIPA	Dianion	Salicylaldehyde and 2,2'-diamino-biphenyl
SAL ₂ DPT	Dianion	Salicylaldehyde and dipropylenetriamine
SAL ₂ MeDPT	Dianion	Salicylaldehyde and methyldipropylenetriamine
FSALDTS	Trianion	3-formylsalicylaldehyde and thiosemicarbazide
PY ₃ TAE	Neutral	Pyridine-2-carboxaldehyde and 1,1,1,-tris (aminomethyl)ethane
PY ₃ TACH	Neutral	Pyridine-2-carboxaldehyde and 1 ϵ ,3 ϵ ,5 ϵ tri- aminocyclohexane
PY ₃ TREN	Neutral	Pyridine-2-carboxaldehyde and triethylene- tetraamine
SALPAH	Monoanion	Salicylaldehyde and 3-aminopropanol (alcohol proton present)
SALPA	Dianion	Salicylaldehyde and 3-aminopropanol
SAL ₂ DIAPS	Dianion	Salicylaldehyde and 2,2'-diamino-diphenyldisulfide
SALETA	Dianion	Salicylaldehyde and 2-aminoethanol
SALPDA	Monoanion	Salicylaldehyde and N-methyl-1,3-propanediamine

chelate (9).

One of the most interesting bidentate Schiff base compounds is $\text{Cu}(\text{SALMA})_2$ (Figure 2, Ligand type I, $\text{R}=\text{CH}_3$). There are three crystalline modifications of this compound. The α -form contains molecules in a planar configuration, but packed together such that a chain of copper ions 3.33 \AA apart is formed (10) (Figure 1, Structure type I). The β -form is isomorphous with the β -form of $\text{Ni}(\text{SALMA})_2$, i.e., square planar coordination of the metal ion (11). The γ -form contains dimeric units of the complex $[\text{Cu}(\text{SALMA})_2]_2$, in which the copper ion from one molecule bonds to one of the oxygens on the chelate of the other copper ion (Figure 1, Structure type II). As a result, each metal ion is five-coordinate and has a distorted square-pyramidal arrangement with the metal out of the base approximately 0.1 \AA (12).

Additional divalent transition metal ions form complexes with the ligand SALMA. An X-ray structure determination of the complex $\text{Zn}(\text{SALMA})_2$ revealed a dimeric complex (Figure 1, Structure type II) in which the zinc ions are five-coordinate and trigonal bipyramidal. In addition, it was found that cobalt(II) and manganese(II) form complexes which are isomorphous and isostructural with $\text{Zn}(\text{SALMA})_2$ (13).

Tridentate Ligands

Much of the early interest in tridentate Schiff base ligands was due to the fact that several tridentate Schiff base ligands formed copper(II) complexes which had reduced magnetic moments. Investigation of the nature of tridentate Schiff base complexes revealed a variety of coordination numbers and stereochemistries for mononuclear complexes and

polynuclear complexes held together by a variety of bridging groups. However, in all cases those complexes having subnormal magnetic moments have a polynuclear structure.

One of the most common features of polynuclear Schiff base complexes is the formation of a four-membered ring consisting of the metal ions and the bridging atoms. As shown by the drawings of Figure 1 on page 7, a variety of stereochemistries is possible for the metal ion in polynuclear Schiff base complexes. However, the majority of the complexes possess a four-membered ring consisting of the metal ions and the bridging atoms.

Numerous X-ray structure determinations have been performed for mononuclear complexes with tridentate ligands as well as for polynuclear complexes. Among those determinations relevant to the research performed are the SALGLY copper(II) complexes (Figure 2, Ligand type I, $R = -CH_2-CO_2^-$) both as the hemihydrate and the tetrahydrate. The basic environment of the copper(II) ion is square pyramidal in both cases with four short and one long coordination bond. The complex of the tetrahydrate is held in a three-dimensional network by nine hydrogen bonds (14); whereas, the hemi-hydrate has a coordinate bond (2.33 \AA) between the copper ion and an oxygen from the carboxyl group of the adjacent molecule as well as hydrogen bonding (15).

It has been found that not all the coordination sites of potentially tridentate ligands are bonded to the metal ion in certain complexes. For instance, the complex $Cu(SALETAH)_2$ (Figure 2, Ligand type I, $R = -CH_2-CH_2-OH$) has square planar coordination of the copper by

trans ligands. Both the phenolic oxygens and the azomethine nitrogens are bonded to the copper ion, but the alcohol oxygens are not. However, the alcohol oxygens form hydrogen bonds with the alcohol oxygens of adjacent molecules with contacts of 2.65 \AA and 2.70 \AA . Thus, the structure consists of two-dimensional sheets of hydrogen bonded molecules (16).

The tridentate Schiff base ligands EIA and PIA (Figure 2, Ligand type II, $R = -\text{CH}_2-\text{CH}_2-\text{O}^-$ and $R = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}^-$, respectively) give different types of polynuclear complexes with copper(II). Cu(EIA) is a tetrameric complex which has a "cubane" structure (Figure 1, Structure type III). The "cubane" unit consists of bipyramidal copper ions held in a distorted tetrahedral arrangement with oxygen atoms above each face of the tetrahedron. In general, the unit can be thought of as two dimers held together by copper-oxygen bonds. The metal-metal distance between "dimers" is 3.26 \AA , whereas the metal-metal distance within the "dimer" is 3.01 \AA . The normal magnetic moment is attributed to the lack of available low energy orbitals for π -type superexchange, since all of the outer orbitals of the oxygens are involved in σ bonding (17).

In contrast to Cu(EIA) , Cu(PIA) is a planar dimeric complex with a subnormal magnetic moment (Figure 1, Structure type II). The coordination of the copper ions is square planar and bridging occurs through the alcohol oxygens of the PIA ligand. Overall, the entire complex is planar within 0.03 \AA . Here the copper-copper distance was found to be 3.03 \AA . The subnormal magnetic moment of 0.41 B.M. is consistent with

superexchange through a π bonding scheme since there are low energy orbitals available on the bridging oxygens (17).

Nickel(II) forms a unique "bent dimer" with EIA (Figure 1, Structure type IV). Here the M_2O_2 four-membered ring is still present, but the dihedral angle between the two O-Ni-O planes of the ring is 39° . The coordination around each nickel is planar with the greatest distance of any atom from their least squares plane being 0.01 \AA (18).

Displaced dimers are formed by the tridentate Schiff base ligand AIA (Figure 2, Ligand type II, $R = C_6H_4O^-$) with copper(II) (Figure 1, Structure type V). The structure of $Cu(AIA)$ consists of two copper ions of the asymmetric unit bridged by the phenolic oxygens of the AIA ligand, with a copper-copper distance of 2.99 \AA . Association between the dimers takes place through a weak bond between the copper ion of one molecule and the oxygen atom of the other (Cu—O distance of 2.64 \AA). The geometry of one copper ion is a distorted square pyramid, whereas the other copper ions have square-planar coordination. A subnormal magnetic moment of 1.3 B.M. was found (19).

An additional type of structure based on dimeric units is formed by copper(II) and N-2-pyridylsalicylaldehyde (Figure 2, Ligand type I, $R = C_5N_2H_4$), (hereafter SALPYA). Although magnetic studies had previously indicated a trimeric structure, an X-ray structure determination revealed that the polynuclear species was $[Cu(SALPYA)(H_2O)]_4(NO_3)_4$, a "stacked dimer" (Figure 1, Structure type VI). As is shown schematically on page 7 the SALPYA ligands coordinate to three different copper ions; the phenolic oxygens act as bridges between the copper ions forming

two dimeric units and the nitrogen of the pyridines link the two dimeric units together. As a result of coordinated waters, the copper ions are five-coordinate and have a distorted square pyramidal arrangement. The nitrate ions are not coordinated and are disordered between two sites in the lattice. This tetranuclear unit is unique in that the dimers are held together by the ligand rather than the bridging atoms being shared by three metal ions as in the cubane type unit. The copper-copper distances within the dimers are 3.07 \AA , whereas the copper-copper distances between ions in different dimers is 3.17 \AA . Magnetic susceptibility measurements indicate an antiferromagnetic coupling between the pairs of oxygen bridged copper ions, but little or no interaction between the dimers (20).

Tetradentate Ligands

The majority of tetradentate Schiff base ligands are formed by reacting salicylaldehyde or acetylacetone with diamines (Ligand type III). When the carbon chain linking the nitrogen atoms is short ($n = 2$ to 4) the ligands appear to be restricted to coordinate in a planar cis fashion for the majority of complexes. However, other effects can cause variations from coplanarity (21).

One of the most extensively investigated tetradentate Schiff base complexes is $\text{Co}(\text{SAL}_2\text{EN})$ (Figure 2, Ligand type III, $n = 2$). The initial reason for interest in this compound was its ability to absorb oxygen. Although the first form investigated was found to absorb one oxygen molecule per three cobalt ions (22), an inactive form of $\text{Co}(\text{SAL}_2\text{EN})$ as well as a form that would reversibly carry one oxygen per two cobalt

ions was later prepared (23). An incomplete X-ray study of the different forms of $\text{Co}(\text{SAL}_2\text{EN})$ was performed and a model for the molecule with reasonable values for the bond angles and distances was constructed to accommodate the measured unit cell dimensions and the symmetry of the modification studied. The molecules were found to be arranged in layers so as to produce large or small holes in the active or inactive oxygen carriers, respectively.

Although decomposition occurred while the data set was being collected, sufficient data were obtained to determine the structure of the oxygen-carrying cobalt complex $\text{Co}(\text{BZAC}_2\text{EN})(\text{Pyridine})\text{O}_2$ (Figure 2, Ligand type IV, $n = 2$). The structure of the complex consists of monomeric molecular units in which the cobalt is approximately octahedral with the four Schiff base ligand atoms and phenyl rings coplanar with the metal ion. The oxygen molecule and pyridine occupy the remaining axial positions. The angle observed for the $\text{Co}-\text{O}-\text{O}$ (oxygen molecule) is 126° , which is in agreement with that predicted by Pauling and differs from the sideways coordination postulated by Griffith. The oxygen-oxygen distance of 1.26 \AA is comparable with the superoxide ion value (1.28 \AA) (24).

Although not an oxygen-carrier, $\text{Cu}(\text{SAL}_2\text{EN})$ is unique in that the complex is dimeric. The five-coordinate copper results from intermolecular bonding to the oxygen in an adjacent molecule (Figure 1, Structure type II). The ethylene bridge is twisted into a "gauche" configuration while the benzene rings and chelate rings slope slightly away from the copper atoms such that the separation of the chelate rings

is 4.0 \AA at the extremities, but the Cu—Cu distance is 3.18 \AA . No significant magnetic interaction between the metal ions occurs down to 83°K , presumably due to the long Cu—O bonds or the Cu—O—Cu angle (25).

The metal ions in several mononuclear complexes formed from tetradentate Schiff base ligands have the same general stereochemistry as the copper(II) in $\text{Cu}(\text{SAL}_2\text{EN})$. These complexes include NN'-ethylene-bis-(acetylacetoniminato) copper monohydrate, NN'-disalicylidene-propane-1,2-diamine copper monohydrate (26) and NN'-disalicylidene-ethylene diamine zinc(II) (27); all of which have a water molecule completing the tetragonal pyramidal configuration.

Also, iron(III) forms a number of complexes with unusual structures and magnetic properties with SAL_2EN . The complex $\text{Fe}(\text{SAL}_2\text{EN})\text{Cl}$ has been shown to possess a binuclear structure in the solid state in which each iron(III) achieves six-coordination by intermolecular metal-oxygen bonding similar to $\text{Cu}(\text{SAL}_2\text{EN})$ (Figure 1, Structure type II). The Fe—O "in plane" length is 1.98 \AA , while the bridging length is greater (2.18 \AA). The complex showed a slightly reduced high-spin moment (5.36 B.M. at 300°K), which was suggested as being due to super-exchange via the Fe—O—Fe grouping (28). A five-coordinate monomer was also produced by crystallizing the complex from nitromethane. However, the nitromethane was retained in the crystal lattice as solvent of crystallization. The moment of the monomeric form was found to be 5.9 B.M. as opposed to the subnormal moment of the dimeric form.

The oxo-bridged dimer $[\text{Fe}(\text{SAL}_2\text{EN})]_2\text{O}$ has an abnormally low

magnetic moment of 1.87 B.M., which is temperature dependent. The structure of $[\text{Fe}(\text{SAL}_2\text{EN})_2\text{O} \cdot 2 \text{ Pyridine}]$ was found to consist of a five-coordinate iron dimer with an oxo-bridge (Figure 1, Structure type VII). The Fe—O—Fe angle was found to be 139° , and the Fe—Fe distance was 3.36 \AA . The pyridines are not bonded to the iron ions, but exist as solvent of crystallization. The configuration of the ligand is very similar to that of the monomeric $\text{Fe}(\text{SAL}_2\text{EN})\text{Cl}$ (29).

In general with tetradentate Schiff base ligands (Figure 2, Ligand type III) increasing the length of the methylene chain may cause a change in the stereochemistry of the complex from a cis-planar coordination by the ligand to tetrahedral coordination. Weigold has prepared cobalt salicylaldehyde complexes with methylene chains up to ten units in length and has obtained magnetic moments consistent with tetrahedral cobalt for the complexes with ligands having methylene chains of C_7 to C_{10} (21).

An interesting example of the effect of the steric bulk of a tetradentate ligand on the stereochemistry of a metal ion is found in $\text{Cu}(\text{SAL}_2\text{BIPA})$ (Figure 2, Ligand type V). The complex was predicted to be tetrahedral due to the steric requirements of the bulky ligand. However, the stereochemistry of the copper is almost square planar with a dihedral angle of 39° between the planes defined by CuON and $\text{CuO}'\text{N}'$. This is in contrast to the 90° angle expected for a tetrahedral arrangement and has been achieved by twisting the ligand framework, including the bond joining the phenyl rings (30).

Pentadentate Ligands

Pentadentate ligands in general have not been thoroughly studied. Attachment to a metal ion by a pentadentate ligand in which the donor atoms are members of a continuous chain of atoms can lead to a variety of stereochemical arrangements, but the ligand framework must be sufficiently flexible to allow all of the donor atoms to bond to the metal ion if the ligand is to act as a pentadentate.

The pentadentate Schiff base ligand SAL₂DPT (Figure 2, Ligand type VI, R = H, n = 3) has given complexes with manganese, cobalt, nickel, copper, and zinc. Molecular weight studies indicated that the complexes are monomeric and X-ray powder photographs indicate the complexes are isomorphous. In addition, all the complexes except zinc have high spin magnetic moments and the spectrum of the nickel complex was similar to that of a known five-coordinate nickel complex (31).

A three-dimensional X-ray analysis of Ni(SALMeDPT) (Figure 2, Ligand type VI, R = CH₃, n = 3) revealed a monomeric solid-state structure in which the nickel ion was coordinated by the three nitrogens and the two oxygens. The structure is a distorted trigonal bipyramid with two oxygens and one nitrogen in the equatorial plane and two nitrogens in the axial position (32).

The macrocyclic ligand, 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo [12.3.1]-octadeca-1(18),2,12,14,16 pentaene, (ML) (Figure 2, Ligand type VII), yields a dimeric complex with iron(III). The X-ray structure of the dimer [(H₂O)MLFe]₂O (ClO₄)₄ revealed an approximately pentagonal bipyramidal configuration about the iron ion with one shortened axial

distance. A water molecule occupies the outer axial positions, and the dimer is composed of two $\text{FeML}(\text{H}_2\text{O})$ (Figure 1, Structure type VIII) units linked by a linear oxo bridge with an iron-oxygen distance of 1.8 \AA (33).

A recent X-ray structure determination has shown that the binucleating, pentadentate ligand FSALDTS (Figure 2, Ligand type VIII, $\text{B} = -\text{OC}_2\text{H}_5$, $\text{X} = -\text{N}=\text{C} \begin{smallmatrix} \text{S}^- \\ \text{NH}_2 \end{smallmatrix}$) yields a dimeric complex with nickel(II) (Figure 1, Structure type IX). In $\text{Ni}(\text{SALDTS})(\text{OC}_2\text{H}_5)$ the Ni-Ni distance of 2.38 \AA is significantly shorter than the sum of the Van der Waals radii ($\sim 2.8 \text{ \AA}$) (34). In addition, copper(II) complexes with this type of ligand are known to have subnormal magnetic moments and the available information indicates a binuclear structure similar to the nickel complex (35).

Hexadentate and Heptadentate Ligands

Considerable preparative work and resolution of the resulting complexes of different isomers of hexadentate Schiff base ligands has been done. The structural designs of hexadentate ligands has been considered on a general basis by Lions (36), who recognized that there were at least 36 possible structural patterns for hexadentate ligands. The most common type of linear hexadentate ligand is represented by Ligand type IX (Figure 2). Complexes of cobalt(III) where $\text{L} = \text{S}$ and $x=y=z=2$ have been prepared and resolved. In addition, complexes of the related ligand with $\text{L} = \text{NH}$ and $x=y=z=2$ have been prepared and complexes of cobalt(III), iron(III), and aluminum(III) resolved (37,38).

In addition to complexes of linear hexadentate ligands, several

complexes of branched hexadentate ligands have been prepared and studied. Of the more common are Ligand type X (Figure 2, R = salicylidene, $C_7H_4O^-$) and Ligand type XI (Figure 2, $R' = H$, R = salicylidene, $C_7H_4O^-$). These ligands have been shown to form inner complexes with iron(III) and cobalt(III) (39,40) and are presumed to be octahedral complexes with the chelate rings disposed in either a right- or left-handed spiral. Thus, the result must be a cis isomer.

X-ray studies of the complexes formed by the ligand PY_3TAE (Figure 2, Ligand type XI, $R' = -CH_3$, $R = -C_6H_5N$) have revealed considerable difference in the amount of twist between the respective trigonal faces. The complex $Zn(PY_3TAE)$ has a geometry approximately midway between trigonal prismatic and octahedral (twist angle = 28°). The zinc, nickel, cobalt, and manganese complexes crystallize in the same space group and are isomorphous and, therefore probably isostructural (41).

However, trigonal prismatic coordination with only slight distortion can be achieved by using the ligand PY_3TACH (Figure 2, Ligand type X, $R = -C_6H_5N$). The complex $Zn(PY_3TACH)$ has an average twist of the trigonal faces of only 4° . Presumably the added rigidity of the cyclohexane backbone is responsible for the trigonal-prismatic arrangement (42).

In general, heptadentate Schiff base ligands are rather uncommon. Several workers have reported preparation of what could be complexes formed from heptadentate Schiff base ligands (43,44). Most of the complexes were prepared from the ligands SAL_3TREN (Figure 2, Ligand type

XII, $R = C_7H_4O^-$) or PY_3TREN (Figure 2, Ligand type XII, $R = -C_6H_5N$). An X-ray structure determination of $Ni(PY_3TREN)$ revealed a structure that can be described as a capped octahedron. The three imine nitrogen atoms and the three pyridine nitrogen atoms are disposed approximately at the apices of an octahedron with metal-nitrogen distances of 2.10 \AA . This distance is close to that predicted by Pauling's covalent radii and very similar to nickel-nitrogen distances found for related complexes. The unique tertiary amine nitrogen is at a significantly greater distance from the nickel, 3.25 \AA . This, at very best, is a very weak nickel-nitrogen interaction (44). Hence, a clear-cut case of a heptadentate Schiff base complex remains unknown.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes

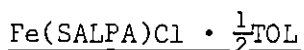
All the Schiff base ligands employed except SALGLYH₂ and SALDIAPSH₂ were prepared by mixing salicylaldehyde with the respective amine; in the preparations of SALGLY and SAL₂DIAPS the preparative method for the ligand is included with the preparation of the complex. The analytical data for all of the complexes prepared are given in Table 2 on page 28.

Cu(SALPAH)Cl

A methanol solution (100 ml) of SALPAH₂ (0.1 mole) was added to a methanol solution (150 ml) of anhydrous copper chloride (0.05 mole); the resulting solution was stirred and heated to reflux. Filtering the hot solution yielded a brown crystalline product which was dried in vacuo.

Fe(SALPA)Cl

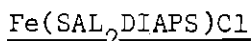
To the ligand SALPAH₂ (0.01 mole) was added a methanol solution (100 ml) of lithium methoxide (0.02 mole); the resulting solution of the dianion of the ligand was added dropwise to a stirred methanol solution of FeCl₃ · 6H₂O (0.01 mole). Upon heating the solution to reflux, a dark brown crystalline product precipitated and was filtered off. The product, Fe(SALPA)Cl, was recrystallized from tetrahydrofuran prior to further study.



In an attempt to find a solvent from which $\text{Fe}(\text{SALPA})\text{Cl}$ would crystallize as larger crystals suitable for single crystal X-ray diffraction studies, toluene was employed as a solvent. The complex was dissolved in hot toluene and the solution filtered. On standing, the saturated solution yielded large crystals of the complex $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$.



The initial preparation of this complex was performed following the preparative scheme given by Ray and Mukherjee (45). Glycine was added to a distilled water solution (150 ml) of ferrous sulfate; the resulting solution was heated, and an ethanol solution (50 ml) of salicylaldehyde was added. The ratios were 3:2:2 moles for glycine: salicylaldehyde:ferrous sulfate. A dark red crystalline material precipitated from the refluxing solution and was filtered off; allowing the filtrate to stand yielded additional product. After the true composition of the complex had been established by analyses, the reactants were mixed in the stoichiometric ratio, 4:4:3 moles, and the same crystalline material was obtained. The material analyzed was air-dried since it was found that by heating (100°C) under vacuum for 24 hours, approximately 7.5 waters were lost.



The ligand $\text{SAL}_2\text{DIAPSH}_2$ was made by adding a methanol solution (50 ml) of salicylaldehyde (0.02 mole) dropwise to a methanol solution (100 ml) of 2,2'-diaminodiphenyldisulfide (0.01 mole). A methanol

solution (75 ml) of lithium methoxide (0.02 mole) was added as base and the ligand solution was added dropwise to a hot methanol solution (100 ml) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mole). Filtering the hot solution yielded a black crystalline product and the filtrate gave additional crystals which were suitable for analyses and a structure determination.

$\text{LiFe}(\text{SALETA})_2$

A methanol solution (125 ml) of lithium methoxide (0.04 mole) was added to neat SALETAH_2 (0.02 mole); the resulting ligand solution was added dropwise to a stirred methanol solution (100 ml) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mole). The solution was heated to reflux and filtered while hot; dark red crystalline material formed in the filtrate, but upon exposure to air the material appeared to lose solvent. Recrystallization from ethanol yielded an air-stable red crystalline material which analyzed for $\text{LiFe}(\text{SALETA})_2$.

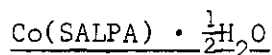
$\text{Cu}(\text{SALPDA})\text{Cl}$

A methanol solution (75 ml) of lithium methoxide (0.01 mole) was mixed with SALPDAH (0.01 mole) and the ligand solution added dropwise to a refluxing methanol solution (150 ml) of anhydrous copper chloride (0.01 mole). The solution was filtered while hot and the filtrate saved. Over a period of several weeks, green crystals formed from the filtrate. The material was filtered and allowed to air dry.

$\text{Ni}(\text{SALPDA})_2$

A methanol solution (75 ml) of lithium methoxide (0.02 mole) was mixed with SALPDA (0.02 mole); to the ligand solution a methanol solution (150 ml) of nickel chloride (0.01 mole) was added dropwise. The

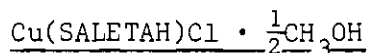
solution was heated to reflux and filtered while hot. Upon standing, the filtrate yielded reddish-brown crystals which appeared to lose solvent upon exposure to air but air-stable crystals were formed by recrystallization from m-xylene.



To SALPAH₂ (0.01 mole) was added a methanol solution (50 ml of KOH (0.02 mole)); the resulting ligand solution was added to a stirred methanol solution (125 ml) of CoAc₂ · 4H₂O and heated to reflux. The filtrate of the hot solution yielded a red crystalline product which was filtered off and air dried.



A methanol solution (75 ml) of lithium methoxide (0.02 mole) was mixed with SALETAH₂ (0.01 mole) and the ligand solution added to a stirred methanol solution (125 ml) of CoAc₂ · 4H₂O (0.01 mole). The resulting red solution was filtered while hot and yielded a red-orange precipitate; additional microcrystalline material was deposited from the filtrate.



The addition of a methanol solution (75 ml) of SALETAH₂ (0.02 mole) to a methanol solution (125 ml) of CuCl₂ (0.02 mole) immediately produced a flocculant green precipitate. The resulting slurry was stirred and allowed to stand for five minutes. Filtering yielded several grams of dark green product which was washed with methanol and dried in vacuo over H₂SO₄.

Cu(SALETA) $\cdot \frac{1}{2}$ H₂O

A methanol solution (50 ml) of KOH (0.017 moles) was mixed with SALETAH₂ (0.02 mole) and the ligand solution added to CuAc₂ \cdot H₂O (0.02 mole) partially dissolved in methanol (125 ml). Immediate precipitation of dark green material resulted, while some of the CuAc₂ \cdot H₂O remained undissolved. Methanol (125 ml) was added and stirring and heating were continued until solution was complete. After filtering the hot solution, the volume of the solvent was reduced by flash evaporation. Several grams of dark green material separated and was recrystallized from an acetone-methanol mixture and dried in vacuo over H₂SO₄.

Ni(SALETAH)Ac \cdot CH₃OH

The addition of a methanol solution (50 ml) of SALETAH₂ (0.02 mole) to NiAc₂ \cdot 4H₂O (0.02 mole) partially dissolved in methanol (125 ml) resulted in precipitation of considerable green material and undissolved NiAc₂ \cdot 4H₂O remained. Additional methanol (100 ml) was added and the mixture heated until solution was complete. Filtering the hot solution and allowing the filtrate to stand produced large green crystals.

Sources of Analytical Data

For all of the compounds given in Table 2, the C,H,N,S analyses were performed by Galbraith Laboratories, Knoxville, Tennessee or Atlantic Micro Lab, Atlanta, Georgia. All metal analyses were performed by the author.

It was found that inconsistent results from metal analyses were obtained if the organic ligands were not completely destroyed prior to

Table 2. Analytical Data

Compound	Empirical Formula	Per Cent Metal		Per Cent Carbon		Per Cent Hydrogen		Per Cent Nitrogen		Per Cent Sulfur	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Cu(SALPAH)Cl	$\text{Cu}(\text{C}_{10}\text{NO}_2\text{H}_{12})\text{Cl}$	22.92	22.93	43.33	43.13	4.36	4.40	5.05	5.04	-	-
Fe(SALPA)Cl	$\text{Fe}(\text{C}_{10}\text{NO}_2\text{H}_{11})\text{Cl}$	-	-	44.73	44.68	4.14	4.22	5.22	4.98	-	-
$\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$	$\text{Fe}(\text{C}_{10}\text{NO}_2\text{H}_{11})\text{Cl} \cdot \frac{1}{2}\text{C}_7\text{H}_8$	-	-	51.54	51.58	4.77	4.74	4.27	4.67	-	-
$[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2] \cdot 2\text{H}_2\text{O}$	$\text{Fe}_3\text{C}_{36}\text{O}_{20}\text{N}_4\text{H}_{44}$	16.42	16.63	42.39	42.26	4.31	4.40	5.49	5.32	-	-
$\text{Fe}(\text{SAL}_2\text{DIAPS})\text{Cl}$	$\text{Fe}(\text{C}_{26}\text{N}_2\text{S}_2\text{O}_2\text{H}_{18})\text{Cl}$	10.23	10.24	57.21	56.16	3.33	3.18	5.13	5.06	11.73	11.26
$\text{LiFe}(\text{SALETA})_2$	$\text{LiFe}(\text{C}_9\text{NO}_2\text{H}_{10})_2$	-	-	55.55	55.29	4.67	4.96	7.19	7.15	-	-
$\text{Cu}(\text{SALPDA})\text{Cl}$	$\text{Cu}(\text{C}_{11}\text{N}_2\text{OH}_{15})\text{Cl}$	21.89	21.61	45.51	45.69	5.21	5.38	9.65	9.86	-	-
$\text{Ni}(\text{SALPDA})_2$	$\text{Ni}(\text{C}_{11}\text{N}_2\text{OH}_{15})_2$	-	-	59.88	58.38	6.86	6.90	12.69	12.48	-	-
$\text{Co}(\text{SALPA}) \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{Co}(\text{C}_{10}\text{NO}_2\text{H}_{11}) \cdot \frac{1}{2}\text{H}_2\text{O}$	-	-	48.99	47.88	4.94	4.88	5.71	5.39	-	-
$\text{Co}(\text{SALETA})_2\text{H}$	$\text{Co}(\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4)$	-	-	55.95	56.19	4.97	4.86	7.25	7.27	-	-
$\text{Cu}(\text{SALETAH})\text{Cl} \cdot \frac{1}{2}\text{CH}_3\text{OH}$	$\text{Cu}(\text{C}_9\text{H}_{10}\text{NO}_2)\text{Cl} \cdot \frac{1}{2}\text{CH}_3\text{OH}$	22.76	22.52	40.86	41.03	4.34	4.25	5.02	5.06	-	-
$\text{Cu}(\text{SALETA}) \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{Cu}(\text{C}_9\text{NO}_2\text{H}_9) \cdot \frac{1}{2}\text{H}_2\text{O}$	26.95	26.17	45.85	45.24	4.28	4.30	5.93	5.68	-	-
$\text{Ni}(\text{SALETAH})\text{Ac} \cdot \text{CH}_3\text{OH}$	$\text{Ni}(\text{C}_{12}\text{NO}_5\text{H}_{17})$	-	-	45.91	45.91	5.46	5.46	4.46	4.47	-	-

analyzing. The initial method employed in destroying the organic material consisted of boiling the complex in concentrated H_2SO_4 with a few milliliter of H_2O for approximately 12 hours. Another method was later employed in which the samples to be analyzed were placed in porcelain crucibles and slowly heated to approximately 900°C . The samples were kept at this temperature from two to six hours. After allowing it to cool, the remaining sample material was dissolved in acid (HNO_3 for copper analyses, HCl for iron analyses) by boiling the entire crucible and lid until no sample material remained. The solution was allowed to cool; the crucible and lid were retrieved from the solution using plastic-coated tongs. The volume of the acid solution was then reduced by boiling until approximately 10 milliliters of solution remained.

After allowing the solutions to cool, the copper samples were worked up and copper determined by electrodeposition on a platinum electrode. Iron analyses were performed by a standard potentiometric titration method, using $\text{K}_2\text{Cr}_2\text{O}_7$ as titrant.

Determination of Magnetic Moments

Magnetic measurements were made either by the Gouy method or by the Faraday method. Instrumentation and procedures for the Gouy method have been described elsewhere (46). The equipment set up, calibration and mode of operation for the Faraday method were developed by the author and have been described in detail by Hightower (47).

In general if the field gradient over an element of volume, dV , of the specimen is $\frac{dH}{dl}$, then the force dF is

$$dF = (\kappa - \kappa_0) dV H \frac{dH}{dl} \quad (1)$$

where κ and κ_0 are the susceptibilities per unit volume of the sample and the displaced medium, respectively. For the guoy method the specimen is contained in a cylindrical tube of constant cross-sectional area, the lower end of which extends into the magnetic field of strength H . The tube is filled to the same height each time with finely ground sample. Thus, the volume of material is constant and experiences the same field strengths by virtue of being in the same position in the magnetic field. Integration over the entire length of the specimen from $H = H$ at the lower end of the tube to H_0 at some length l gives

$$F = \frac{(\kappa - \kappa_0)(H^2 - H_0^2)A}{2l} = \Delta w g \quad (2)$$

where A is the cross-sectional area of the sample, Δw is the apparent change in weight of the sample upon turning on the field and g is the gravitational constant. Usually κ_0 is negligible compared to κ , and if the sample extends above the pole pieces a distance greater than eight times the pole gap width, H_0 is negligible compared to H .

Thus, the volume susceptibility, κ , is given by

$$\kappa = \frac{2\Delta w g}{H^2 A} \quad (3)$$

In the Faraday method a very small sample (even one small crystal can suffice) is suspended from a sensitive balance in a very

non-homogeneous magnetic field which is designed to maintain $\frac{dH}{dl}$ constant over the entire region in which the sample is located. If κ_o is negligible, then the expression for κ becomes

$$\kappa = \frac{g\Delta w}{VH \left(\frac{dH}{dl} \right)} \quad (4)$$

The volume susceptibility, κ , is related to the gram susceptibility, χ_g , by the relationship,

$$\chi_g = \frac{\kappa}{\rho} = \frac{\kappa V}{w} \quad (5)$$

where ρ is the density and w the weight of the sample. Applying this relationship to Equations 3 and 4 yields, respectively

$$\chi_g = \frac{2gV}{H^2 A} \cdot \frac{\Delta w}{w} = C \frac{\Delta w}{w} \quad (6)$$

$$\chi_g = \frac{g}{H \left(\frac{dH}{dl} \right)} \cdot \frac{\Delta w}{w} = C' \frac{\Delta w}{w} \quad (7)$$

The values of C and C' can be evaluated by using a standard of known susceptibility. The standard used was HgCo(CNS)_4 with $\chi_g = 4981.32 \times 10^{-6} (T + 10)^{-1}$ where T is the absolute temperature.

In both methods, the relative weight of a sample was measured with and without the magnetic field and the change in weight Δw , was corrected for the diamagnetism of the sample holder. The gram

susceptibility of the sample, χ , was then calculated from Equations (6) and (7), using the value of C or C' determined from the standard.

$$\chi g_{\text{samp}} = \frac{\Delta w_{\text{samp}}}{w_{\text{samp}}} \cdot \frac{w_{\text{std}}}{\Delta w_{\text{std}}} \cdot \chi g_{\text{std}} \quad (8)$$

The molar susceptibility, χ_m , was calculated using expression (9), where M.W. is the molecular weight of the complex and the diamagnetic corrections are calculated from the atomic values given by Figgis and Lewis (48).

$$\chi_m = \chi g \times \text{M.W.} + \text{Diamagnetic Corrections} \quad (9)$$

The magnetic moments, μ_{eff} , were then calculated using the equation,

$$\mu_{\text{eff}} = 2.84(\chi_m T)^{1/2} \quad (10)$$

where T is the absolute temperature. Table 3 gives the information obtained from the magnetic studies.

Crystallographic Data

Experimental Methods

As a result of the extremely dark color of most of the crystals investigated, no information as to the orientation of the axes or singularity of the crystal could be obtained by viewing the crystals under the polarizing microscope. Hence, the choice of crystal was made by

Table 3. Magnetic Data

Compound	Method	$\chi_g \times 10^6$	$\chi_m \times 10^6$	Temp°K	Dimag Corr $\times 10^6$	μ_{eff} (B.M.)
Cu(ALPAH)Cl	Gouy	1.18	461	299	133	1.05
Fe(SALPA)Cl	Faraday	26.7	7430	299	131	4.23
$[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}^*$	Faraday	39.0**	40200**	299**	456**	9.84**
Fe(SAL ₂ DIAPS)Cl	Faraday	26.0	14400	299	278	5.90
Fe(SAL ₂ DIAPS)Cl	Faraday	40.2	22250	196	278	5.89
Cu(SALETAH)Cl $\cdot \frac{1}{2} \text{CH}_3\text{OH}$	Faraday	5.18	1590	299	143	1.96
Cu(SALPDA)Cl	Faraday	3.00	935	299	148	1.50
Co(SALETA) ₂ H	Gouy	Diamag- netic				
Co(SALPAM) $\cdot \frac{1}{2} \text{H}_2\text{O}$	Gouy	33.26	8267	296	113	4.44

* This measurement was run in the Faraday Apparatus, but the system was not evacuated since the complex lost H_2O under vacuum.

** These values are for the formula unit, which contains three iron ions, rather than per metal ion.

visual examination under the stereoscopic microscope. Normally the crystal was mounted on a thin glass fiber which had been glued into a mounting pin. In the structure determination of $[\text{Fe}(\text{SALPA})\text{Cl}]_2 \cdot \text{TOL}$, the crystal decomposed (probably due to loss of toluene of crystallization) when exposed to the atmosphere for an extended period of time. To prevent decomposition, the crystal was glued on the tip of a small Lindemann glass capillary; a slightly larger capillary was placed over the crystal and the two capillaries were sealed in a very small torch flame. The sealed section (approximately 10 mm in length) containing the crystal was then glued into the screw base mounting pin used on the goniometer head. With this arrangement, there was no noticeable decomposition during data collection.

After the crystal was mounted on the goniometer head, coarse adjustments of the arcs were made by visual examination. Exact orientation of the crystal was carried out on a Burger precession camera using unfiltered molybdenum radiation (49).

Unit cell parameters, diffraction symmetry and other data necessary to define the unit cell and determine the space group were obtained from measurements and inspection of zero and upper level photographs taken with zirconium-filtered molybdenum radiation. The densities of all the crystals were determined by the flotation method. Solutions of methylene iodide and various organic solvents in which the complexes were not soluble were employed. Table 4 on page 44 contains the cell parameters, volumes, number of formula units per unit cell and densities (calculated and observed) for all the crystals investigated.

Collection of Intensity Data Using Film Methods

After the unit cell parameters and space group information had been determined, intensity data were collected on the Burger precession camera or on the Picker Automated Diffractometer. With the camera, timed exposures of 50, 5.0 and 0.5 hours were collected for each level on Ilford Industrial G X-ray film. Three timed exposures were developed simultaneously using freshly prepared Kodak developer and fixer. Crystal misalignment was determined by the presence of doubling of spots on the photographs; any misalignment was corrected before continuing with data collection. The intensities of the reflections were estimated by visual comparison of the blackness of the spot to a standard series, both of which were illuminated simultaneously by a Kodak Illuminator.

Collection of Intensity Data Using Counter Methods

Crystals for which intensity data were to be collected on the Picker Four-Circle Automated Diffractometer were initially aligned on the precession camera. However, the crystals were further aligned on the diffractometer using published instructions (50), since the alignment is far more critical than on the precession camera. For 20 reflections (including reflections along each of the reciprocal axes), the values of ϕ , χ , ω , and 2θ (these four angles define the position of the crystal and detector) were determined by manually centering the reflection in the exit collimator. A least-squares refinement of the data using the Carter program (51) yielded refined cell parameters and from these parameters the angle settings for the remaining reflections were calculated. The take-off angle and crystal

to scintillation counter distance were 2.0° and 21 cm, respectively. Zirconium-filtered Molybdenum $K\alpha$ radiation (wave length = $.7107 \text{ \AA}$) was used for all data collection. Using the theta-two theta scan technique, reflections were scanned at a rate of 1° per minute for a total scan of 2° . Symmetry-forbidden reflections were collected to insure that the proper space group had been chosen and that conditions for these extinctions were met.

Stationary background counts of 20 seconds each were collected for the 20 settings corresponding to the beginning and end of the scan after the reflection had been scanned. Copper attenuators (which had previously been calibrated by collecting intensities on several different reflections of varying magnitudes) were used. The threshold point was set so that attenuators would be inserted when the counting rate exceeded 10,000 counts/second. The pulse height analyzer was set for approximately a 90 per cent window, centered on the molybdenum $K\alpha$ peak. Corrected intensities (CI) were obtained by the relationship

$$CI = CT - 3(bg1 + bg2)$$

where CT is the total integrated peak count for the two degree scan, while 3 is the factor of the scan time to the total background counting time. Standard deviations, σ , for the corrected intensities were assigned according to the formula (52)

$$\sigma(CI) = [CT + 0.25(tc/tb)^2(bdg1 + bdg2) + (PI)^2]^{1/2}$$

where t_c is the total scan time, t_b is the counting time of each background, and P is an "ignorance" factor introduced to keep the very strong reflections from having unreasonably high weights. The weighting scheme employed was based upon counting statistics where W_i , the weights, are derived from the following relationship

$$W_i = 4(CI)/\sigma(CI)^2$$

A standard reflection was run approximately every 50 reflections to check for decomposition, loss of alignment due to mechanical slippage of the drives, crystal movement, or changes in the electrical circuitry of the instrument. If the standard reflection's point of maximum intensity deviated significantly from the mid-point of the scan or its total integrated intensity had changed significantly, the arcs of the goniometer head were reset. It was necessary in certain cases, i.e. slippage of drives, to totally realign the crystal prior to resuming data collection.

Calculations

F. L. Carter's program for calculating diffractometer settings was run on the Burroughs 5500 computer. All other calculations were carried out on the Univac 1108 computer. Programs used included Zalkins FORDAP Fourier summation program (53), Busing, Martin and Levy's ORFLS (54), XLFS, and ORFFEE, a program for calculating Lorentz-polarization corrections by Bertrand (55), a data reduction program by Kirkwood (56), a program for calculating the best least-squares plane

for a set of atoms, and Johnson's ORTEP (57) for drawing crystal structure illustrations.

Two additional programs, RBANG and BECLS6, were adapted to the Univac 1108 for the purpose of trying a group refinement on the disordered portion of the structure $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$. RBANG is a direct rewrite (58) of the Ibers/Doedens program of the same name. The program defines a set of orthogonal axes from the crystal axes and provides input for the orientation angles phi, theta, and rho for rigid body refinements. BECLS6 (59) is a locally modified version of Ibers/Doedens program NUCLS5, which is a highly modified version of ORFLS in which least-squares refinement of individual atoms and/or rigid groups is possible.

Location of Atomic Positions and Structure Refinement of the Ordered Structures

All the structure determinations reported in this thesis were performed by the heavy atom method. The Patterson Function was used to locate the heavy atoms in the structure; once the heavy atoms were found, they served as a phasing model (from which the remaining atomic positions were located).

For the monoclinic space group, $P2_1/c$, there is 2-fold screw axis parallel to b and a c glide perpendicular to b. As was indicated in Table 4 all of the crystal structures studied crystallized in this space group. The equivalent positions for $P2_1/c$ (no. 14) are x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$. In this space group the screw and glide do

not pass through the origin, but are offset from it. In order to locate the heavy atom positions in a cell the Patterson function is employed. For the space group $P2_1/c$ the vectors between symmetry related atoms (Harker relationships) have the coordinates $\pm 2x, \pm 2y, \pm 2z$; $\mp 2x, \pm \frac{1}{2}, \pm \frac{1}{2}, \mp 2z$; and $0, \pm \frac{1}{2}, \pm 2y, \pm \frac{1}{2}$. From the larger peaks on the plane $\mp 2x, \pm \frac{1}{2}, \pm \frac{1}{2}, \mp 2z$ the x and z coordinates may be found and from the peaks on the line $0, \pm \frac{1}{2}, \pm 2y, \pm \frac{1}{2}$, the y coordinate may be obtained. Employing the peaks between centrosymmetrically related atoms, $\pm 2x, \pm 2y, \pm 2z$ the coordinates already found may be verified.

A noteworthy feature of the Patterson map for the complexes which had subnormal magnetic moments was a very strong metal-metal vector of $3.0 - 3.2 \text{ \AA}$ in length. This vector arises from the two metal ions in the four-membered M_2O_2 ring. The coordinates found by assuming that this vector corresponds to $2x, 2y, 2z$ were consistent with those atomic positions found for the heavy atoms by use of the other Harker relationships.

Once the heavy atom positions were determined, several cycles of full-matrix least-squares refinement yielded conventional R values of .3 to .4 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). A Fourier synthesis was then computed using the phases calculated for the known positions of the structures. From the resulting electron density map, additional atom positions were located. The addition of these atom positions led to an even better phasing and repetition of the sequence of least-squares refinement and difference Fourier synthesis was continued until all atomic positions were located and nothing but residual electron densities,

corresponding to a fraction of an electron, remained in the electron density maps.

Refinement of the temperature factors, atomic coordinates, and scale factor(s) was done each time additional atoms were located. In all structure factor calculations, the scattering factors for neutral atoms by Ibers (60) were employed. After most of the atomic positions were located, a weighting scheme was applied to the data collected by counter methods. Anisotropic parameters were also assigned to describe the thermal motion of the heavy atoms in the structure; the final ratio of the number of reflections to parameters varied was at least 9 to 1. Least-squares refinement was continued using the weighting scheme and anisotropic temperature factors until no significant change in parameters, R_1 (the conventional R), or the weighted R_2

$$R_2 = \left\{ \sum_i w_i (|F_o| - |F_c|)^2 / \sum_i w_i (|F_o|)^2 \right\}^{1/2}$$

were observed.

Table 5 contains the final weighted and unweighted R values, total number of parameters varied, ignorance factor (if used), and number of reflections used in the refinement. Final positional parameters, thermal parameters, and $F_o - F_c$ tables are given for each structure in Tables 11 through 14.

Location of Atomic Positions and Structure Refinement of the Disordered Structures

In an attempt to obtain larger crystals of the $\text{Fe}(\text{SALPA})\text{Cl}$ complex, the material was recrystallized from toluene. Preliminary X-ray

measurements indicated that the complex had crystallized in the same space group, but the crystals contained a molecule of toluene per dimeric unit of the complex. The first attempt to collect diffractometer data was thwarted by decomposition of the crystal, but sealing the crystal inside a Lindemann glass capillary solved that problem and diffractometer data were collected.

The heavy atom method was again employed. Positions for the heavy atoms were found from the three-dimensional Patterson. Several cycles of least-squares refinement, followed by an electron density calculation revealed the positions of all remaining non-hydrogen atoms except for the carbons of the toluene. Additional cycles of least-squares refinement followed by a Difference Fourier revealed a region of high electron density around an inversion center, $(\frac{1}{2}, \frac{1}{2}, 0)$. However, this region did not contain one set of distinct peaks corresponding to toluene carbons but consisted of a broad continuum of electron density with maxima in several areas. Disorder of the methyl group is required because of the presence of only two toluene molecules per unit cell, but the appearance of the difference Fourier in this region suggested disorder of the toluene ring as well. Four of the strongest peaks were chosen which, from construction of a three-dimensional model, were reasonable for half of a toluene. Attempts at least-squares refinement of these positions led to very large shifts in coordinates and widely varying temperature factors. Plotting these refined positions revealed that the resulting geometry was absurd for a toluene molecule. These atomic positions were removed from the refinement and the weighting

scheme was introduced; anisotropic temperature factors were assigned to the iron and chlorine atoms. The calculation of an additional difference Fourier was performed and again a continuum appeared. Several additional attempts to refine the toluene positions by adding one atomic position, refining, running a difference Fourier and then locating additional carbon peaks met with no success.

After least-squares refinement, using the weighting scheme described, coordinates and anisotropic temperature factors for the iron and chlorine, the calculated phases of the structure factors were used with the observed structure factors to calculate an electron density map.

It appeared as if there might be atomic positions for toluenes in two locations, twisted about 20° with respect to each other, and possibly too far from the center of inversion. However, a refinement was attempted using these positions. Again, refinement led to a geometry and bond distances which were unreasonable. In addition, some of the positions which appeared to approximate the second ring had refined to the positions initially ascribed to the first ring. At this stage it was apparent that least-squares refinement of individual atom positions could not handle the disorder problem.

An ideal geometry was assumed for the toluene and a single rigid group constrained about the inversion center at $(\frac{1}{2}, \frac{1}{2}, 0)$ was introduced. The orientation angles ϕ , θ , and ρ as well as a group temperature factor were refined. After four cycles of refinement, neither the angles nor the temperature factor changed significantly.

However, an electron density map revealed some remaining electron density around the inversion center. A second group was added in an attempt to find if there was the possibility that the disorder resulted from packing of the toluene in more than one orientation around the inversion center. Several refinements were made with two orientations, each having a fractional occupancy. From the R-factors and Hamilton's significance test (61), there did not appear to be any justification for such a model.

Releasing the atoms from their restraints as a rigid group and refining temperature factors and coordinates on separate cycles resulted in significantly better R values (61), but again the resulting geometry was unreasonable. The same procedure was followed, but anisotropic temperature factors were used for the toluene atoms. Again, significantly better R values were obtained, but the geometry was unreasonable. An ORTEP drawing of the toluene atoms with anisotropic motion revealed that there was both in-plane motion and out-of-plane motion.

An oblique calculation was performed in the vicinity of the toluene using the plane described by the toluene positions of the best rigid body refinement. The peak positions in the oblique calculations differed significantly from those found by rigid body refinement. As was found in all of other non-rigid refinements, the geometry of the toluene molecule was unreasonable.

Results of the rigid body refinements along with other pertinent information are given in Table 6.

Table 4. Cell Parameters for Structures

	Method of Data Collected	Formula Units Per Unit Cell	a	b	c	β	Density Theory g/cm ³	Density Found g/cm ³
Cu(SALPAH)Cl	Counter	4	8.564(3)	12.353(5)	10.305(4)	98.43 (3)	1.71	1.69(2)
Fe(SALPA)Cl	Film	4	9.85 (2)	14.86 (2)	9.39 (2)	124.25(10)	1.57	1.59(2)
Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL	Counter	4	11.548(3)	9.143(2)	18.683(4)	134.43 (5)	1.48	1.47(2)
[Fe(H ₂ O) ₆][Fe(SALGLY) ₂] ₂ \cdot 2H ₂ O	Counter	2	18.14 (3)	12.18 (2)	9.48 (1)	90.41 (4)	1.62	1.60(2)
Fe(SAL ₂ DIAPS)Cl	Film	2	10.02 (2)	21.76 (4)	11.06 (2)	96.17(10)	1.52	1.55(2)

NOTE: All these complexes crystallized in the space group $P_{21/C}$.

Table 5. Final Refinement Data

	R	wR	Number of Parameters Varied	Number of Reflections Used	SC* Value	Ignorance Factor	Number of Anisotropic Atoms
Cu(SALPAH)Cl	.089	.081	72	644	.05	.00	2
Fe(SALPA)Cl	.121	-	65	418	-	-	0
Fe(SALPA)Cl· $\frac{1}{2}$ TOL	.099	.091	76	851	.30	.01	2
[Fe(H ₂ O) ₆][Fe (SALGLY) ₂] ₂ ·2H ₂ O	.078	.047	144	1428	.30	.00	3
Fe(SAL ₂ DIAPS)Cl	.095	-	190	2163	-	-	8

$$*SC = \frac{\sigma(CI)}{CI} .$$

Table 6. Rigid Refinement Data for Toluene of $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$

Description of Refinement	NV	NO	P	Starting Values of occ	Final Values of occ	G β	R ₁	R ₂
One rigid group Refined orientation angles and G β	75	851	.01	-	-	12.97	.099	.091
Two rigid groups Refined orientation angles and G β	79	842	.02	.50		13.46		
Two rigid groups Refined orientation angles, occupancies, and G β 's	80	851	.01	.25	1.01	13.55		
Two rigid groups Refined orientation angles and occupancy of groups while G β 's were constrained to same value	79	851	.01	.82	1.00	-5.05	.101	.092
Two rigid groups Refined orientation angles, occupancies, and G β 's on separate cycles	81	851	.01	.18	.00	13.36	.102	.093
Two rigid groups continued refinement of orientation angles, occupancies, and G β (G β 's set at 10.00 prior to refining)	81	851	.01	.75	.66	11.88		
Positions found for one rigid group were refined as non-rigid. Alternated co- ordinates and isotropic temperature factors	81	851	.01	.25	.34	9.09	.098	.089
Positions found for one rigid group refined as non- rigid. Alternately refined coordinates and anisotropic temperature factors	87	851	.01	.66	.70	11.87		
Simultaneously refined co- ordinates and anisotropic temperature factors	107	851	.01	.34	.30	7.89	.098	.091
Simultaneously refined co- ordinates and anisotropic temperature factors	107	851	.01	-	-	-	.090	.083
Simultaneously refined co- ordinates and anisotropic temperature factors	107	851	.01	-	-	-	.077	.069
Simultaneously refined co- ordinates and anisotropic temperature factors	107	851	.01	-	-	-	.076	.069

NV = Number of variables.

NO = Number of observations (Reflections).

P = Ignorance factor.

G β = Group Temperature Factors.R₁ = Unweighted R value.R₂ = Weighted R value.

occ = Occupancy of the atom.

Table 7. Final Positional and Thermal
Parameters for Fe(SALPA)Cl

Atom	x	y	z	B, Å ²
Fe	.0436	.4639	.3741	4.83(15)
Cl	-.1688	.3947	.1543	6.63(31)
O2	-.0377	.5634	.4237	7.45(77)
O14	.2295	.3926	.4576	4.51(53)
C3	.3380	.3928	.4153	5.10(90)
C4	.4464	.3104	.4753	7.13(117)
C5	.5512	.3071	.4198	6.73(109)
C6	.5601	.3737	.3172	6.67(109)
C7	.4600	.4432	.2592	6.16(103)
C8	.3539	.4575	.3132	4.81(83)
C9	.2513	.5346	.2454	4.74(78)
N10	.1305	.5480	.2584	6.56(84)
C11	.0408	.6475	.1632	10.85(164)
C12	-.0950	.6606	.1813	8.10(131)
C13	-.1102	.6591	.3386	8.85(137)

Table 8. Final Positional and Thermal
Parameters* for $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$

Atom	x	y	z	B, Å ² or β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Fe	.1389	.0335	.0072	136(5)	94(4)	54(2)	20(5)	67(2)	3(3)
Cl	.3412	.1576	.1449	188(12)	203(12)	77(5)	-53(9)	86(6)	-54(6)
O2	.0798	.1092	-.1066	5.12(30)					
O14	.0538	-.1208	.0298	4.53(30)					
C3	.1409	.0849	-.1469	3.45(40)					
C4	.0848	.1850	-.2266	6.01(52)					
C5	.1442	.1596	-.2711	6.03(52)					
C6	.2643	.0677	-.2331	6.09(51)					
C7	.3223	-.0301	-.1530	5.44(46)					
C8	.2582	-.0145	-.1107	3.39(38)					
C9	.3234	-.1233	-.0320	3.71(39)					
N10	.2769	-.1213	.0143	3.25(31)					
C11	.3541	-.2396	.0942	5.81(52)					
C12	.2212	-.3383	.0659	4.70(45)					
C13	.1222	-.2604	.0846	4.41(44)					

* Anisotropic 3's given are $\times 10^4$.

Table 9. Final Positional and Thermal Parameters*
for $[\text{Fe}(\text{H}_2\text{O})_6][(\text{Fe}(\text{SALGLY})_2)_2 \cdot 2\text{H}_2\text{O}]$

Atom	x	y	z	B, Å ² or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe2	.0000	.0000	.0000	14(1)	34(3)	54(4)	-1(2)	0(2)	1(3)
Fe3	.7656	-.0288	.3806	22(1)	23(2)	51(3)	0(1)	11(1)	2(2)
O3	.0261	.0283	.2169	3.01(33)					
O4	.0009	.1714	-.0333	3.11(37)					
O5	.8868	.0176	.0421	2.48(30)					
O6	.7822	.0278	.8233	4.66(41)					
O7	.6808	-.0018	.4921	3.37(35)					
O8	.8517	-.1079	.2747	2.11(30)					
O9	.9169	-.2623	.2389	2.93(35)					
O10	.7112	-.0328	.2074	3.05(33)					
O11	.8380	.0210	.5374	2.97(33)					
O12	.9279	.1363	.5959	3.77(40)					
N13	.7623	-.1849	.4654	1.78(36)					
N14	.8003	.1283	.3166	1.91(37)					
C15	.6381	-.0655	.5721	2.54(53)					
C16	.5721	-.0183	.6230	4.24(57)					
C17	.5215	-.0806	.7142	3.94(61)					
C18	.5400	-.18515	.75186	4.28(63)					
C19	.6052	-.2271	.7082	3.90(61)					
C20	.6567	-.1702	.6105	2.91(52)					
C21	.7184	-.2258	.5558	1.87(43)					

Table 9. (Continued)

Atom	x	y	z	B, Å ² or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C22	.8248	-.2592	.4211	2.91(52)					
C23	.8664	-.2050	.2990	2.24(47)					
C24	.6827	.0507	.1334	1.76(46)					
C25	.6211	.0286	.0337	3.70(55)					
C26	.5907	.1126	-.0475	3.62(60)					
C27	.6161	.2142	-.0299	3.75(60)					
C28	.6728	.2423	.0589	2.58(51)					
C29	.7074	.1595	.1442	2.06(46)					
C30	.7653	.1871	.2290	2.66(51)					
C31	.8660	.1645	.3857	3.57(57)					
C32	.8774	.1061	.5187	2.24(47)					

* Anisotropic β 's are given $\times 10^4$.

Table 10. Final Positional and Thermal
Parameters* for Fe(SAL₂DIAPS)Cl

Atom	x	y	z	B, Å ² or					
				β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	.2441	.1142	.0549	65(1)	16(0)	71(2)	5(1)	- 2(1)	-2(1)
C12	.2143	.0583	-.1239	76(2)	20(0)	71(3)	2(1)	0(2)	-5(2)
S3	.0911	.0326	.1284	59(2)	21(7)	92(3)	1(1)	7(2)	4(2)
S4	.0591	.0464	.3059	104(3)	31(1)	108(4)	6(2)	45(3)	6(2)
O5	.3890	.1666	.0380	94(8)	20(2)	85(8)	- 4(3)	- 4(7)	-2(5)
O6	.1030	.1707	.0056	91(8)	21(2)	70(7)	13(3)	-17(6)	7(5)
N7	.2325	.1519	.2348	100(11)	28(3)	81(10)	3(5)	2(9)	4(7)
N8	.3885	.0440	.1302	79(8)	21(2)	76(9)	3(4)	7(7)	-2(6)
C9	.5131	.1689	.0906	3.41(36)					
C10	.5791	.1156	.1461	3.54(37)					
C11	.5867	.2238	.0860	5.49(53)					
C12	.5132	.0581	.1574	3.70(37)					
C13	.7182	.1176	.1931	4.41(43)					
C14	.7878	.1704	.1800	5.10(50)					
C15	.7261	.2255	.1270	5.48(53)					
C16	.3451	-.0176	.1440	2.94(32)					
C17	.2469	-.1370	.1578	3.81(40)					
C18	.2069	-.0289	.1404	2.64(30)					
C19	.2080	.2131	.2494	4.74(47)					
C20	.1434	.2503	.1583	3.61(39)					
C21	.0847	.2284	.0421	3.41(37)					

Table 10. (Continued)

Atom	x	y	z	B, Å ² or β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
C22	.0045	.2678	-.0340	4.02(42)					
C23	.1204	.3103	.1856	5.68(56)					
C24	.1591	-.0890	.1480	3.87(39)					
C25	.3815	-.1271	.1669	3.41(37)					
C26	-.0155	.3283	.0036	4.97(50)					
C27	.2838	.1203	.3400	4.97(48)					
C28	.4087	.1367	.4051	5.43(53)					
C29	.0404	.3503	.1139	5.29(52)					
C30	.2176	.9687	.3775	4.42(44)					
C31	.2654	.0343	.4828	6.47(62)					
C32	.4594	.1050	.5128	7.25(71)					
C33	.3841	.0519	.5449	7.03(68)					
C34	.4316	-.0664	.1530	3.20(35)					

* Anisotropic β's are given × 10⁴.

Table 11. Observed and Calculated Structure Factors for Fe(SALPA)Cl

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
K=0				-3	8	12	10	-2	4	31	32	-7	1	9	14
				-4	8	26	25	0	4	14	16	1	1	119	119
2	0	94	88	-6	8	9	7	1	4	7	10	3	1	12	18
4	0	24	18	-8	8	12	12	-5	5	28	32	-3	2	17	25
5	0	19	16	-9	8	16	15	-6	5	37	40	-4	2	35	33
0	2	56	54	-4	10	13	9	-7	5	30	30	-5	2	33	28
1	1	49	54	-5	10	30	21	-8	5	25	28	-6	2	28	32
3	2	33	33	-6	10	13	8	-9	5	14	17	-7	2	28	32
4	2	36	36	-7	10	23	13	-4	5	45	45	0	2	59	49
5	2	12	12	-8	10	13	10	-2	5	40	35	1	1	69	65
6	2	18	20	6	0	13	10	-1	5	75	71	2	2	16	24
-1	2	112	117					0	5	30	27	3	2	35	44
-2	2	59	59	K=1				1	5	9	10	4	2	20	24
-3	2	14	17					2	5	13	14	5	2	16	19
-5	2	17	13	-2	1	86	84	3	5	22	23	6	2	11	16
-6	2	51	51	-3	1	33	42	4	5	23	20	-3	3	22	23
-7	2	32	41	-4	1	21	10	-6	6	12	13	-4	3	15	14
-8	2	18	19	-5	1	28	31	-7	6	13	12	-5	3	26	26
0	4	58	55	-6	1	24	32	-3	6	14	12	-6	3	23	20
1	4	59	62	-7	1	17	21	-2	6	14	13	-7	3	26	28
2	4	47	43	0	1	134	122	-1	6	17	13	-8	3	16	18
3	4	24	27	1	1	68	67	-7	7	7	10	-2	3	87	77
-1	4	76	75	2	1	41	44	-5	7	12	13	-1	3	12	12
-2	4	30	31	4	1	54	66	-4	7	29	24	0	3	48	52
-3	4	21	25	5	1	26	33	-3	7	4	37	1	3	22	22
-5	4	40	42	-2	2	41	33	-2	7	40	33	2	3	16	16
-6	4	21	17	-3	2	28	29	-1	7	23	21	-4	4	13	11
-7	4	20	26	-6	2	12	10	-5	8	9	9	-5	4	26	24
-8	4	30	36	0	2	35	37	-4	8	9	6	-7	4	18	19
-9	4	18	24	1	2	43	46	-3	8	9	10	-8	4	22	23
2	6	20	13	2	2	20	24	-9	9	20	17	-9	4	16	19
3	6	16	14	3	2	20	26	-10	9	15	11	-3	4	32	32
4	6	13	11	-3	3	86	79	-8	9	17	15	-2	4	41	47
-1	6	19	11	-4	3	47	50	-5	9	24	23	-1	4	41	41
-2	6	27	20	-5	3	13	17	-4	9	8	7	0	4	32	31
-3	6	17	15	-6	3	26	27	-3	9	8	5	1	4	42	43
-4	6	17	13	-2	3	65	67					2	4	24	30
-5	6	34	37	0	3	15	17	K=2				3	4	15	23
-6	6	43	40	1	3	16	16					-5	5	25	26
-7	6	36	37	2	3	35	37	3	0	42	47	-6	5	35	34
-8	6	21	23	3	3	23	24	-2	1	55	41	-7	5	14	19
0	8	13	10	4	3	9	13	-3	1	12	13	-4	5	14	16
1	8	19	14	5	3	10	12	-4	1	16	19	-2	5	12	11
2	8	13	8	-4	4	43	45	-5	1	31	35	-1	5	28	29
-1	8	15	8	-3	4	38	36	-6	1	36	40	0	5	19	16

Table 11. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
0	10	17	29	-3	4	65	66	0	6	16	7	-1	10	14	19
1	10	12	10	-4	4	67	64	1	6	37	37	-3	10	15	15
0	11	16	15	-5	4	47	46	-1	7	37	38	-4	10	19	23
1	11	29	16	-6	4	16	12	-2	7	45	46	-5	10	12	15
2	11	17	23	1	4	16	14	-3	7	13	8	0	10	21	22
3	11	15	17	2	4	16	19	-4	7	10	15	-1	11	30	22
-1	12	31	30	3	4	15	22	-5	7	15	17	-2	11	21	20
0	12	24	21	4	4	11	19	0	7	58	67	-3	11	19	17
0	13	18	20	5	4	17	21	1	7	55	62	0	11	22	19
1	13	15	14	-1	5	59	53	2	7	25	28	2	11	17	13
2	13	11	14	-2	5	70	64	-1	8	13	10	3	11	17	17
3	13	16	15	-3	5	22	23	-2	8	25	23	-1	12	11	7
4	13	16	17	-4	5	22	21	-1	9	46	42	-2	12	16	9
				-7	5	12	18	-2	9	33	30	-3	12	20	13
	L=2			0	5	39	40	-3	9	25	20	-4	12	21	17
				1	5	29	32	-4	9	15	9	-1	14	21	17
2	0	42	46	3	5	18	21	0	9	43	41	-2	14	17	10
4	1	16	17	-3	6	31	30	1	9	19	21	-3	14	18	10
-7	3	9	19	-4	6	38	32	3	9	16	18	-4	14	13	7
-2	4	37	36	-5	6	15	18								

Table 12. (Concluded)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-4	1	14	13	-3	5	10	8	-6	2	18	19	-6	0	15	16
-3	1	13	13	-2	5	15	17	-5	2	13	14	-3	0	17	18
-7	2	28	26	-7	6	9	11	-4	2	12	14	-1	0	20	23
-5	2	13	14	-4	6	13	12	-6	3	16	16	-7	1	16	16
-4	2	29	30	-7	7	20	21	-5	3	10	7	-6	2	9	6
-3	2	14	14	-6	7	19	18	-4	3	24	26	-5	2	11	8
-2	2	15	12	-5	7	10	8	-2	3	16	19	-4	2	22	24
-1	2	14	13	-3	7	12	15	-1	3	13	10	-2	2	10	8
-6	3	35	32	-2	7	11	10	-7	4	12	12	-1	2	12	11
-5	3	15	17					-6	4	14	18	-4	3	9	8
-4	3	14	18					-3	4	17	16	-3	3	10	9
-3	3	10	12					-5	5	16	14	-5	4	19	16
-2	3	11	11					-4	5	17	18	-4	4	20	21
1	3	11	7	-7	1	25	27	-7	6	24	23	-7	5	20	20
-5	4	21	22	-6	1	9	8	-6	6	19	17	-6	5	9	10
-4	4	23	25	-5	1	11	11	-5	6	10	9	-5	5	15	16
-2	4	16	19	-4	1	22	23	-3	6	16	13	-3	5	14	14
-1	4	12	11	-3	1	17	19					-7	7	12	11
-7	5	26	27	-1	1	19	18					-6	7	21	20
-6	5	17	18	-7	2	20	23	-7	0	25	14	-5	7	10	4

Table 13. Observed and Calculated Structure Factors
for $[\text{Fe}(\text{H}_2\text{O})_6] [\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
H=0				5	-6	29	33	10	4	54	57	4	3	27	28
0	-8	45	50	5	-5	82	80	10	5	25	30	4	4	41	42
0	-4	71	74	5	-4	41	42	10	7	39	38	4	5	74	72
0	-2	71	90	5	-3	30	31	H=1				4	6	85	83
0	2	92	90	5	-2	56	58	0	-6	32	33	4	7	18	14
0	4	72	74	5	2	57	58	0	-4	24	18	4	8	25	20
0	8	50	50	5	3	30	31	0	-2	62	73	5	-7	32	31
1	-5	107	103	5	4	37	42	0	4	109	110	5	-6	39	36
1	-3	59	61	5	5	76	80	0	6	76	71	5	-5	39	38
1	-1	43	45	5	6	29	33	0	8	31	30	5	-4	43	46
1	1	56	45	6	-8	39	44	1	-7	49	46	5	-2	67	64
1	3	66	61	6	-6	39	39	1	-6	41	37	5	0	68	83
1	5	98	103	6	-5	56	58	1	-5	80	83	5	1	74	90
2	-8	47	51	6	-3	21	25	1	-4	20	14	5	3	94	93
2	-7	21	10	6	-2	69	68	1	-1	71	57	5	4	56	55
2	-6	57	55	6	2	68	68	1	1	131	143	5	5	32	32
2	-5	31	31	6	3	24	25	1	2	18	17	5	8	21	22
2	-4	20	20	6	5	53	58	1	3	58	60	6	-4	25	29
2	-3	45	43	6	6	38	39	1	4	16	15	6	-3	51	54
2	-2	65	64	6	8	42	44	1	7	24	21	6	-2	80	83
2	-1	23	34	7	-5	49	48	1	8	20	13	6	-1	87	92
2	0	146	153	7	-3	23	28	2	-6	31	36	6	0	58	66
2	1	30	34	7	-2	45	49	2	-5	27	30	6	1	96	90
2	2	68	64	7	2	48	49	2	-3	35	32	6	2	44	37
2	3	49	43	7	3	26	28	2	-2	84	82	6	3	23	23
2	4	22	20	7	5	51	48	2	0	15	38	6	5	38	39
2	5	27	31	8	-7	23	19	2	1	121	124	6	6	40	33
2	6	54	55	8	-4	33	27	2	2	19	20	6	7	23	24
2	7	19	10	8	-3	31	31	2	3	17	11	7	-8	26	28
2	8	45	51	8	-2	40	39	2	4	83	76	7	-7	23	23
3	-7	25	31	8	-1	28	29	2	6	86	83	7	-5	34	32
3	-6	26	25	8	0	60	58	2	8	30	31	7	-4	31	34
3	-5	86	84	8	1	25	29	3	-8	26	33	7	-3	25	21
3	-4	19	21	8	2	37	39	3	-7	48	50	7	-1	22	8
3	-2	33	31	8	3	29	31	3	-6	36	36	7	0	42	39
3	-1	17	21	8	4	32	27	3	-5	52	46	7	1	53	52
3	2	33	31	8	6	22	17	3	-4	38	34	7	2	17	18
3	4	23	21	8	7	21	19	3	-3	71	70	7	3	59	57
3	5	80	84	9	-6	34	29	3	-2	61	56	7	4	60	56
3	6	25	25	9	-4	49	45	3	-1	72	78	7	5	32	33
3	7	24	31	9	-3	28	29	3	0	32	33	8	-7	41	42
4	-8	26	31	9	-2	57	54	3	1	83	81	8	-5	50	39
4	-7	44	46	9	2	57	54	3	3	79	78	8	-3	59	64
4	-5	39	36	9	3	30	29	3	5	23	23	8	-2	20	20
4	-4	37	36	9	4	43	45	3	7	26	27	8	-1	42	47
4	-2	67	66	9	6	37	29	4	-7	29	29	8	0	51	54
4	-1	75	74	10	-7	36	38	4	-6	58	60	8	1	27	28
4	0	211	215	10	-6	23	21	4	-5	44	43	8	4	39	43
4	1	78	74	10	-5	28	30	4	-4	49	47	8	5	54	48
4	2	69	66	10	-4	58	57	4	-3	56	55	8	6	18	14
4	4	34	36	10	-3	24	23	4	-2	36	39	8	7	36	35
4	5	35	36	10	-1	40	37	4	-1	31	37	8	8	30	27
4	7	43	46	10	1	36	37	4	0	38	31	9	-8	31	34
4	8	27	31	10	3	23	23	4	2	22	28	9	-4	46	47

Table 13. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
9	-3	23	25	4	-1	113	112	9	2	35	32	3	4	27	28
9	0	21	17	4	0	61	59	9	4	28	30	3	5	47	46
9	4	28	24	4	1	85	84	9	5	20	22	3	7	56	57
9	7	25	19	4	2	62	54	9	6	42	39	3	8	27	24
9	8	32	31	4	3	43	42	9	7	23	24	4	-7	23	24
10	-7	26	19	4	4	59	59	10	-7	19	21	4	-6	65	63
10	-6	30	27	4	6	42	44	10	-5	27	30	4	-5	37	35
10	-3	24	27	4	7	22	17	10	-4	22	27	4	-4	79	73
10	-1	34	36	5	-7	43	40	10	-1	36	35	4	-3	71	69
10	0	24	16	5	-6	71	74	10	0	23	30	4	-2	62	62
10	1	25	17	5	-5	19	16	10	1	54	47	4	-1	43	41
10	5	45	42	5	-3	29	28	10	2	20	31	4	0	64	71
H=2				5	-2	43	46	10	3	37	36	4	1	29	32
0	-8	32	37	5	-1	113	108	10	7	26	25	4	2	66	61
0	-4	54	55	5	0	37	44	10	8	25	24	4	4	91	90
0	2	87	110	5	1	102	105	H=3				4	8	23	15
0	4	200	199	5	2	57	57	0	-6	75	79	5	-4	45	44
0	6	31	33	5	3	92	89	0	-2	24	6	5	-3	21	18
0	8	35	31	5	4	42	40	0	0	33	37	5	-1	90	89
1	-7	59	61	5	5	19	7	0	2	234	239	5	0	18	27
1	-4	56	50	5	6	41	39	0	4	83	82	5	2	43	43
1	-3	63	51	5	7	25	26	1	-7	33	34	5	3	39	43
1	-1	131	111	5	8	34	31	1	-6	24	22	5	4	24	24
1	1	191	178	6	-5	19	21	1	-5	28	25	5	5	23	18
1	2	36	37	6	-4	24	21	1	-4	71	67	5	7	53	57
1	3	94	99	6	-2	49	53	1	-3	45	46	6	-6	43	40
1	7	20	23	6	-1	91	91	1	-2	143	137	6	-3	64	64
2	-8	30	36	6	0	25	17	1	2	173	181	6	-1	17	7
2	-7	26	27	6	1	89	92	1	3	79	75	6	0	49	47
2	-5	25	26	6	2	40	39	1	5	81	81	6	1	47	55
2	-4	40	33	6	3	46	40	1	6	33	31	6	2	59	60
2	-3	53	51	6	4	61	63	1	7	62	61	6	4	79	80
2	-2	42	42	6	5	27	23	2	-7	33	32	6	5	38	37
2	-1	90	87	6	6	37	39	2	-6	65	67	6	7	24	19
2	0	28	35	7	-7	32	26	2	-5	29	28	6	8	31	32
2	2	58	56	7	-5	42	41	2	-4	16	11	7	-4	50	48
2	3	34	28	7	-3	19	18	2	-3	28	22	7	-3	38	37
2	4	122	119	7	-2	62	58	2	-2	142	137	7	-1	37	42
2	5	21	21	7	-1	57	54	2	-1	30	29	7	0	50	51
2	6	34	39	7	0	42	38	2	0	20	24	7	5	33	32
3	-7	58	56	7	1	39	40	2	1	55	58	7	7	30	21
3	-6	37	39	7	2	49	47	2	2	102	104	7	8	23	23
3	-3	28	26	7	3	19	19	2	4	100	98	8	-8	24	22
3	-2	26	24	8	-3	49	50	2	5	42	39	8	-7	26	23
3	-1	125	124	8	-1	51	49	2	8	31	30	8	-6	26	20
3	0	64	69	8	1	48	41	3	-8	26	23	8	-4	40	44
3	2	57	58	8	2	31	33	3	-7	32	38	8	-3	70	67
3	3	43	38	8	4	32	32	3	-5	62	62	8	-1	29	25
3	4	36	34	9	-6	65	64	3	-4	34	36	8	0	25	5
3	5	46	39	9	-5	31	26	3	-3	24	23	8	1	46	47
3	6	44	42	9	-3	31	24	3	-1	26	23	8	2	45	41
3	7	20	23	9	-2	25	26	3	0	67	68	8	3	26	34
4	-5	32	28	9	-1	23	12	3	2	39	35	8	4	21	22
4	-4	79	77	9	1	35	35	3	3	24	23	8	5	40	42

Table 13. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
9	-8	19	22	3	2	28	34	9	-6	46	51	3	4	44	47
9	-4	48	44	3	3	85	85	9	-5	30	21	3	5	44	48
9	0	46	48	3	4	45	42	9	-4	60	55	4	-8	23	29
9	3	20	16	3	5	86	86	9	-2	55	55	4	-7	39	37
9	4	19	19	3	6	26	31	9	-1	22	15	4	-4	25	23
9	5	24	20	3	8	37	35	9	3	23	29	4	-3	34	29
9	6	25	27	4	-8	49	50	9	4	25	22	4	-2	88	87
10	-5	49	48	4	-5	29	30	9	5	37	37	4	0	47	49
10	-3	26	21	4	-4	34	34	9	6	25	26	4	1	21	21
10	-2	39	36	4	-3	19	23	9	8	28	29	4	2	39	40
10	1	29	31	4	-1	50	56	10	-5	42	39	4	3	23	27
10	5	23	23	4	0	63	69	10	-4	22	16	4	4	27	25
10	6	21	17	4	3	58	61	10	-2	42	39	4	5	50	51
10	8	24	21	4	5	25	22	10	-1	23	35	4	6	30	28
H=4				4	7	21	14	10	3	33	30	4	8	46	44
0	-8	51	55	4	8	41	37	10	7	26	30	5	-8	32	30
0	-6	45	43	5	-6	20	26	H=5				5	-7	30	34
0	-4	45	38	5	-5	52	53	0	-8	33	36	5	-6	21	18
0	-2	214	209	5	-4	43	45	0	-4	60	63	5	-5	50	53
0	2	107	108	5	-2	50	48	0	-3	21	0	5	-4	29	27
0	8	35	36	5	-1	29	27	0	-2	126	126	5	-3	20	10
1	-7	39	39	5	1	22	14	0	0	75	75	5	-2	40	43
1	-6	29	34	5	4	40	35	0	4	31	39	5	1	48	47
1	-5	83	83	5	5	63	59	0	6	56	59	5	2	37	34
1	-4	27	21	5	6	33	29	1	-8	29	26	5	3	57	59
1	-3	25	25	6	-8	27	27	1	-7	34	31	5	4	29	27
1	-2	50	45	6	-6	38	36	1	-6	22	19	5	5	45	41
1	0	24	25	6	-4	52	47	1	-5	100	97	6	-5	30	27
1	1	26	22	6	-1	46	47	1	-3	18	18	6	-4	38	36
1	2	16	11	6	0	91	96	1	-2	70	71	6	-3	66	67
1	3	35	30	6	1	58	60	1	-1	65	64	6	-2	44	42
1	4	29	27	6	5	32	28	1	0	25	25	6	1	48	57
1	5	90	94	6	7	20	17	1	3	159	158	6	4	31	28
1	7	22	22	6	8	23	24	1	5	48	44	6	5	45	41
2	-8	48	53	7	-6	37	38	2	-8	26	23	7	-8	36	36
2	-7	25	25	7	-4	23	27	2	-8	26	23	7	-5	29	25
2	-6	44	41	7	-3	44	40	2	-3	31	28	7	-4	23	23
2	-3	88	86	7	-2	55	60	2	-2	103	106	7	-3	42	40
2	-2	70	66	7	-1	41	41	2	0	64	69	7	-2	20	14
2	0	102	105	7	2	51	51	2	1	17	21	7	0	77	81
2	1	29	31	7	3	36	34	2	2	94	104	7	1	24	25
2	2	94	91	7	4	23	23	2	3	47	53	7	2	24	27
2	3	74	73	7	5	40	35	2	4	30	36	7	4	35	28
2	4	93	89	7	6	41	46	2	6	19	13	8	-7	27	23
2	5	25	20	7	7	36	30	2	7	25	20	8	-4	25	15
2	8	44	38	7	8	38	37	2	8	33	34	8	-3	61	61
3	-8	22	23	8	-5	23	18	3	-8	24	29	8	1	39	40
3	-7	23	21	8	-3	27	33	3	-7	58	60	8	5	45	45
3	-6	57	56	8	-1	60	62	3	-6	19	15	9	-5	21	23
3	-5	60	61	8	0	22	11	3	-5	80	83	9	-4	29	30
3	-4	17	10	8	1	42	38	3	-1	62	68	9	-3	25	22
3	-3	57	51	8	2	22	23	3	0	23	20	9	-1	50	50
3	-1	79	76	8	3	65	65	3	2	18	17	9	0	56	56
3	0	24	10	8	6	25	30	3	3	47	46	9	3	24	22

Table 13. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
10	-7	29	26	4	1	24	27	H=7				6	-4	36	33
10	-5	38	35	4	2	38	41	0	-6	94	97	6	-3	24	24
10	-3	34	34	4	4	39	33	0	-4	56	61	6	-1	33	33
10	-1	26	31	4	6	39	36	0	0	54	45	6	0	30	33
10	5	32	30	5	-7	46	45	0	2	120	119	6	1	71	77
H=6				5	-6	57	53	0	4	108	110	6	2	45	48
0	-6	45	46	5	-4	27	26	1	-4	59	61	6	4	36	39
0	-4	84	82	5	-3	20	20	1	-3	39	36	7	-8	29	30
0	-2	167	164	5	-2	25	23	1	-2	17	15	7	-4	35	38
0	0	22	14	5	-1	66	66	1	-1	138	138	7	-3	30	31
0	2	39	31	5	1	41	39	1	1	23	25	7	-1	47	50
0	4	91	90	5	2	18	13	1	3	36	31	7	0	25	20
0	5	18	0	5	3	19	15	1	4	27	35	7	1	26	31
0	6	31	35	5	5	20	11	1	7	34	34	7	2	54	56
0	8	31	29	6	-7	25	21	2	-8	34	31	7	4	43	43
1	-8	21	20	6	-6	26	29	2	-6	62	68	8	-7	32	31
1	-7	65	65	6	-5	34	33	2	-5	39	45	8	-6	23	17
1	-5	22	21	6	-4	52	47	2	-4	105	105	8	-4	26	25
1	-4	27	28	6	-2	63	58	2	-3	36	38	8	-2	42	44
1	-3	56	58	6	-1	54	54	2	-2	35	30	8	1	64	73
1	-2	48	48	6	3	48	51	2	-1	54	52	8	2	21	17
1	-1	98	92	6	4	71	69	2	0	24	24	8	4	26	28
1	2	30	31	6	6	34	34	2	2	46	48	8	5	28	29
1	4	53	51	6	7	25	24	2	3	40	41	9	-8	34	36
1	5	52	53	7	-2	64	60	2	4	51	57	9	-4	32	33
1	7	28	27	7	0	41	39	2	5	26	28	9	-3	26	18
2	-6	22	22	7	2	34	40	2	6	35	31	9	-2	38	38
2	-5	38	38	7	4	55	61	2	7	28	29	9	-1	20	19
2	-4	71	74	8	-7	40	40	3	-8	22	25	9	0	35	33
2	-3	98	95	8	-6	31	28	3	-6	25	30	9	2	24	15
2	-2	81	77	8	-5	39	42	3	-4	59	57	9	4	21	14
2	-1	53	60	8	-4	43	43	3	-3	31	40	9	6	25	24
2	0	22	19	8	-3	23	18	3	-1	44	40	10	-3	52	52
2	2	67	67	8	-2	42	44	3	1	21	19	10	-2	22	25
2	3	27	28	8	-1	64	60	4	-7	22	25	10	0	34	34
2	4	169	172	8	0	23	13	4	-6	57	54	10	1	42	49
2	6	39	38	8	1	26	28	4	-4	29	34	10	6	24	15
2	7	21	21	8	3	33	29	4	-2	20	16	H=8			
2	8	22	25	8	4	35	34	4	1	26	31	0	-6	55	52
3	-7	59	63	8	5	21	14	4	2	59	60	0	-4	42	47
3	-6	22	20	8	7	29	26	4	4	26	26	0	-2	32	26
3	-5	19	14	8	-6	47	50	4	5	48	52	0	0	112	105
3	-3	127	125	9	-3	20	12	5	-8	31	29	0	2	106	105
3	-2	88	87	9	0	29	23	5	-7	24	20	0	4	28	32
3	-1	24	21	9	2	21	24	5	-5	27	26	0	8	47	50
3	0	22	24	9	3	21	20	5	-3	56	57	1	-8	28	20
3	4	18	26	9	6	23	22	5	-2	20	19	1	-5	64	62
3	5	52	58	9	8	27	20	5	-1	72	78	1	-4	42	47
3	8	24	24	10	-8	26	22	5	0	42	40	1	-3	147	148
4	-5	29	21	10	-4	38	37	5	1	18	18	1	-1	43	42
4	-4	72	73	10	-1	22	19	5	4	45	49	1	1	36	38
4	-3	21	21	10	3	28	27	5	6	36	36	1	2	37	32
4	-2	148	147	10	7	27	27	5	7	28	29	1	3	33	33
4	-1	67	70					6	-6	41	44	1	4	23	25

Table 13. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
1	5	50	58	7	-2	57	57	3	6	39	44	0	2	43	36
2	-8	32	32	7	-1	56	61	4	-8	30	28	0	4	70	67
2	-6	26	23	7	0	33	37	4	-7	36	36	0	6	50	50
2	-5	21	18	7	1	35	41	4	-4	24	31	1	-7	47	46
2	-1	39	37	7	3	29	33	4	-2	56	51	1	-6	60	55
2	0	62	51	7	4	39	41	4	0	63	59	1	-4	24	25
2	2	85	88	7	5	22	25	4	1	24	22	1	-3	55	44
2	6	30	30	7	8	22	24	4	5	37	37	1	-2	34	30
2	8	23	11	8	-6	25	21	4	7	22	24	1	-1	73	75
3	-7	29	22	8	-5	33	34	4	8	37	36	1	0	27	27
3	-5	44	44	8	-1	51	55	5	-5	58	54	1	1	123	127
3	-4	27	21	8	1	31	33	5	-4	40	34	1	3	70	65
3	-3	109	112	8	3	30	32	5	-3	25	29	1	6	21	19
3	-2	72	78	8	5	26	28	5	-2	54	53	2	-6	25	18
3	-1	83	82	9	-7	31	27	5	1	33	38	2	-5	32	34
3	2	22	20	9	-3	34	33	5	2	54	53	2	-4	52	50
3	3	22	29	9	-2	24	33	5	3	70	66	2	-3	26	28
3	4	31	37	9	-1	34	39	5	5	32	29	2	-2	70	70
3	5	55	62	9	1	24	23	6	-4	23	24	2	-1	38	41
3	7	47	49	10	-5	33	30	6	-2	63	61	2	2	30	24
4	-8	21	22	10	0	31	33	6	0	84	81	2	4	41	42
4	-7	36	38	10	3	22	20	6	1	42	42	2	6	28	26
4	-6	33	30	10	4	33	30	6	3	28	29	2	8	22	14
4	-5	46	41	10	7	29	29	6	5	32	27	3	-7	29	25
4	-3	29	25					6	6	26	20	3	-6	32	32
4	-2	32	27					7	-5	30	26	3	-5	39	38
4	-1	35	39					7	-2	26	18	3	-4	29	30
4	0	50	46					7	0	37	31	3	-3	44	44
4	1	27	28					7	2	28	19	3	-1	50	53
4	2	60	63					7	3	56	61	3	0	27	31
4	3	38	40					7	4	30	29	3	2	20	15
4	5	41	44					7	5	22	20	3	3	34	42
4	7	38	36					7	6	24	20	4	-5	32	24
5	-8	22	16					8	-7	29	23	4	-4	35	33
5	-6	33	32					8	-2	31	24	4	-2	26	25
5	-5	64	67					8	1	27	24	4	-1	34	35
5	-3	98	100					8	5	35	35	4	0	20	24
5	-2	32	40					8	6	25	28	4	3	35	35
5	-1	66	71					9	-4	36	33	4	4	60	68
5	2	23	24					9	-2	21	20	4	5	24	27
5	3	52	52					9	1	28	34	4	7	33	36
5	5	26	29					9	4	25	23	5	-7	27	25
5	7	23	20					10	-7	31	37	5	-4	26	25
6	-7	25	30					10	-3	24	28	5	-2	27	25
6	-5	23	24					10	1	26	24	5	-1	40	41
6	-1	71	72					10	2	23	28	5	1	72	77
6	0	47	53					10	4	29	23	5	2	23	22
6	1	40	35					10	5	36	28	5	3	44	45
6	2	60	67									5	5	21	32
6	3	65	65									5	6	22	25
6	7	28	21									5	7	25	29
7	-5	34	36									5	8	24	27
7	-4	28	25									6	-5	22	17
7	-3	29	24									6	-4	42	40

Table 13. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
6	-2	57	58	3	4	21	14	2	-6	47	50	1	-2	22	28
6	-1	29	27	3	5	39	43	2	-5	27	25	1	3	55	51
6	1	30	34	3	7	42	45	2	-1	37	34	2	-6	25	19
6	3	55	56	4	-4	43	44	2	2	71	67	2	-4	34	40
6	6	32	35	4	-3	49	50	2	3	33	40	2	-3	30	25
7	-8	25	16	4	2	43	36	2	5	20	17	2	-2	45	46
7	-7	22	21	4	4	60	59	2	8	23	19	2	0	35	37
7	-2	25	30	5	-4	20	21	3	-6	22	18	2	1	32	34
7	-1	42	48	5	-3	21	19	3	-5	20	27	2	3	23	22
7	0	56	55	5	-2	24	20	3	-4	26	32	2	8	36	36
7	3	26	31	5	-1	68	66	3	-3	39	42	3	-6	22	20
8	-5	31	30	5	1	60	59	3	0	21	23	3	-5	46	48
8	-1	30	38	5	2	51	53	3	1	36	39	3	-2	34	34
8	0	34	37	5	6	24	32	3	5	24	22	3	-1	34	39
8	1	39	39	5	7	23	27	3	7	39	38	3	2	24	30
8	3	39	39	6	-7	21	21	3	8	22	15	3	3	39	35
8	4	29	29	6	-6	24	27	4	-8	23	23	4	-7	32	30
9	-8	23	17	6	-4	23	24	4	-6	34	39	4	-2	33	31
9	-4	32	28	6	-3	48	52	4	-3	21	27	4	-1	24	26
9	-3	24	21	6	-2	26	18	4	0	36	38	4	0	50	52
9	0	22	27	6	1	22	13	4	2	55	51	4	1	24	27
9	5	25	24	6	4	39	40	4	3	37	34	4	6	25	26
9	8	29	25	6	5	36	31	4	5	23	22	4	8	26	32
10	-2	22	23	7	-6	22	19	4	8	30	28	5	-6	21	19
10	-1	49	49	7	-4	42	45	5	-3	35	34	5	-2	32	30
10	2	31	34	7	-2	20	9	5	-2	28	28	5	3	26	20
10	3	34	32	7	1	52	58	5	0	24	12	5	5	22	18
10	5	23	24	7	2	53	56	5	1	35	37	6	-3	45	48
H=11				7	4	25	25	5	2	21	22	6	-2	43	43
0	-8	22	27	7	7	29	29	5	4	35	33	6	0	41	41
0	-4	55	52	8	-3	41	40	5	7	22	14	6	2	29	35
0	0	30	38	8	5	22	28	6	-6	33	33	6	3	22	29
0	2	37	33	9	-6	23	28	6	0	21	19	7	-6	25	29
0	4	61	60	9	-2	26	24	6	1	33	35	7	-2	26	25
1	-7	20	13	9	-1	27	17	6	2	69	69	7	2	39	37
1	-1	80	79	10	-3	44	46	6	3	43	44	7	6	28	24
1	0	21	23	10	-1	28	29	6	4	23	24	8	-3	35	32
1	1	53	56	H=12				7	-4	31	32	8	-1	27	21
1	2	30	28	0	-8	27	27	7	-2	32	33	8	1	29	28
1	3	40	47	0	-6	26	21	7	5	30	27	9	-2	37	39
1	6	28	33	0	-4	30	23	8	-4	21	17	9	2	21	15
1	7	47	49	0	2	101	100	8	-1	29	26	10	-4	26	28
2	-6	38	29	0	4	34	37	8	0	25	23	10	-3	23	19
2	-4	40	44	0	6	24	21	9	-5	21	15	10	-1	25	24
2	0	35	37	0	8	40	34	9	-4	26	25	10	1	25	26
2	1	28	27	1	-7	25	29	9	1	23	20	H=14			
2	2	36	34	1	-4	24	21	10	3	32	32	0	-2	30	27
2	4	57	55	1	-3	63	62	H=13				0	2	21	28
2	5	21	15	1	-1	34	30	0	-8	45	51	0	6	31	28
3	-6	32	31	1	1	50	49	0	-4	47	37	1	-7	44	50
3	-5	43	48	1	2	32	31	0	-2	31	31	1	-5	50	44
3	-2	24	19	1	5	36	34	0	0	102	104	1	-4	35	26
3	-1	58	56	1	7	46	41	0	8	33	34	1	1	41	38
3	2	26	22	2	-8	32	37	1	-5	46	50	1	3	42	43

Table 14. Observed and Calculated Structure Factors
for Fe(SAL₂DIAPS)Cl

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
K=0				3	4	85	83	-4	5	37	40	2	6	43	44
0	6	72	71	3	6	86	86	-4	7	41	44	2	7	24	26
0	8	23	18	3	8	42	38	-4	9	24	24	2	9	13	11
0	0	36	39	3	0	28	28	-4	0	16	14	2	0	9	8
0	2	21	21	3	2	13	16	-4	1	10	10	2	1	10	10
-1	4	114	106	4	4	16	15	-4	2	10	8	2	2	10	9
-1	6	81	80	4	6	25	22	-5	4	11	14	2	3	10	12
-1	8	66	57	4	8	10	11	-5	5	51	53	3	2	9	11
-1	0	7	9	4	0	27	30	-5	6	37	40	3	3	56	46
-1	2	39	45	6	6	7	7	-5	7	32	35	3	4	10	14
-2	4	41	42	6	0	20	22	-5	8	9	8	3	5	83	86
-2	0	39	40	6	2	21	19	-5	9	23	23	3	6	22	21
-3	2	108	110	7	6	34	41	-6	5	32	33	3	7	20	17
-3	6	86	80	8	8	13	11	-6	7	18	17	3	8	8	4
-3	0	47	50	8	0	14	11	-6	8	16	18	3	0	27	29
-4	4	73	75	9	6	20	20	-6	9	9	6	3	1	17	20
-4	6	102	100	9	8	13	12	-6	1	17	15	4	5	18	15
-4	8	31	30	10	6	10	10	-6	2	17	17	4	6	34	34
-4	0	10	10	10	8	21	24	-7	5	15	17	4	7	39	40
-5	4	69	74	K=1				-7	6	20	23	4	8	18	20
-5	8	16	15	0	3	139	134	-7	7	25	24	4	9	29	24
-5	0	17	17	0	4	80	73	-7	8	9	11	4	0	10	10
-5	2	21	21	0	5	81	76	-7	9	22	22	4	1	17	19
-6	6	18	19	0	6	59	55	-7	0	10	8	5	5	38	39
-6	8	23	25	0	7	54	50	-7	1	14	18	5	7	20	22
-6	0	11	7	0	9	15	18	-8	5	9	11	5	8	9	12
-7	6	20	26	0	1	44	43	-8	6	13	13	5	0	17	16
-7	8	22	25	0	2	75	75	-8	7	19	20	5	2	14	11
-7	2	20	20	-1	3	159	146	-8	8	10	9	6	6	46	51
-8	4	10	9	-1	4	81	82	-8	9	17	19	6	7	16	20
-8	6	21	23	-1	5	20	20	-9	5	24	24	6	8	9	6
-8	8	10	14	-1	6	21	20	-9	6	14	16	6	9	14	14
-8	0	17	20	-1	7	43	45	-9	7	14	12	6	0	10	10
-9	6	10	12	-1	8	33	34	-9	8	14	12	6	1	17	21
-9	8	20	28	-1	9	16	15	-9	9	10	1	7	5	38	39
-9	0	20	22	-1	1	26	28	-10	5	14	18	7	7	17	14
-9	2	11	9	-1	2	60	64	-10	7	17	18	7	0	14	8
-10	2	7	8	-2	3	42	44	-10	9	14	13	7	1	10	7
-10	6	24	24	-2	5	9	7	-11	6	14	9	8	5	14	9
-10	8	26	27	-2	6	72	80	-11	8	14	14	8	6	14	14
-10	0	10	7	-2	7	38	40	-11	9	9	9	8	7	14	16
-11	4	13	14	-2	9	8	7	-12	5	14	10	8	8	10	7
-11	6	7	9	-2	0	9	9	-12	7	13	11	9	5	24	25
-12	6	12	13	-2	1	13	17	1	2	53	57	9	8	14	11
-12	8	9	10	-2	2	25	26	1	3	14	12	9	0	13	11
1	4	37	34	-3	3	28	21	1	4	24	25	10	5	17	19
1	6	41	34	-3	5	84	87	1	5	47	53	10	9	22	18
1	8	27	32	-3	6	67	68	1	6	43	40	11	8	12	9
1	0	18	21	-3	7	36	32	1	7	20	19	12	5	9	8
1	2	13	14	-3	8	8	14	1	0	21	19	K=2			
2	6	61	55	-3	0	9	10	1	1	9	10	0	3	58	60
2	8	9	10	-3	1	26	29	2	2	21	18	0	4	122	125
2	0	34	34	-4	3	18	22	2	3	20	19	0	5	120	101
2	2	16	18	-4	4	35	40	2	4	29	33	0	6	38	31
3	2	42	42	-4				2	5	12	16				

Table 14. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
0	7	37	35	2	6	20	21	-3	5	23	29	5	6	34	36
0	8	26	26	2	7	14	11	-3	6	26	27	5	9	18	23
-1	3	206	197	2	8	15	11	-3	7	10	12	5	0	13	18
-1	4	23	35	3	2	72	82	-3	9	11	12	6	7	12	12
-1	5	60	47	3	3	8	3	-3	0	20	20	7	6	12	12
-1	6	60	54	3	6	55	60	-4	3	52	54	7	7	34	38
-1	7	66	59	3	7	46	50	-4	4	48	52	7	0	23	23
-1	0	11	13	3	8	11	9	-4	5	16	21	7	1	13	14
-2	2	185	187	3	9	28	29	-4	6	34	35	7	2	13	11
-2	3	16	14	3	0	20	15	-4	7	14	14	8	6	13	16
-2	4	20	23	4	5	42	46	-4	8	22	21	3	6	14	17
-2	5	67	78	4	6	46	51	-4	9	11	9	6	5	58	50
-2	6	8	5	4	7	49	54	-4	0	17	18				
-2	7	50	53	4	8	11	13	-4	1	22	19				
-2	8	14	14	4	0	12	14	-4	2	18	15				
-3	4	51	49	5	5	18	23	-5	4	22	28	0	4	47	38
-3	5	38	42	5	7	25	18	-5	5	20	25	0	5	40	33
-3	6	65	70	5	9	27	21	-5	6	48	50	0	6	14	10
-3	7	34	39	6	5	36	42	-5	8	26	24	0	7	22	20
-3	8	25	24	6	6	11	14	-5	1	22	21	0	8	54	44
-3	9	22	19	6	8	17	16	-6	5	15	18	0	9	21	24
-3	0	30	27	7	5	16	13	-6	9	25	27	0	0	15	14
-4	4	25	29	7	6	21	23	-6	2	27	24	-1	4	99	93
-4	5	59	59	7	8	17	19	-7	5	62	61	-1	5	63	62
-4	6	43	43	8	5	32	38	-7	6	12	13	-1	6	49	45
-4	7	14	11	9	5	12	14	-7	9	12	14	-1	9	20	21
-4	8	10	13	9	6	12	15	-8	5	28	31	-1	1	13	14
-4	9	11	11	9	7	12	15	-8	6	25	30	-2	3	19	19
-4	0	16	21	9	8	12	11	-8	8	18	16	-2	4	26	33
-5	5	56	62	9	9	12	13	-9	6	35	35	-2	5	46	43
-5	7	24	26					-9	8	19	16	-2	6	17	15
-5	8	11	11					1	3	22	19	-2	7	26	35
-5	9	11	13					1	5	36	43	-2	8	34	42
-6	5	26	29	0	3	79	86	1	6	64	59	-2	9	11	17
-6	7	25	22	0	4	107	105	1	7	13	18	-2	0	23	21
-6	0	17	14	0	5	86	78	1	8	10	8	-2	1	24	23
-7	5	19	20	0	6	62	60	1	9	11	11	-2	2	13	9
-7	7	26	25	0	7	67	65	1	1	17	16	-3	3	19	18
-8	5	26	25	0	9	29	31	1	2	23	24	-3	4	91	90
-8	6	12	12	0	2	13	11	2	4	80	75	-3	5	28	29
-9	5	12	11	-1	3	15	16	2	5	21	22	-3	7	19	23
-9	7	17	18	-1	4	82	78	2	6	85	82	-3	8	11	14
-9	8	18	16	-1	5	127	125	2	7	22	22	-3	9	18	17
-9	9	22	18	-1	6	19	22	2	8	15	17	-3	0	8	9
-10	5	22	26	-1	2	18	22	2	0	32	32	-3	1	9	7
-10	6	18	20	-2	2	118	112	2	1	18	12	-3	2	22	22
-10	8	22	22	-2	3	45	41	3	2	15	21	-4	5	70	64
-10	0	18	13	-2	6	113	113	3	4	19	17	-4	6	18	22
1	2	71	72	-2	7	9	10	3	7	15	17	-4	7	15	15
1	3	97	84	-2	8	10	11	3	8	11	16	-4	8	24	30
1	4	56	54	-2	9	19	20	3	0	33	40	-4	0	24	24
1	5	25	24	-2	0	23	24	4	5	25	26	-5	5	72	69
1	7	16	16	-2	2	13	11	4	6	84	91	-5	6	29	37
1	0	20	18	-3	2	107	97	4	7	30	34	-5	7	8	8
2	2	45	43	-3	3	53	45	4	0	28	27	-5	8	8	9
2	5	94	94	-3	4	8	8	5	5	22	22	-5	9	12	13

Table 14. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-5	0	13	10	7	5	13	14	-8	6	25	26	K=6			
-5	1	9	6	7	6	33	40	-8	7	26	23				
-5	2	17	13	7	7	13	15	-8	8	18	20	0	8	15	16
-6	5	24	32	7	8	17	20	-9	0	14	12	0	0	22	22
-6	6	17	19	8	8	14	18	-10	5	14	15	0	1	19	14
-6	7	23	24	8	0	15	16	-10	7	14	12	-1	5	13	16
-6	8	22	25	9	5	17	21	1	4	29	34	-1	6	18	16
-6	0	13	17	9	6	14	14	1	5	20	26	-1	7	40	45
-7	6	12	18	9	8	10	13	1	6	12	11	-1	8	11	11
-7	7	9	9	9	9	15	12	1	7	43	47	-1	9	26	27
-7	0	10	11	11	5	10	12	1	8	31	32	-1	0	28	30
-8	5	16	17	11	6	15	14	1	9	15	15	-2	4	42	39
-8	8	13	17	K=5				1	0	20	16	-2	5	69	66
-8	9	17	17					1	1	22	21	-2	6	32	40
-8	1	14	13	0	5	23	27	1	2	18	17	-2	9	12	10
-10	5	17	20	0	6	48	51	2	3	49	45	-2	0	12	12
-10	6	14	15	0	7	35	34	2	4	7	11	-2	1	13	17
-10	9	14	12	0	9	38	37	2	5	11	15	-3	5	40	37
-10	0	15	14	0	0	11	12	2	6	13	15	-3	6	56	51
-11	7	15	14	0	1	12	9	2	7	17	17	-3	8	16	20
1	3	36	30	0	4	88	91	2	8	10	5	-3	9	12	9
1	4	81	71	-1	5	33	34	2	9	16	18	-3	0	22	20
1	5	57	54	-1	6	51	50	2	1	12	12	-3	1	36	36
1	6	84	75	-1	7	18	17	2	2	19	19	-4	4	12	19
1	9	8	9	-1	8	14	12	3	3	105	104	-4	1	14	10
1	0	8	12	-1	9	19	13	3	4	8	9	-4	2	14	13
1	2	9	13	-1	0	11	7	3	5	41	49	-5	5	40	37
2	3	53	50	-1	4	74	78	3	6	31	34	-5	6	16	20
2	4	8	8	-2	5	13	10	3	7	23	24	-5	7	27	26
2	5	81	79	-2	6	23	21	3	8	27	28	-5	8	21	20
2	6	15	14	-2	7	50	55	3	9	24	23	-5	9	37	38
2	7	10	12	-2	9	15	16	3	0	12	9	-5	1	14	10
2	8	63	59	-2	0	26	19	3	2	13	8	-6	5	67	73
2	0	24	25	-2	3	46	45	4	6	10	10	-6	6	24	29
3	3	14	20	-3	5	16	17	4	7	11	8	-7	5	18	19
3	4	61	56	-3	6	29	26	4	8	16	15	-7	7	19	13
3	5	58	55	-3	7	34	33	4	9	21	17	-7	9	25	23
3	6	10	12	-3	8	18	15	4	0	18	15	-8	5	48	49
3	7	13	14	-3	0	24	20	5	1	19	13	-8	6	28	31
3	8	12	16	-3	1	17	14	5	5	35	40	-8	9	33	30
3	9	15	14	-3	7	27	25	5	6	46	45	-12	5	23	21
3	0	9	8	-4	8	29	30	6	0	51	42	1	5	24	22
4	5	17	17	-4	0	21	17	6	6	38	45	1	6	67	58
4	6	11	13	-4	1	18	17	6	8	13	13	1	7	59	58
4	8	12	15	-4	5	32	28	6	9	27	27	1	8	22	24
4	9	9	9	-5	7	38	31	7	5	22	28	1	9	34	33
4	0	16	16	-5	8	26	25	7	6	18	21	1	0	18	13
4	1	14	16	-5	0	40	45	7	7	23	27	1	1	19	15
4	2	10	9	-5	1	18	19	7	8	27	25	2	4	30	26
5	5	8	11	-5	2	13	15	8	5	18	18	2	5	15	14
5	6	27	29	-6	7	33	31	8	9	24	24	2	7	38	42
5	9	16	16	-6	9	17	14	9	5	19	17	2	8	20	24
5	1	10	10	-6	0	22	18	9	6	20	21	2	9	17	14
6	7	16	17	-7	5	20	20	9	7	14	14	2	2	14	12
6	8	16	22	-8	5	18	19					2	3	22	17
6	0	22	23									3	4	39	50

Table 14. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	K	FO	FC
3	5	37	42	1	8	51	53	-5	10	11	7	0	12	95	91
3	6	15	17	1	9	12	12	-6	5	11	10	0	14	84	80
3	9	13	11	1	0	35	39	-6	6	29	29	0	18	61	63
3	1	14	14	2	4	65	69	-6	8	20	18	0	20	22	23
4	5	28	32	2	5	15	10	-6	9	38	37	0	22	20	22
4	9	19	15	2	6	14	13	-6	10	12	9	1	4	108	108
5	6	21	29	2	7	24	25	-7	5	25	20	1	6	17	18
5	7	37	42	2	8	31	33	-7	9	28	26	1	7	40	35
6	5	18	20	2	9	12	12	-7	10	18	14	1	8	30	33
6	7	24	30	2	0	23	24	-7	11	12	14	1	9	24	28
7	6	14	13	3	7	16	15	-8	5	26	19	1	10	27	35
8	5	20	23	3	8	12	10	-8	6	35	31	1	13	27	24
8	6	21	16	3	0	14	10	-8	9	18	14	1	14	32	31
8	7	21	21	3	2	15	12	-9	6	19	14	1	15	66	73
8	8	15	10	4	4	34	43	-9	7	19	17	1	16	26	26
8	0	16	13	4	5	10	10	-9	9	13	9	1	17	33	32
9	5	21	20	4	7	21	23	-10	5	20	15	1	18	21	17
K=7				4	8	18	20	1	5	21	26	1	19	15	17
0	5	63	58	4	9	14	13	1	6	57	58	1	21	26	27
0	6	41	47	5	6	44	52	1	8	9	14	1	22	11	9
0	7	25	26	5	8	24	25	1	9	13	12	1	23	16	12
0	9	21	18	6	9	20	21	1	10	10	9	2	2	36	33
-1	6	58	55	6	6	36	37	2	5	12	15	2	4	91	98
-1	8	44	39	7	6	14	13	2	7	23	25	2	5	90	94
-1	9	12	12	7	8	31	29	2	8	34	41	2	6	44	47
-1	0	13	15	8	5	21	19	2	9	17	18	2	7	23	24
-2	6	9	7	8	8	16	19	2	10	10	6	2	8	73	76
-2	9	17	20	K=L				3	5	44	49	2	9	45	39
-3	5	26	23	0	5	21	27	3	6	17	17	2	10	53	51
-3	6	22	13	0	7	24	26	3	7	18	15	2	11	23	17
-3	8	40	42	0	8	42	42	3	8	24	26	2	12	51	46
-3	9	17	23	0	9	27	36	3	9	15	20	2	15	14	17
-3	0	26	27	0	10	13	12	4	10	11	10	2	16	35	33
-4	5	13	13	0	11	14	15	4	7	22	23	2	18	21	21
-4	6	37	35	0	12	15	13	4	8	28	28	2	22	31	30
-4	7	30	26	-1	5	30	34	5	9	16	17	3	3	74	70
-4	0	23	23	-1	6	16	16	5	5	44	40	3	5	43	40
-4	1	14	12	-1	8	8	9	5	6	31	29	3	6	38	40
-5	5	29	29	-1	10	9	8	5	8	17	16	3	7	154	146
-5	6	23	22	-1	11	10	12	6	8	22	17	3	8	50	49
-5	8	18	17	-1	12	14	17	6	9	18	15	3	9	61	58
-5	0	31	29	-2	5	10	10	7	5	29	28	3	11	31	32
-6	5	21	21	-2	6	42	40	7	6	19	13	3	12	26	21
-6	6	47	47	-2	8	43	51	7	8	13	16	3	13	36	35
-6	9	14	15	-2	9	32	44	8	5	27	18	3	15	27	28
-6	0	20	17	-3	6	47	51	8	6	19	16	3	16	14	10
-7	5	18	15	-3	10	17	18	9	5	20	17	3	17	15	15
-7	6	40	39	-3	11	14	18	9	8	20	19	3	19	45	51
-7	8	38	35	-4	7	26	26	11	5	19	15	3	21	37	40
-8	5	14	14	-4	8	32	31	H K FO FC				3	22	11	10
-8	8	21	18	-4	10	24	21	L=0				4	0	82	80
-8	9	15	16	-5	5	34	28					4	1	21	18
-8	0	15	9	-5	6	19	20					4	3	23	21
-10	6	22	20	-5	8	22	19	0	6	22	23	4	4	93	98
								0	10	111	109	4	5	27	31
								0	10	111	109	4	6	46	43

Table 14. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
4	7	43	51	7	18	11	14	0	21	31	36	12	5	14	13
4	8	38	38	7	19	16	16	0	22	16	19	12	6	9	10
4	9	37	34	8	0	44	40	0	24	13	13	12	7	9	8
4	10	13	16	8	1	29	27	1	4	75	74	12	8	14	12
4	11	16	14	8	2	25	24	1	5	13	9	12	9	19	18
4	12	29	30	8	3	29	30	1	6	23	22	2	11	40	37
4	13	17	15	8	4	41	43	1	7	51	44	2	12	17	17
4	16	26	25	8	5	27	25	1	8	23	22	2	13	49	52
4	17	15	14	8	8	34	32	1	10	27	29	2	14	13	13
4	21	26	26	8	10	16	15	1	11	31	30	2	15	29	33
4	22	23	21	8	14	16	18	1	12	25	31	2	16	16	13
4	23	20	11	8	16	16	12	1	14	27	27	2	17	20	20
5	0	58	54	9	5	23	26	1	15	10	8	2	19	15	18
5	1	31	40	9	7	43	46	1	16	47	53	2	20	12	10
5	3	113	110	9	11	16	18	1	20	20	21	2	23	13	10
5	4	29	35	10	4	31	27	1	21	9	10	2	24	13	11
5	6	25	24	10	6	16	13	1	24	13	15	3	1	123	118
5	7	21	24	10	7	16	18	1	25	10	9	3	2	52	58
5	8	13	12	10	8	23	29	2	2	46	45	3	3	80	83
5	9	26	29	10	10	23	20	2	3	25	25	3	5	24	33
5	11	45	51	11	4	16	16	2	4	128	120	3	6	117	110
5	14	24	26	11	5	16	12	2	5	76	74	3	7	63	59
5	15	19	21	11	7	16	16	2	6	121	117	3	8	65	64
5	16	15	16	11	11	19	17	2	7	12	11	3	9	105	102
5	17	19	19	12	3	15	11	2	8	65	56	3	10	24	25
5	18	23	19	12	8	28	19	2	9	78	77	3	11	43	47
5	19	11	10	12	10	14	9	2	10	36	38	3	13	10	9
5	21	11	12					9	3	28	30	3	14	35	45
6	0	141	142			L=1		9	4	21	22	3	15	21	21
6	1	26	27					9	5	13	12	3	17	14	15
6	2	34	38	8	1	29	33	9	6	57	58	3	18	12	16
6	3	56	56	8	5	13	14	9	8	30	32	3	20	41	42
6	4	49	50	8	6	16	17	9	9	16	17	3	21	9	9
6	5	37	42	8	7	29	34	9	10	13	12	3	22	16	17
6	7	14	13	8	9	37	38	9	11	9	11	3	23	9	8
6	8	25	28	8	10	26	26	9	12	27	23	4	1	29	33
6	11	28	31	8	13	33	29	9	13	13	13	4	2	62	64
6	12	61	64	8	14	13	11	9	7	9	8	4	3	72	70
6	13	44	43	8	15	13	17	10	1	17	17	4	4	52	44
6	14	29	30	0	16	47	55	10	2	9	10	4	5	96	100
6	17	20	22	8	16	9	8	10	3	26	25	4	6	29	30
6	18	23	22	8	20	10	7	10	5	29	28	4	7	18	15
6	20	11	10	8	21	14	15	10	7	9	13	4	8	32	36
6	21	20	19	9	1	27	25	10	9	37	41	4	9	69	75
6	22	11	12	0	5	13	14	10	11	14	14	4	11	18	17
7	0	67	67	0	6	35	29	11	1	14	15	4	12	24	24
7	1	47	48	0	8	19	19	11	2	10	7	4	13	8	7
7	2	67	61	0	9	21	28	11	3	10	8	4	14	21	20
7	3	42	48	0	10	76	68	11	4	14	9	4	15	35	41
7	8	40	40	0	11	16	14	11	6	31	30	4	17	15	15
7	10	33	34	0	12	9	9	11	8	17	16	4	18	15	16
7	11	19	24	0	13	39	41	11	9	14	11	4	19	15	15
7	12	22	22	0	15	28	34	11	10	14	12	4	21	9	11
7	13	30	26	0	17	39	43	11	12	14	9	4	22	13	16
7	15	23	21	0	18	22	18	12	1	14	12	4	23	17	18
7	17	11	13	0	19	19	12	12	3	14	12	5	4	42	45

Table 14. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
5	5	26	29	-1	11	25	25	-4	6	40	42	-7	18	13	14
5	6	72	67	-1	12	23	23	-4	8	31	31	-7	20	19	20
5	7	13	9	-1	13	39	42	-4	11	34	33	-8	1	24	21
5	8	49	54	-1	14	23	23	-4	13	66	63	-8	2	31	34
5	10	18	14	-1	15	20	18	-4	14	21	26	-8	3	25	31
5	11	21	22	-1	16	44	47	-4	15	20	16	-8	4	20	21
5	12	37	37	-1	17	39	43	-4	16	12	11	-8	5	40	44
5	15	21	19	-1	18	11	10	-4	17	39	44	-8	8	13	9
5	19	16	14	-1	19	15	17	-4	19	22	27	-8	10	13	14
5	20	19	19	-1	20	33	39	-4	20	20	25	-8	15	13	12
6	1	76	76	-1	21	9	6	-4	22	13	14	-8	16	13	15
6	2	16	17	-1	24	9	9	-4	23	13	12	-8	17	26	30
6	3	45	50	-2	2	88	90	-5	1	40	43	-8	19	17	16
6	6	11	11	-2	3	129	119	-5	2	45	49	-8	20	14	9
6	7	16	12	-2	4	71	76	-5	4	92	84	-9	1	19	21
6	8	23	28	-2	5	83	80	-5	5	39	44	-9	2	26	25
6	9	48	51	-2	6	88	82	-5	9	7	4	-9	4	21	19
6	10	38	47	-2	7	52	48	-5	10	39	42	-9	5	23	25
6	11	30	29	-2	8	64	60	-5	11	19	20	-9	6	13	12
6	12	26	24	-2	10	57	53	-5	12	21	25	-9	7	9	8
6	13	43	40	-2	12	12	15	-5	13	37	38	-9	8	9	11
6	14	12	14	-2	13	21	21	-5	14	27	28	-9	9	9	9
6	15	29	31	-2	14	10	7	-5	15	12	14	-9	10	9	6
6	17	21	20	-2	15	26	29	-5	16	21	22	-9	13	13	14
6	20	13	16	-2	17	49	52	-5	17	12	9	-9	14	27	28
6	21	17	17	-2	18	19	22	-5	18	16	14	-9	15	9	7
6	22	14	14	-2	19	17	17	-5	19	18	20	-9	16	17	16
7	2	67	68	-2	20	22	21	-5	20	16	17	-9	17	14	13
7	3	12	14	-2	22	9	8	-5	24	10	12	-9	18	9	9
7	4	15	17	-2	23	16	18	-6	1	27	30	-9	19	9	9
7	5	21	23	-2	24	17	14	-6	3	31	36	-9	20	14	16
7	6	12	10	-2	25	10	4	-6	4	34	34	-10	2	9	10
7	7	17	17	-2	26	10	8	-6	5	30	30	-10	4	13	14
7	8	19	17	-3	2	75	80	-6	9	25	27	-10	5	24	24
7	12	24	28	-3	3	122	116	-6	10	26	30	-10	6	13	11
7	14	9	6	-3	4	107	108	-6	12	21	21	-10	9	22	24
7	16	30	32	-3	5	17	23	-6	13	12	10	-10	13	14	13
7	18	13	12	-3	6	66	70	-6	14	8	6	-10	14	22	21
7	20	9	7	-3	7	26	25	-6	15	15	16	-10	16	14	15
7	22	10	10	-3	8	81	86	-6	16	29	31	-10	17	9	10
8	2	22	24	-3	10	27	29	-6	17	28	30	-10	20	13	11
8	3	22	24	-3	11	21	22	-6	20	13	13	-11	1	14	19
8	4	18	16	-3	13	10	11	-6	21	22	17	-11	5	20	19
8	12	9	5	-3	14	74	76	-6	23	14	12	-11	6	14	12
12	10	9	3	-3	16	28	30	-7	1	60	65	-11	7	10	10
12	13	13	11	-3	17	12	11	-7	2	45	48	-11	8	10	8
13	2	13	13	-3	18	12	8	-7	6	34	39	-11	10	24	21
13	10	12	13	-3	19	8	7	-7	7	24	31	-11	12	9	11
13	12	15	12	-3	20	24	25	-7	8	8	7	-11	17	16	17
-1	4	68	62	-3	22	21	23	-7	10	31	32	-11	19	9	12
-1	5	46	53	-3	23	13	10	-7	11	23	23	-12	1	14	12
-1	6	105	97	-4	1	60	57	-7	12	22	26	-12	2	14	12
-1	7	55	54	-4	2	28	34	-7	13	20	19	-12	4	14	11
-1	8	42	39	-4	3	38	34	-7	15	18	18	-12	9	14	12
-1	9	57	53	-4	4	9	12	-7	16	25	23	-13	1	13	12
-1	10	27	27	-4	5	66	66	-7	17	9	9	-13	2	13	10

Table 14. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-13	5	9	7	3	3	18	21	6	13	16	18	10	5	15	14
-13	6	13	9	3	4	55	47	6	14	25	25	10	6	11	6
				3	6	21	7	6	17	17	21	10	7	27	23
				3	7	50	36	6	18	14	11	10	8	15	25
				3	8	56	57	6	20	15	15	10	10	27	26
				3	9	39	38	6	21	10	8	10	12	11	9
				3	10	35	36	6	22	15	13	11	0	22	24
				3	11	82	76	6	23	11	9	11	5	25	25
				3	13	19	17	6	25	11	10	11	7	33	34
				3	15	48	52	6	26	11	10	11	11	16	12
				3	18	13	8	7	0	55	65	12	2	16	15
				3	23	14	12	7	1	29	33	12	3	16	15
				4	3	47	44	7	2	26	27	12	4	16	15
				4	4	30	33	7	3	18	24	12	5	16	15
				4	5	98	95	7	5	40	45	12	7	11	9
				4	6	59	62	7	6	13	12	12	8	25	21
				4	7	80	78	7	7	9	10	12	9	11	10
				4	8	63	59	7	8	9	8	12	10	11	12
				4	9	18	17	7	10	27	23	13	0	16	14
				4	10	61	54	7	11	26	26	13	2	11	12
				4	11	25	23	7	12	31	34	13	3	11	9
				4	12	23	23	7	14	27	22	13	9	11	8
				4	14	35	38	7	15	14	13	13	10	11	7
				4	15	15	19	7	17	15	18	13	11	11	10
				4	16	20	16	7	21	15	9	13	12	10	8
				4	19	22	26	7	23	19	14	-1	7	34	31
				4	26	15	13	8	0	50	54	-1	8	96	99
				5	0	37	40	8	1	14	14	-1	9	16	18
				5	2	23	20	8	2	14	14	-1	10	33	42
				5	4	38	42	8	3	28	28	-1	11	16	17
				5	5	79	74	8	5	14	13	-1	12	9	4
				5	6	25	25	8	6	17	11	-1	13	7	4
				5	7	96	97	8	7	10	9	-1	14	34	39
				5	8	35	34	8	8	45	40	-1	15	61	60
				5	9	18	12	8	10	27	23	-1	16	14	15
				5	10	25	26	8	12	33	35	-1	17	34	37
				5	11	46	45	8	14	36	42	-1	18	19	21
				5	13	15	17	8	15	15	14	-1	19	40	41
				5	15	18	21	8	16	18	18	-1	20	21	22
				5	16	13	13	8	17	10	4	-1	22	14	13
				5	19	14	13	8	18	11	4	-1	26	11	11
				5	20	10	10	8	20	19	17	-1	27	11	10
				5	21	14	13	8	22	11	9	-2	6	43	49
				5	29	16	13	8	26	15	13	-2	7	105	112
				6	0	22	25	9	2	14	17	-2	8	58	54
				6	1	27	26	9	3	14	19	-2	9	27	26
				6	2	21	18	9	4	28	28	-2	10	9	11
				6	3	22	22	9	5	21	19	-2	11	30	38
				6	4	49	49	9	7	33	31	-2	12	40	49
				6	5	21	20	9	8	15	14	-2	13	23	30
				6	6	12	11	9	11	40	44	-2	14	11	7
				6	8	75	70	9	14	15	12	-2	15	8	8
				6	9	22	19	9	15	15	12	-2	16	41	49
				6	10	41	44	9	16	15	14	-2	17	12	13
				6	11	53	56	9	17	11	5	-2	18	38	38
				6	12	16	15	10	4	24	23	-2	19	13	14

Table 14. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-2	20	16	16	-6	2	16	16	-9	12	10	13	0	24	18	20
-2	22	10	9	-6	5	11	10	-9	13	18	17	0	25	13	11
-3	4	112	104	-6	6	36	39	-9	14	10	8	1	9	69	71
-3	5	59	56	-6	7	29	32	-9	15	10	9	1	10	45	49
-3	7	21	22	-6	8	19	18	-9	16	22	24	1	11	40	41
-3	10	67	65	-6	9	21	20	-9	18	15	19	1	12	52	53
-3	11	36	40	-6	11	54	59	-9	19	15	15	1	13	40	40
-3	12	32	34	-6	13	32	37	-9	21	11	11	1	15	37	41
-3	13	27	25	-6	16	19	19	-10	2	15	14	1	17	10	9
-3	14	14	19	-6	17	10	10	-10	3	15	9	1	18	29	33
-3	15	29	32	-6	18	14	16	-10	4	15	11	1	19	25	25
-3	16	12	9	-6	19	10	10	-10	5	10	10	1	21	21	25
-3	17	12	10	-6	22	10	9	-10	6	10	11	1	24	18	14
-3	18	16	15	-6	23	11	13	-10	7	28	32	1	25	19	14
-3	25	15	10	-6	25	15	14	-10	8	10	9	2	8	31	33
-4	0	58	55	-7	0	40	46	-10	15	15	16	2	9	90	87
-4	2	24	23	-7	1	40	42	-10	12	15	18	2	10	68	61
-4	3	78	76	-7	2	18	17	-10	19	11	9	2	11	25	29
-4	5	83	78	-7	3	34	35	-10	21	11	12	2	12	38	40
-4	6	21	17	-7	4	31	31	-11	0	15	14	2	13	25	30
-4	7	54	55	-7	5	13	13	-11	3	15	17	2	14	26	28
-4	8	32	35	-7	8	24	19	-11	4	19	21	2	15	23	21
-4	9	16	17	-7	9	13	13	-11	5	15	14	2	17	15	14
-4	10	18	23	-7	10	9	7	-11	6	15	13	2	18	16	18
-4	11	25	29	-7	11	9	6	-11	7	11	3	2	19	16	13
-4	12	21	25	-7	12	26	24	-11	8	11	8	2	20	21	21
-4	13	11	9	-7	13	14	16	-11	9	11	6	2	21	21	20
-4	14	22	20	-7	14	31	35	-11	10	11	12	2	23	13	10
-4	15	23	23	-7	15	30	34	-11	11	15	14	2	24	19	21
-4	16	12	16	-7	16	10	9	-11	16	15	12	3	6	65	63
-4	17	9	8	-7	18	10	12	-11	18	11	9	3	9	31	29
-4	18	9	9	-7	19	21	22	-12	0	27	24	3	10	69	60
-4	19	16	18	-7	21	11	10	-12	1	11	9	3	12	59	59
-4	20	10	9	-7	22	11	9	-12	2	16	11	3	13	31	39
-4	21	14	11	-8	0	27	35	-12	3	19	20	3	17	22	22
-4	22	14	15	-8	1	25	28	-12	11	16	15	3	19	21	21
-4	24	15	9	-8	3	29	34	-12	12	11	9	3	21	12	10
-5	0	22	23	-8	4	29	27	-12	15	15	11	3	22	13	14
-5	1	47	53	-8	5	22	23	-13	0	28	27	3	24	19	18
-5	3	56	59	-8	6	26	24	-13	2	16	14	4	2	19	20
-5	4	48	53	-8	8	31	36	-13	7	11	9	4	3	36	36
-5	5	37	38	-8	10	14	17	-13	12	15	13	4	4	17	10
-5	7	29	31	-8	12	14	10	-13	14	10	8	4	5	81	75
-5	8	42	42	-8	15	31	30	-10	10	11	9	4	6	48	42
-5	9	14	19	-8	16	26	28					4	7	35	32
-5	10	18	22	-8	17	15	14					4	8	48	47
-5	11	25	29	-8	18	28	31					4	9	46	44
-5	12	15	17	-8	19	15	11					4	10	19	15
-5	14	20	14	-8	20	11	9					4	12	10	8
-5	15	20	19	-9	0	32	37					4	13	37	38
-5	17	13	14	-9	1	10	11					4	14	27	25
-5	19	17	17	-9	3	17	22					4	16	28	32
-5	22	10	10	-9	4	32	40					4	17	11	12
-5	25	15	16	-9	5	14	16					4	18	17	14
-6	0	36	38	-9	6	29	28					4	20	18	24
-6	1	21	24	-9	8	27	25					4	25	14	14

Table 14. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
5	1	31	34	9	12	20	21	-4	13	32	38	-8	3	27	27
5	2	31	31	9	17	14	16	-4	14	10	6	-8	5	21	20
5	3	34	37	10	1	14	17	-4	18	16	18	-8	11	26	24
5	5	40	40	10	6	20	18	-4	20	12	11	-8	12	13	14
5	6	69	64	10	8	20	21	-4	21	12	12	-8	15	13	15
5	8	30	29	10	13	20	21	-4	22	13	13	-8	16	19	18
5	9	36	30	-10	14	20	17	-4	24	19	21	-8	17	13	14
5	10	24	22	11	3	14	12	-5	1	25	18	-8	19	14	9
5	13	30	26	11	4	14	12	-5	2	57	57	-8	20	14	13
5	14	26	24	11	5	14	15	-5	3	8	12	-9	2	13	16
5	16	24	23	11	6	21	16	-5	4	27	27	-9	3	29	29
5	17	35	37	11	8	21	16	-5	5	43	50	-9	5	35	34
5	20	13	9	12	2	21	15	-5	6	28	29	-9	8	13	14
5	21	13	11	12	3	15	10	-5	7	29	31	-9	9	38	40
6	2	36	40	12	5	15	14	-5	8	21	23	-9	11	13	15
6	3	32	41	-1	9	52	45	-5	9	70	71	-9	17	20	17
6	4	15	17	-1	10	10	12	-5	10	17	18	-10	1	34	31
6	5	15	13	-1	12	14	10	-5	11	14	13	-10	3	19	19
6	6	15	12	-1	13	75	69	-5	12	15	17	-10	6	28	21
6	7	15	12	-1	16	22	22	-5	13	33	36	-10	11	24	28
6	8	30	34	-1	17	31	35	-5	14	19	25	-10	12	20	23
6	9	28	29	-1	18	15	16	-5	15	11	10	-10	13	20	18
6	10	33	29	-1	20	23	20	-5	16	16	22	-11	1	20	23
6	11	31	34	-1	21	17	16	-5	21	18	18	-11	2	14	13
6	12	12	11	-1	22	12	12	-6	1	29	29	-11	4	32	29
6	14	17	19	-1	25	13	11	-6	2	43	50	-11	6	20	22
6	15	22	19	-1	25	13	11	-6	3	17	15	-11	9	14	15
6	16	18	15	-1	27	14	10	-6	4	14	13	-11	10	14	11
6	17	22	20	-2	8	45	48	-6	6	23	24	-11	12	14	10
6	18	13	12	-2	9	22	21	-6	7	23	20	-11	13	14	15
7	1	47	54	-2	10	11	7	-6	8	10	7	-12	2	21	23
7	2	16	18	-2	11	11	17	-6	9	10	9	-12	4	15	15
7	4	31	36	-2	12	35	38	-6	10	59	65	-12	10	21	19
7	6	63	66	-2	13	13	15	-6	12	49	48	-12	10	21	19
7	7	21	22	-2	14	23	20	-6	16	17	14	-13	1	21	16
7	8	32	30	-2	15	14	17	-6	17	18	20				
7	11	17	14	-2	16	29	33	-6	19	18	16				
7	12	28	26	-2	17	24	25	-6	22	13	16				
7	13	41	37	-2	18	11	10	-6	24	14	15				
7	16	19	11	-2	19	11	14	-7	1	38	43	0	10	54	51
7	18	19	15	-3	7	37	35	-7	2	31	28	0	11	40	42
8	2	51	51	-3	8	41	39	-7	3	33	33	0	12	31	36
8	4	28	27	-3	9	94	95	-7	4	35	36	0	14	10	10
8	9	35	32	-3	10	70	68	-7	5	34	33	0	15	26	28
8	10	18	17	-3	11	21	23	-7	6	28	32	0	16	11	13
8	11	19	18	-3	13	38	40	-7	8	28	26	0	17	25	24
8	13	19	19	-3	17	29	31	-7	9	29	26	0	18	12	16
8	14	23	21	-3	21	17	15	-7	12	17	18	0	19	27	27
8	15	19	18	-3	22	12	9	-7	13	21	25	1	10	26	32
8	16	19	20	-4	5	37	33	-7	14	12	17	1	11	37	40
8	21	14	15	-4	6	76	69	-7	15	18	20	1	12	31	36
9	1	23	22	-4	8	48	56	-7	16	18	18	1	14	46	51
9	4	19	16	-4	9	63	60	-7	17	18	18	1	15	15	16
9	5	13	14	-4	10	20	17	-7	18	13	15	1	17	16	17
9	6	13	10	-4	11	21	20	-7	19	13	10	1	18	21	24
9	10	19	21	-4	12	53	54	-7	20	13	13	1	22	24	23
								-8	2	21	20	2	9	36	32

L=4

CHAPTER III

RESULTS AND DISCUSSION

Complexes of N-(3-hydroxypropylsalicylimine)

Several new complexes of the Schiff base ligand N-(3-hydroxypropylsalicylimine), SALPAH_2 , have been prepared and studied. As was indicated in the experimental section, these include complexes of Cu, Co, Ni and Fe.

Analytical data for the product of the reaction of equimolar amounts of nickel acetate and SALPAH_2 in methanol indicated that the resulting green complex corresponded to one ligand and one molecule of solvent per metal ion. Kirkwood (56) prepared the same complex, using ethanol as the solvent, by adding two moles of sodium ethoxide per mole of ligand. It was found that the green solvated species could be converted into a reddish-brown unsolvated material by recrystallization from anhydrous m-Xylene. This behavior was exactly the same that Kirkwood found for the Ni(EIA) complex (18). The solvated Ni(EIA) was also green and paramagnetic, while the unsolvated complex could also be prepared by recrystallization from m-Xylene. The unsolvated, reddish-brown Ni(EIA) was found to be diamagnetic and to have a bent dimeric structure in which the nickel coordination was square planar.

Attempts at obtaining a single crystal of the green Ni(SALPA)•
ETOH suitable for X-ray studies were not successful. For all of the
crystals, examination through the polarizing microscope revealed several

micro crystals stacked together or the precession photographs indicated a polycrystalline material. The red unsolvated Ni(SALPA) complex appeared to give single crystals, but the systematic absences were not consistent with any space group.

Based upon the information known about the Ni(EIA) complexes and the available analytical data, the red, unsolvated Ni(SALPA) complex is probably polynuclear with square planar coordination of the nickel ions, whereas the solvated Ni(SALPA) \cdot EtOH complex is probably polynuclear with a higher coordination number.

The cobalt(II) complex obtained with the ligand SALPAH₂ using two moles of KOH per mole of ligand and a ratio of ligand to CoAc₂ \cdot of 1:1, analyzed for one ligand per metal ion, but as a hemihydrate, Co(SALPA) \cdot $\frac{1}{2}$ H₂O. With $\mu_{\text{eff}} = 4.41$ B.M. the magnetic moment appears reasonable for a cobalt(II) complex (μ_{eff} is found to be 4.1-5.2 B.M. for cobalt(II) (62)). Since there is only one ligand per metal ion, there is a good possibility that the complex has associated into a polynuclear unit in order for the metal ion to be at least four-coordinate. However, single crystals sufficiently large for X-ray investigations were not obtained.

The Cu(SALPAH)Cl complex was made by mixing the free ligand, SALPAH₂, with CuCl₂ in a 2:1 ratio in a methanol solution without base. However, the Fe(SALPA)Cl complex was prepared using two equivalents of lithium methoxide per equivalent of ligand and a ratio of ligand to FeCl₃ \cdot 5H₂O of 1:1. In the copper(II) complex, the ligand had to exist as a monoanion in order for a chloride to be present in a neutral

complex. It was assumed that the proton had not been removed since the acidity of this proton is normally less than that of a phenolic proton; whereas, in the case of the iron(III) complex it appeared that the ligand was a dianion with the chloride balancing the remaining charge of the metal ion.

Interestingly enough, the $\text{Cu}(\text{SALPAH})\text{Cl}$ complex was brown, whereas both $\text{Cu}(\text{PIA})$ and $\text{Cu}(\text{SALPA})$ gave deep purple complexes with subnormal magnetic moments. As indicated in the introductory section, $\text{Cu}(\text{PIA})$ was found to be a square-planar dimer and based on the similarity of the magnetic properties and the ligands, the complexes are presumed to be isostructural. In addition, attempts at recrystallization of $\text{Cu}(\text{SALPAH})\text{Cl}$ from methanol yielded the purple $\text{Cu}(\text{SALPA})$ complex reported by Yamada (63). In order to recrystallize $\text{Cu}(\text{SALPAH})\text{Cl}$, the addition of a few drops of HCl was necessary to prevent the complex from going to $\text{Cu}(\text{SALPA})$ via loss of HCl .

The X-ray structure determinations of the complexes $\text{Cu}(\text{SALPAH})\text{Cl}$ * $\text{Fe}(\text{SALPA})\text{Cl}$ and the solvated form of the iron complex, $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$, revealed that, with both copper(II) and iron(III), dimeric, five-coordinate complexes were formed. Since the alcohol oxygen retained the proton and would have to be bonded to four sites if it acted as a bridging group, the phenolic oxygen is the bridging group in $\text{Cu}(\text{SALPAH})\text{Cl}$. As is normally found in Schiff base complexes formed from β -diketones and salicylaldehyde with amino alcohols, the less-sterically hindered alcohol oxygen acts as the bridging group in the $\text{Fe}(\text{SALPA})\text{Cl}$

*This structure was performed by co-worker, J. A. Kelley (5).

complex. The structure of the solvated iron complex, $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$ was determined since only very small crystals of $\text{Fe}(\text{SALPA})\text{Cl}$ could be obtained. Structurally, the two iron complexes are identical except for distortions that result from the packing of one toluene molecule per dimer in the crystal lattice. The closest contact of the toluene with any atoms within the structure is approximately 4 \AA , with the closest approach to the iron(III) being $5-6 \text{ \AA}$.

Perspective drawings of the molecular structures of $\text{Cu}(\text{SALPAH})\text{Cl}$ and $\text{Fe}(\text{SALPA})\text{Cl}$ are given in Figures 3 and 4, respectively. Since all of the molecules contain an inversion center, the four-membered metal-oxygen ring is exactly planar. The Cu-O distances within the M_2O_2 four-membered ring for $\text{Cu}(\text{SALPAH})\text{Cl}$, 1.78 \AA and 2.22 \AA show a much larger difference than the corresponding distances in $\text{Cu}(\text{PIA})$, 1.86 \AA and 1.92 \AA . Also these metal oxygen distances for $\text{Cu}(\text{SALPAH})\text{Cl}$ differ more than those in $\text{Fe}(\text{SALPA})\text{Cl}$ or $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$, 1.86 \AA and 1.97 \AA , and 1.93 \AA and 1.98 \AA , respectively. The metal-metal distance in $\text{Cu}(\text{SALPAH})\text{Cl}$ is 3.29 \AA which is considerably longer than is found in dimeric $\text{Cu}(\text{PIA})$, 3.01 \AA (17), in the "cubane" $\text{Cu}(\text{EIA})$, 3.01 \AA and 3.26 \AA (17), or in the "stacked dimer" $\text{Cu}(\text{SALPYA})$, 3.07 \AA and 3.17 \AA (20). In addition, the metal-metal distance in $\text{Cu}(\text{SALPAH})\text{Cl}$ is longer than the distances for $\text{Fe}(\text{SALPA})\text{Cl}$, 3.12 \AA or $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$, 3.09 \AA .

As in $\text{Cu}(\text{PIA})$, the coordination of the bridging oxygen is essentially planar in $\text{Cu}(\text{SALPAH})\text{Cl}$. The carbon bonded to the phenolic oxygen, C3, is only 0.08 \AA out of the plane defined by the central four-membered ring. Table 16 gives the plane of the Cu-O four-membered ring

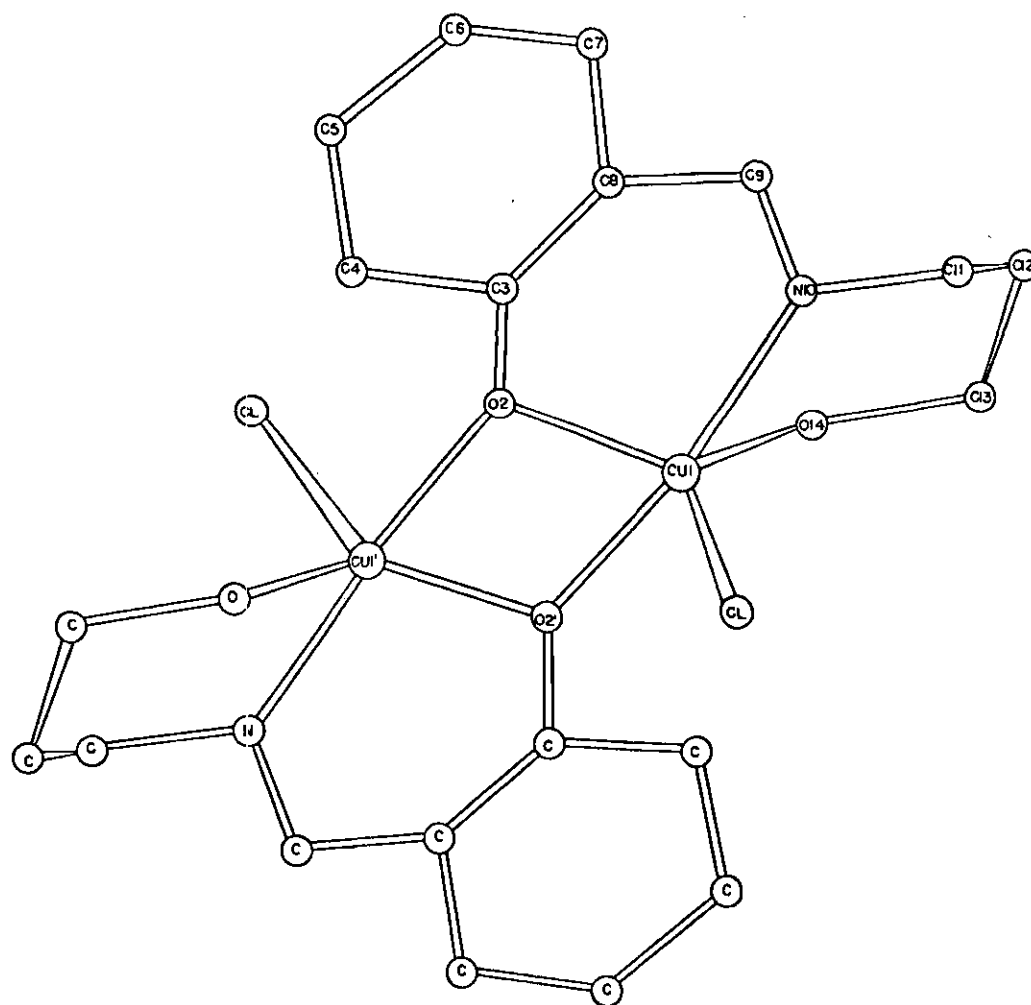


Figure 3. A Perspective Drawing of the Structure of Cu(SALPAH)Cl

and the best least-squares plane of the benzene ring portion of the ligand; the distances of the other atoms of the structure from these planes are indicated.

In $\text{Fe}(\text{SALPA})\text{Cl}$, the carbon which is bonded to the bridging alkoxyl oxygen, Cl3, is also only 0.08 \AA out of the plane of the M_2O_2 four-membered ring. Thus, the coordination of the oxygen does not differ significantly from planarity. In the complex $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$ the coordination of the oxygen is not as planar as in either $\text{Cu}(\text{SALPAH})\text{Cl}$ or $\text{Fe}(\text{SALPA})\text{Cl}$ since Cl3 is displaced 0.28 \AA from the plane of the M_2O_2 four-membered ring. The plane for the M_2O_2 four-membered rings, the best least squares planes for the benzene rings of the ligand, and the distances of the other atoms in the structure from each of these planes are given in Table 17.

Because of the long M-M distances there appears to be no reason for considering the possibility of explaining the lowering of the room temperature magnetic moments through direct M-M interactions. However, both $\text{Cu}(\text{SALPAH})\text{Cl}$ and $\text{Fe}(\text{SALPA})\text{Cl}$ have room temperature magnetic moments considerably below the values expected. The $\text{Cu}(\text{SALPAH})\text{Cl}$ complex has a magnetic moment of 1.05 B.M. as compared to the spin-only value of 1.86 B.M. for copper(II) and $\text{Fe}(\text{SALPA})\text{Cl}$ gave a room temperature magnetic moment of 4.23 B.M. as compared to the normal values for an iron(III) complex of $\sim 5.9 \text{ B.M.}$ (62). As in other polynuclear structures in which the coordination of the bridging oxygen is planar, a plausible explanation of the spin coupling in terms of a delocalized π -system involving the $3d_{xz}$ and $3d_{yz}$ orbitals of the oxygen is possible (17).

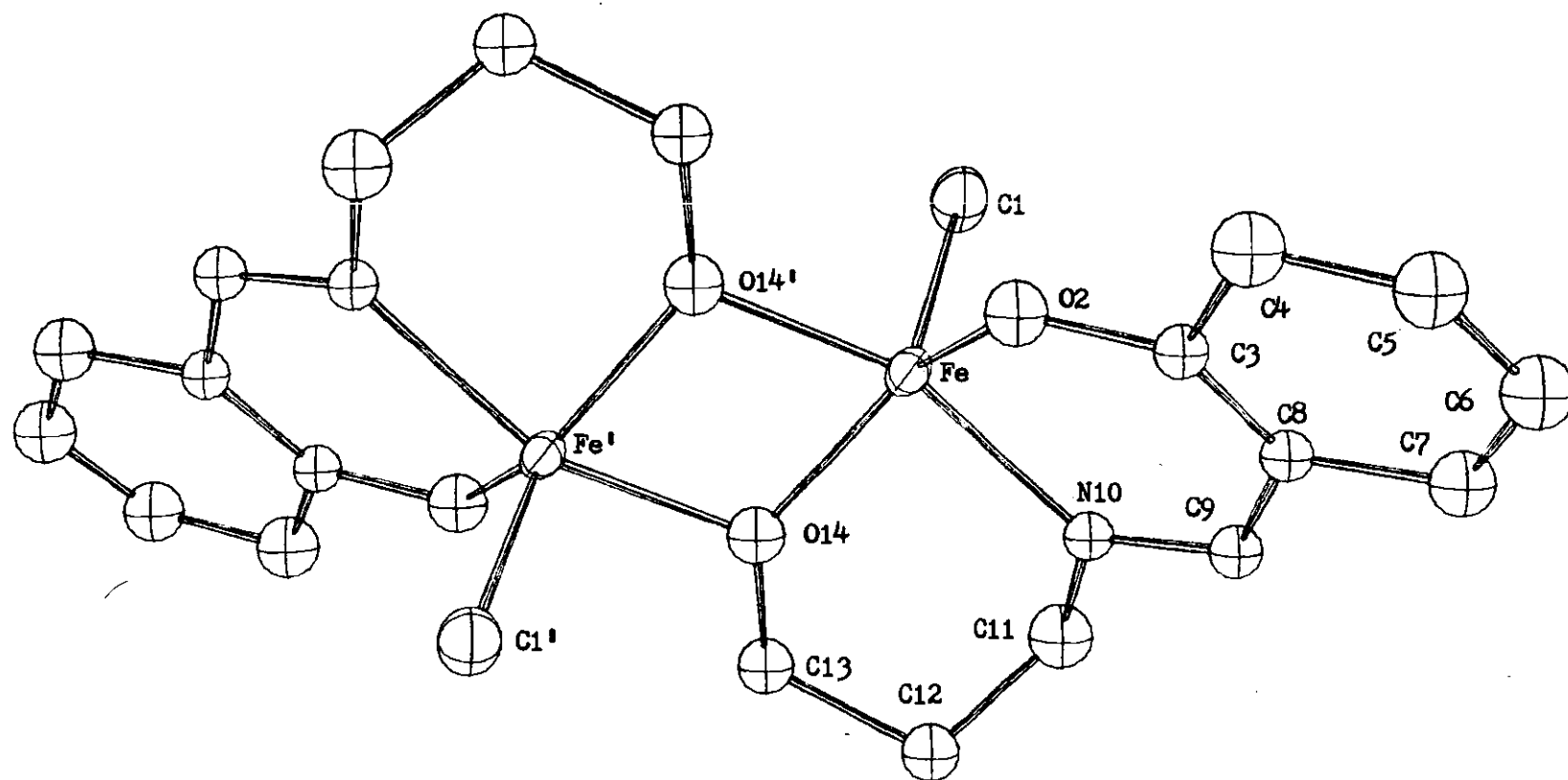


Figure 4. A Perspective Drawing of the Structure of Fe(SALPA)Cl

Table 15. Comparison of Bond Distances and Angles for
 $\text{Cu}(\text{SALPAH})\text{Cl}$, $\text{Fe}(\text{SALPA})\text{Cl}$, $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$

Atoms	$\text{Cu}(\text{SALPAH})\text{Cl}$ Distance, Å	$\text{Fe}(\text{SALPA})\text{Cl}$ Distance, Å	$\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$ Distance, Å
M1-M1'	3.294(7)	3.12(1)	3.089(6)
M1-Cl	2.115(6)	2.20(1)	2.226(6)
M1-O2	1.78(1)	1.87(2)	1.852(13)
M1-O2'	2.22(1)		
M1-O14'		1.97(3)	1.983(12)
O2-O2'	2.31(3)		
O14-O14'		2.23(3)	2.408(26)
M1-N10	2.18(2)	2.12(4)	2.064(13)
M1-O14	2.24(2)	1.86(3)	1.934(13)
O2-C3	1.34(2)	1.33(4)	1.366(17)
C3-C4	1.39(3)	1.51(6)	1.457(24)
C4-C5	1.38(3)	1.39(5)	1.419(26)
C5-C6	1.53(3)	1.42(5)	1.328(24)
C6-C7	1.34(3)	1.31(5)	1.436(24)
C7-C8	1.41(3)	1.41(5)	1.417(21)
C3-C8	1.48(3)	1.43(5)	1.347(19)
C8-C9	1.41(3)	1.42(5)	1.479(21)
C9-N10	1.19(2)	1.28(4)	1.305(19)
N10-C11	1.54(3)	1.70(7)	1.528(24)
C11-C12	1.60(3)	1.45(6)	1.522(27)
C12-C13	1.63(3)	1.57(6)	1.577(23)
C13-O14	1.53(3)	1.59(6)	1.469(19)

Table 15. (Continued)

Atoms	Cu(SALPAH)Cl Angle, Degrees	Fe(SALPA)Cl Angle, Degrees	Fe(SALPA)Cl· $\frac{1}{2}$ TOL Angle, Degrees
M1-O2-M1'	110.3(6)		
O2-M1-O2'	69.7(6)		
Cl-M1-O2	126.2(5)	108.7(8)	112.5(5)
Cl-M1-O2'	98.6(4)		
Cl-M1-O14	110.1(4)	106.8(9)	113.8(4)
Cl-M1-N10	92.5(5)	103.9(9)	97.9(4)
O2'-M1-O14	99.6(6)		
O2'-M1-N10	168.9(6)		
O14-M1-N10	76.0(6)	90.9(1.4)	88.2(5)
O14-N1-O2	123.4(7)	143.6(1.1)	133.6(5)
N10-M1-O2	104.0(6)	88.1(1.2)	88.8(5)
M1-O2-C3	112.3(1.3)	129.5(2.5)	130.8(1.1)
M1'-O2-C3	137.2(1.2)		
O2-C3-C4	98.0(1.9)	113.9(3.9)	115.4(1.6)
C4-C3-C8	133.1(2.0)	118.3(3.4)	120.1(1.6)
C8-C3-O2	128.9(1.9)	127.6(3.5)	124.2(1.5)
C3-C4-C5	100.6(2.1)	114.0(4.4)	116.7(1.9)
C4-C5-C6	127.6(2.1)	124.8(4.4)	122.2(2.0)
C5-C6-C7	129.8(2.2)	120.7(4.0)	120.7(1.9)
C6-C7-C8	104.4(2.0)	120.2(4.5)	117.7(1.7)
C7-C8-C3	123.9(1.9)	121.6(3.8)	121.9(1.8)
C7-C8-C9	97.1(1.8)	116.5(4.0)	112.2(1.5)
C3-C8-C9	139.0(1.8)	121.7(3.2)	125.9(1.4)
C8-C9-N10	110.2(2.0)	123.4(3.9)	119.2(1.5)
Cl-M1-O14'		106.2(9)	102.2(0.4)
C9-N10-M1	125.4(1.6)	128.4(3.2)	128.8(1.2)
C11-N10-M1	130.7(1.7)	122.8(3.0)	116.5(1.0)
C9-N10-C11	103.9(1.8)	108.9(3.9)	114.0(1.4)
N10-C11-C12	114.1(1.7)	107.3(4.8)	108.8(1.4)
C11-C12-C13	105.0(1.8)		111.5(1.6)
O14-M1-O14'		71.0(1.7)	75.9(0.6)
O2-M1-O14'		91.7(1.1)	91.4(0.6)
O14'-M1-N10		148.3(1.4)	158.1(0.5)
M1-O14-M1'		109.0(1.7)	104.1(0.6)
M1-O14-C13		136.0(2.9)	132.9(0.9)
M1'-O14-C13		114.9(3.0)	
O14-C13-C12		103.4(4.4)	110.7(1.3)

Table 16. Calculated Best Least-Squares Planes and
Distances of Atoms from Planes in Cu(SALPAH)Cl

Atoms Defining Plane: Cu1, Cu1', O2 and O2'		Atoms Defining Plane: C3, C4, C5, C6, C7 and C8	
Equation of Plane: $-0.471x - 0.882y + 0.012z = 0.0$		Equation of Plane: $0.36x + 0.922y + 0.142z - 0.138 = 0$	
Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Cu1	0.00	C3	-0.005
Cu1'	0.00	C4	-0.007
O2	0.00	C5	-0.009
O2'	0.00	C6	-0.001
Cl	-1.70	C7	-0.006
C3	0.08	C8	0.008
C4	-0.013	C9	0.054
C5	-0.04	N10	0.201
C6	0.26		
C7	0.47		
C8	0.35		
C9	0.54		
N10	0.35		
Cl1	0.59		
Cl2	2.00		
Cl3	2.06		
Cl4	1.87		

Table 17. Calculated Best Least-Squares Planes
and Distances of Atoms from Planes

Fe(SALPA)Cl

Atoms Defining Plane:

Fe1, Fe1', O14 and C14'

Equation of Plane: $.7137x + .3563y + .6031z - 3.1075 = 0.00$

Atom	Distance from Plane, Å
Fe1	0.00
Fe1'	0.00
O14	0.00
O14'	0.00
C11	0.76
C12	-0.12
C13	-0.08

Atoms Defining Plane:

O14, O14', N10, and O2

Equation of Plane: $.4204x + .4869y + .7657z - 5.482 = 0.00$

Atom	Distance from Plane, Å
O2	0.02
O14	0.02
O14'	-0.02
N10	-0.01
Fe1	-0.55

Fe(SALPA)Cl · $\frac{1}{2}$ TOL

Atoms Defining Plane:

Fe1, Fe1' O14 and O14'

Equation of Plane: $-.1229x + .3128y + .9418z + .000 = 0.00$

Atom	Distance from Plane, Å
Fe1	0.00
Fe1'	0.00
O14	0.00
O14'	0.00
C11	0.14
C12	-0.35
C13	0.28

Atoms Defining Plane:

O14, O14', N10, and O2

Equation of Plane: $.2949x + .5223y + .802z - .1306 = 0.00$

Atom	Distance from Plane, Å
O2	-0.07
O14	0.06
O14'	-0.32
N10	0.33
Fe1	0.55

Table 17. (Continued)

Atoms Defining Plane:

C3, C4, C5, C6, C7, C8

Equation of Plane: $.2919x + .4950y + .8184z - 5.866 = 0.00$

Atoms Defining Plane:

C3, C4, C5, C6, C7, C8

Equation of Plane: $.3638x + .6713y + .6458z - .5820 = 0.00$

<u>Atom</u>	<u>Distance from Plane, Å</u>	<u>Atom</u>	<u>Distance from Plane, Å</u>
C3	0.03	C3	-0.04
C4	-0.01	C4	0.04
C5	-0.01	C5	-0.04
C6	0.00	C6	0.04
C7	0.02	C7	0.00
C8	-0.04	C8	-0.01
C9	-0.03	C9	-0.09
N10	-0.22	N10	-0.11
O2	-0.11	O2	0.01

In general the coupling constant, J , for binuclear complexes can be calculated from the Van Vleck equation for copper(II) ($S = 1/2$) by expression (1) and for iron(III) ($S = 5/2$) by expression (2).

$$\chi_m = \frac{6K}{T} \left[\frac{1}{3+x^2} \right] + N\alpha \quad (1)$$

$$\chi_m = \frac{6K}{T} \left[\frac{55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}} \right] + N\alpha \quad (2)$$

where $x = \exp J/kT$ and $K = Ng^2\beta^2/3k = 0.125lg^2$, χ_m is the molar susceptibility of the dimer, g is the Lande factor, β is the Bohr magneton, N is Avogadro's number, k is the Boltzmann constant, $N\alpha$ is the temperature independent paramagnetism, and J is the coupling constant (64).

The use of a π -type superexchange mechanism to explain the subnormal magnetic moments of oxygen-bridged copper(II) complexes has been successful in that the J values calculated are in reasonable agreement with those found using expression (1); it is probable that the same explanation applies to other metal ion complexes of similar stereochemistry. The magnetic susceptibility of the dimeric $\text{Fe}(\text{SALPA})\text{Cl}$ complex was studied as a function of temperature by Baker (66) and the values of μ_{eff} compared with values calculated (66) assuming antiferromagnetic spin-spin exchange between two high-spin iron(III) ions. The plot of μ_{eff} versus temperature is given in Figure 5 on page 91, where the black circles indicate experimental points and the line is calculated for $J = -17 \text{ cm}^{-1}$, $g = 2.00$, $N\alpha = 0$ and $S = 5/2$ and $5/2$.

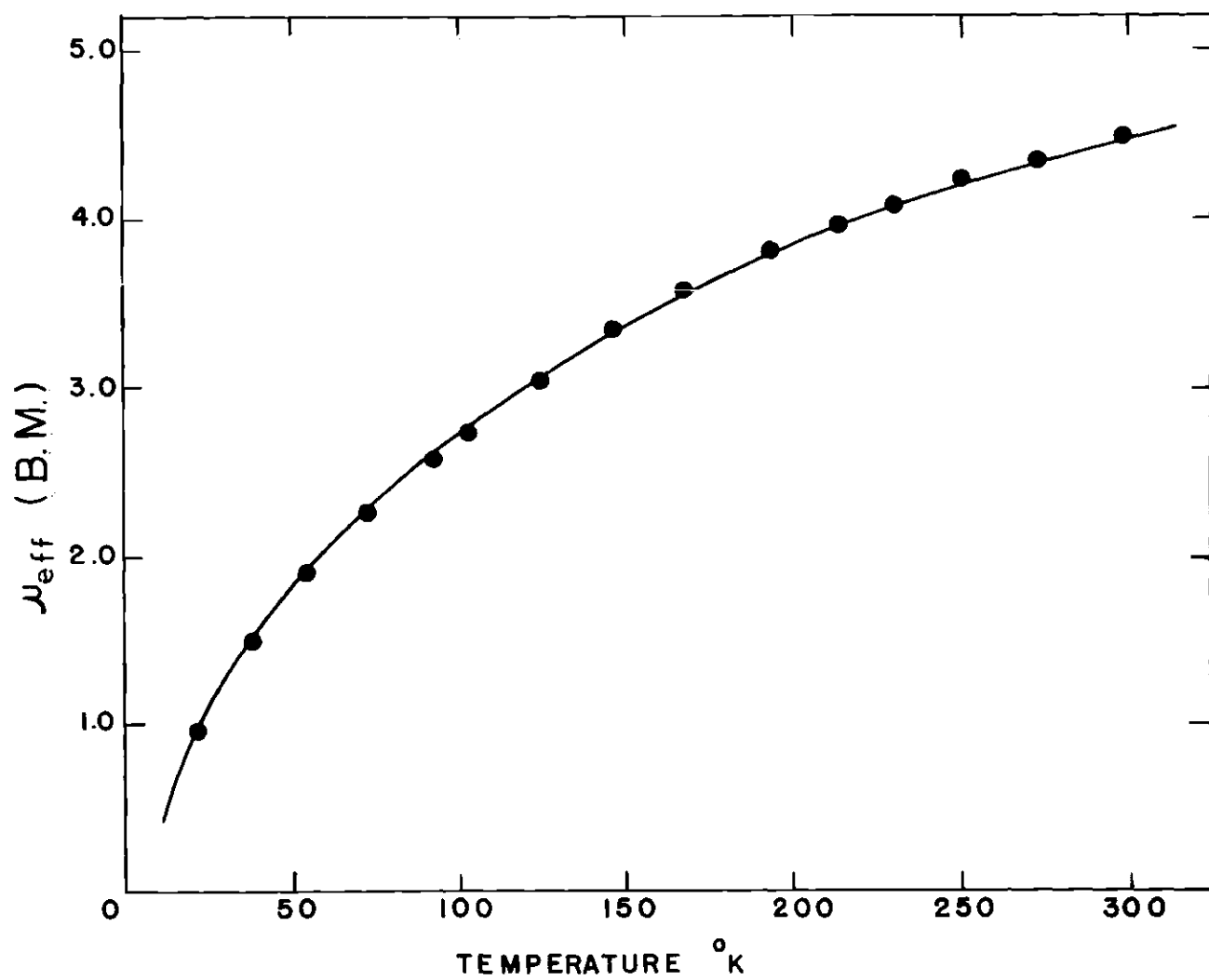


Figure 5. Plot of μ_{eff} vs. temperature for $\text{Fe}(\text{SALPA})\text{Cl}$

An important structural feature has been noted in the copper(II) complexes possessing planar four-membered rings, whether bridged by oxygens (17,19,65,67,68,69,70,71,72,73,74,75,76) or by chlorides (75, 77,78,79,80,81). It appears that in all the oxygen bridged complexes with sub-normal room temperature magnetic moments, the O-M-O angles within the four-membered M_2O_2 ring are significantly less than 90° (normally about 70°); while in the chloride bridged complexes which have normal moments at room temperature, the Cl-Cu-Cl angles are close to 90° .

Although $Cu(SALPAH)Cl$, $Fe(SALPA)Cl$, and $Fe(SALPA)Cl \cdot \frac{1}{2}TOL$ possess different coordination geometries, the O-M-O angles of 76.0° , 71.0° , and 75.9° are in agreement with the observation that oxygen bridged complexes with subnormal moments have an O-M-O angle of approximately 70° . Thus, it appears that the subnormal magnetic moments of $Cu(SALPAH)Cl$ and $Fe(SALPA)Cl$, in light of their structures can be attributed to π bonding, with the important structural feature being the O-M-O angle within the dimer.

Other workers (82) have recently looked at a limited number of oxygen bridged copper(II) complexes and attributed the magnetic exchange properties to superexchange, but have considered the M-O-M angle to be the important structural feature. It is postulated that, since the bridge bonding arrangement consists of hybrid oxygen orbitals, the M-O-M angle reflects the amount of S orbital character and that when this contribution is small, the exchange interaction is ferromagnetic. As the amount of S character increases, the interaction becomes

antiferromagnetic. Using a difference of two degrees in the M-O-M angle from the two complexes with antiferromagnetic interactions, the ferromagnetic behavior of the third complex was rationalized. The two complexes with an antiferromagnetic interaction have planar metal-oxygen four-membered rings, whereas the complex with a ferromagnetic interaction has a bent structure similar to Ni(EIA).

The coordination of the copper in Cu(SALPAH)Cl can be described as bipyramidal. Considering the phenolic oxygen, the oxygen of the aminopropanol of one ligand, and the chlorine as the equatorial groups, the angles within this plane are 126° , 110° , and 123° as opposed to the 120° angles for a regular trigonal bipyramid. The nitrogen of the Schiff base and the phenolic oxygen of the other ligand occupy the axial positions and show a slight distortion from linearity of the N10-Cu1-O2' angle (169°). The copper ion lies only 0.06 \AA out of the equatorial plane described by O2, O14 and Cl, with the displacement toward N10 of the Schiff base.

The iron(III) complexes Fe(SALPA)Cl and Fe(SALPA)Cl $\cdot \frac{1}{2}$ TOL are also five coordinate, but both have a square pyramidal arrangement with the iron displaced 0.55 \AA from the basal plane described by O2, N10, O14 and O14'. Calculating on the basis of electrostatic and non-coulombic repulsive forces, Zemann (83) found a trigonal bipyramidal arrangement to be most favorable, but a distorted square pyramidal arrangement with angles of $104^\circ 4'$ (apex-central-base atoms) only slightly less favorable. A slight deformation of the bond angles is all that is required for the interconversion of these arrangements.

Thus, the rearrangement is expected to require a relatively low energy.

The chloride is at the apex of the distorted square pyramid in both $\text{Fe}(\text{SALPA})\text{Cl}$ and $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$ and the apex-central-base atoms angles of 106.8° , 106.2° , 108.7° , 103.9° , and 113.8° , 102.2° , 112.5° , 97.9° are in reasonable agreement with the angle of $104^\circ 4'$ predicted by Zemann. The angles found within the basal plane for $\text{Fe}(\text{SALPA})\text{Cl}$ and $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2} \text{TOL}$ are 91.7° , 71.0° , 90.9° , 88.1° and 91.4° , 75.9° , 88.2° , and 88.8° , respectively. The 71.0° and 75.9° angles are the O-M-O angles previously discussed.

In light of previous work, the different stereochemistries of the copper(II) and iron(III) complexes are reasonable. In the case of copper(II), five-coordinate complexes of both square pyramidal and trigonal bipyramidal arrangements are known (84) whereas, with five-coordinate iron(III) only square-pyramidal arrangements are known (85).

Complexes of N-(2-hydroxyethylsalicylimine)

As stressed in the introductory section of this thesis, $\text{Cu}(\text{EIA})$ and $\text{Cu}(\text{PIA})$ have radically different structures; in addition $\text{Ni}(\text{EIA})$ has a unique "bent dimer" structure. In an effort to determine whether the same differences occur in the corresponding salicylaldehyde complexes, iron, cobalt, nickel, and copper complexes were prepared from SALETAH_2 and their properties studied.

The green product resulting from the reaction of SALETAH_2 and CuCl_2 analytically corresponds to one monoanion ligand per metal ion with a chloride balancing the remaining charge of the copper(II). However, the compound crystallized with a methanol per two formula units of

complex, i.e., $\text{Cu}(\text{SALETAH})\text{Cl} \cdot \frac{1}{2}\text{CH}_3\text{OH}$. Determination of the magnetic moment by the Gouy method revealed that the complex had a normal magnetic moment ($\mu_{\text{eff}} = 1.96 \text{ B.M.}$). This compound differs from $\text{Cu}(\text{SALPAH})\text{Cl}$, which is brown and has a sub-normal magnetic moment, but is similar to $\text{Cu}(\text{EIA})$, which also had a normal magnetic moment and a dark green color. Based on the magnetic moment and the color, this compound may have a "cubane" type structure similar to $\text{Cu}(\text{EIA})$ or it may be a monomeric copper(II) complex.

A second copper(II) complex was prepared by mixing methanol solutions of SALETAH_2 and copper acetate in the presence of KOH. Analytically the dark green crystalline material corresponded to one dianion ligand per copper(II) ion, as the hemihydrate; i.e. $\text{Cu}(\text{SALETA}) \cdot \frac{1}{2} \text{H}_2\text{O}$. Based on the analyses and similarity of color, this material is presumed to be analogous to $\text{Cu}(\text{EIA})$, which was also dark green and had a "cubane" type structure.

The reaction of a methanol solution of nickel acetate with a methanol solution of the ligand, SALETAH_2 , yielded a dark green crystalline material. Analytically the material corresponds to one acetate and one dianion ligand per nickel(II) with a molecule of methanol per formula unit; i.e., $\text{Ni}(\text{SALETAH})\text{CH}_3\text{OH}$. The green color is characteristic of nickel(II) complexes in which the metal ion is five or six-coordinate. Thus, it appears that this complex may also be polynuclear.

Numerous attempts were made at preparing the previously reported $\text{Fe}(\text{SALETA})\text{Cl}$ complex (86). A deep reddish-purple solution resulted each time the ligand, SALETAH_2 was mixed with a methanol solution of ferric

chloride in the presence of lithium methoxide as base. However, on most attempts no product was isolated, but traces of reddish-brown solid were obtained on occasions. In an attempt to precipitate the complex, a ratio of two ligands per metal ion was employed and a red compound which analyzed as $\text{LiFe}(\text{SALETA})_2$ was obtained. West (86) prepared the complex $\text{Fe}(\text{SALETA})\text{Cl}$ using absolute ethanol as a solvent and triethylamine as base and had found that the iron(III) complex had a sub-normal magnetic moment. Several attempts were made, but no product could be obtained following the preparative directions given.

Later it was realized that this preparation could be extremely sensitive to traces of water and the reaction was run using rigorously anhydrous conditions. The ligand was made by mixing equimolar amounts of salicylaldehyde and ethanolamine and then dissolving the imine in absolute ethanol. Ten milliliters of dimethoxypropane were added as a water scavenger and the ligand solution was added to an absolute ethanol solution containing an equimolar amount of anhydrous ferric chloride. The deep purple solution was refluxed, using a CaCl_2 drying tube to exclude moisture, for one-half hour and no product resulted. At this point, two moles of triethylamine (distilled from P_2O_5) per mole of ligand were added and reflux was continued for an additional one-half hour. Several grams of dark brown microcrystalline material were obtained by filtering the solution. Allowing the filtrate to stand yielded more of the same dark brown crystalline material, which gave good C,H,N,Cl analyses for $\text{Fe}(\text{SALETA})\text{Cl}$. Additional work on this complex will be done by co-workers.

An interesting product results from the reaction of .01 mole of cobalt acetate in methanol with .01 mole of SALETAH_2 in the presence of .02 mole of lithium methoxide. From analyses the resulting red crystalline product appears to correspond to $\text{Co}(\text{SALETA})(\text{SALETAH})$ and is diamagnetic. However, the IR spectrum does not show an -OH stretching band as did the complex prepared by Zelenstov; thus the compound may correspond to the lithium salt $\text{LiCo}(\text{SALETA})_2$. At the time this material was prepared, work by Zelenstov (87) indicated that both a yellowish-pink paramagnetic cobalt(II) complex with one ligand per metal ion and the red, diamagnetic cobalt(III) complex, $\text{Co}(\text{SALETA})(\text{SALETAH})$, could be prepared by mixing equimolar amounts of a benzene solution of SALETAH_2 with a methanol solution of cobalt(II) acetate. (The cobalt(II) complex was prepared under a nitrogen atmosphere.)

Complexes of N-(N-methylaminopropylsalicylimine)

Both nickel and copper complexes of the ligand N-(N-methylaminopropylsalicylimine), SALPDA, have been prepared. The reaction of equimolar amounts of copper(II) chloride, SALPDA, and lithium methoxide in methanol yielded a dark green crystalline product. Analytically the complex corresponds to one ligand and one chloride per metal ion, $\text{Cu}(\text{SALPDA})\text{Cl}$. The sub-normal magnetic moment of 1.5 B.M. is indicative of a dimeric copper(II) complex with bridging probably occurring through the phenolic oxygens of the ligand.

The reaction of methanol solutions of nickel chloride, SALPDA, and lithium methoxide in the ratios of 1:2:2, respectively, yields an unstable reddish-brown material which can be recrystallized from

m-Xylene to give large air-stable reddish-brown crystals. Analytically the complex appears to correspond to two ligands per metal ion and the reddish color of the complex suggests a square planar arrangement of the two tridentate ligands around the metal ion.

Mixed Oxidation State Complexes of Salicylideneglycine

Complexes of a number of first row transition metal ions with the Schiff bases of salicylaldehyde and amino acids have been previously reported (45). From the formulas and magnetic properties, several of these appeared to be polynuclear complexes with unusual magnetic properties. Among those reported were iron and manganese compounds with ratios of metal ion: salicylaldehyde: glycine of 2:2:3 and with magnetic moments of 5.91 B.M. and 5.84 B.M., respectively. In addition a cobalt compound was reported with ratios of 1:1:2 and a magnetic moment of 2.89 B.M.

An X-ray study of the cobalt complex of salicylaldehyde and glycine by Helm (88), showed that the unusual magnetic moment resulted from partial oxidation to cobalt(III) and the correct formulation is $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$ (where SALGLY is the dianion of the imine of salicylaldehyde and glycine). The structure consists of a trimeric unit composed of an octahedral cobalt(II) ion surrounded by six waters and connected by hydrogen bonds to two octahedral cobalt(III) ions. Each cobalt(III) ion is coordinated by two tridentate SALGLY ligands.

The addition of an ethanol solution of salicylaldehyde to a water solution of ferrous sulfate and glycine in the presence of KOH yielded a

deep-red complex which was shown by analyses to have the same formula as the cobalt complex investigated by Helm. Because of the relatively small difference in the magnetic moments of iron(II) and iron(III) complexes, less conclusive evidence for the divalent oxidation state was obtained from magnetic studies. However, the magnetic moment of the compound, based on the formulation $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$ was found to be $\mu_{\text{eff}} = 9.91$ B.M. Considering this as a composite moment of three metal ions and using the value of χ_m obtained by Bailar (38) for $\text{Na Fe}(\text{SALGLY})_2$ for the susceptibilities of the $\text{Fe}(\text{SALGLY})_2$ ions, the value of $\mu_{\text{eff}} = 5.35$ B.M. obtained for the remaining metal ion is consistent with the formulation of the ion as iron(II). (Range of experimental μ_{eff} for iron(II) complexes is 5.1-5.5 B.M. (62)).

The iron(II) ion occupies a crystallographic inversion center as is depicted in the perspective drawing in Figure 6 and has a distorted octahedral arrangement of six waters around it. The three independent iron(II)-oxygen distances are 2.14 Å, 2.11 Å, and 2.11 Å, respectively, and the cis O-Fe(II)-O angles are 88.68°, 76.02°, 88.77°, 91.32°, 103.98°, and 91.23°. Also, the arrangement of the two SALGLY ligands around the iron(III) ions is a distorted octahedron with phenolic oxygen-iron(III) distances of 1.92 Å, and 1.92 Å, carboxy oxygen-iron(III) distances of 2.08 Å and 2.07 Å, and nitrogen-iron(III) distances of 2.07 Å and 2.11 Å, respectively. Bond distances and bond angles for the structure are given in Table 18. As can be seen in Figure 6 the ligands are coordinated such that the azomethine nitrogens are trans to each other, the phenolic oxygen of each ligand is trans to

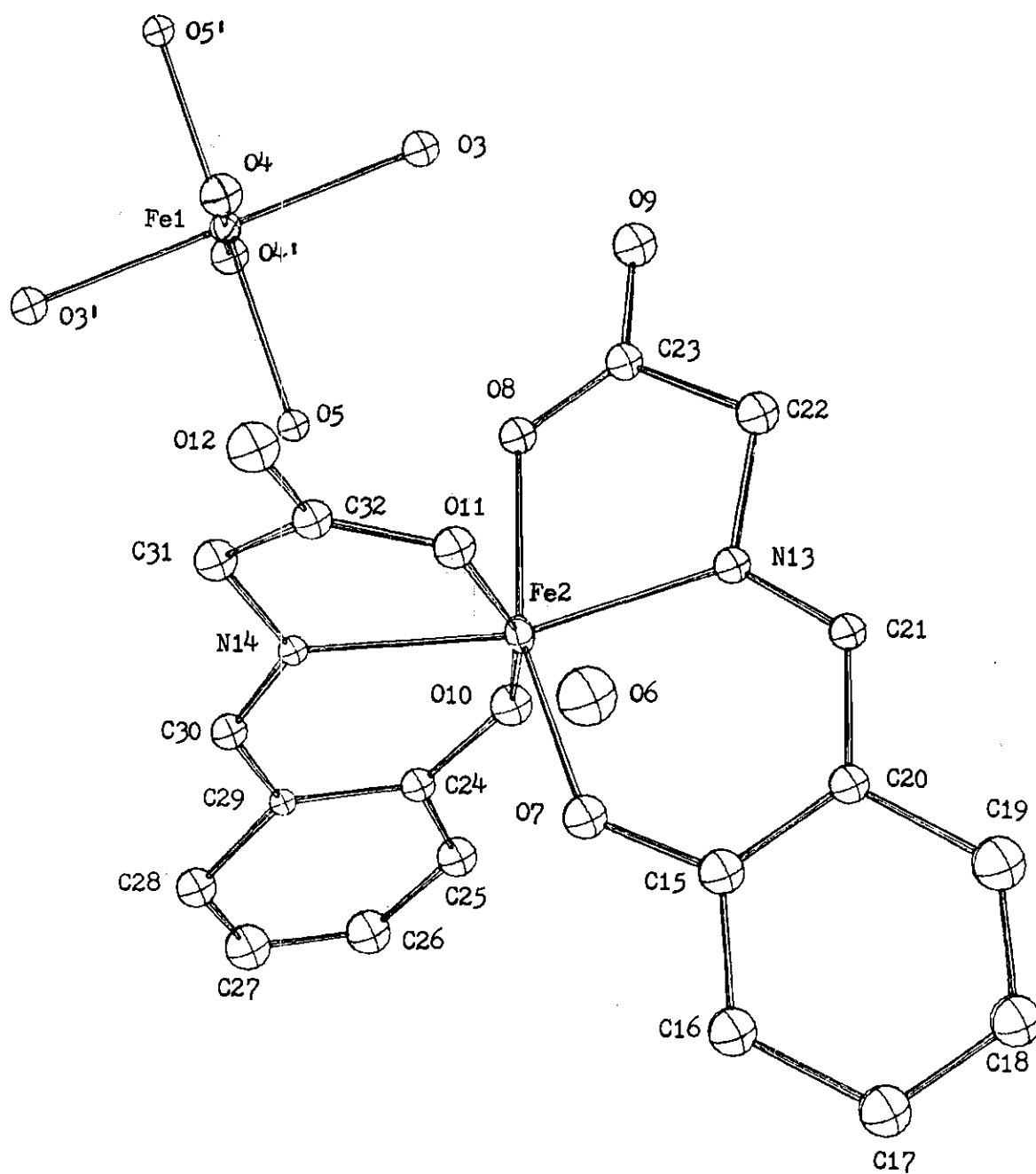


Figure 6. A Perspective Drawing of the Structure of $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$

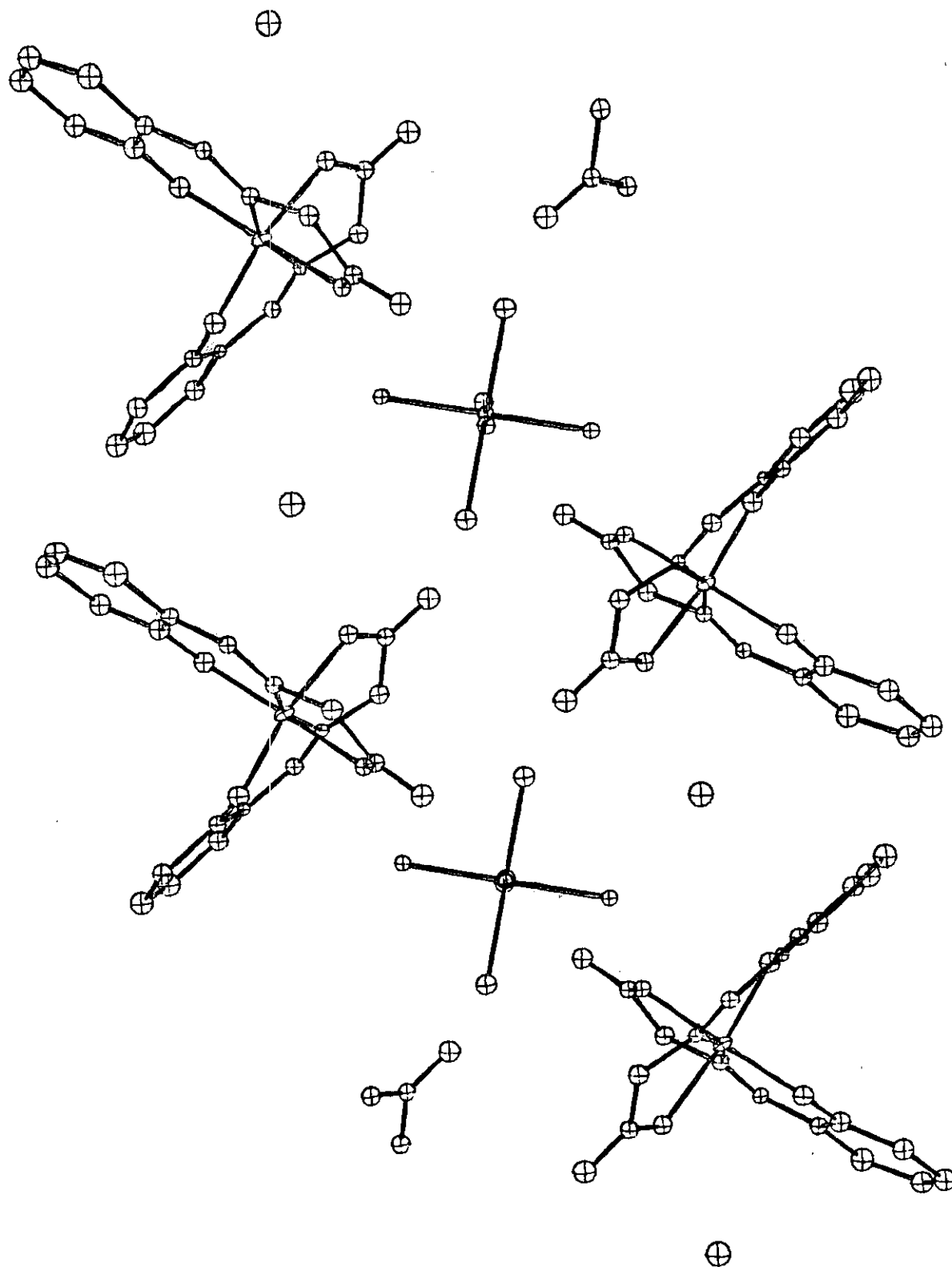


Figure 7. A Perspective Drawing of the Packing in $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$

Table 18. Bond Distances and Angles
 $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$

Atoms	Distance, Å	Atoms	Distance, Å
Fe1-Fe2	5.614(2)	N13-C21	1.288(17)
Fe1-O3	2.142(9)	N13-C22	1.512(19)
Fe1-O4	2.107(11)	N14-C30	1.251(17)
Fe1-O5	2.107(8)	N14-C31	1.436(19)
Fe1-O6	4.292(10)	C15-C16	1.424(19)
Fe2-O6	5.351(10)	C15-C20	1.356(20)
Fe2-O7	1.915(9)	C16-C17	1.482(22)
Fe2-O8	2.075(11)	C17-C18	1.332(22)
Fe2-O10	1.924(11)	C18-C19	1.363(22)
Fe2-O11	2.066(9)	C19-C20	1.531(22)
Fe2-N13	2.067(13)	C20-C21	1.382(20)
Fe2-N14	2.102(13)	C22-C23	1.576(19)
O8-O5	2.755(13)	C24-C25	1.486(19)
O12-O3	2.796(13)	C24-C29	1.425(19)
O7-C15	1.332(16)	C25-C26	1.405(23)
O8-C23	1.254(16)	C26-C27	1.314(23)
O9-C23	1.297(16)	C27-C28	1.373(22)
O10-C24	1.323(17)	C28-C29	1.445(20)
O11-C32	1.263(17)	C29-C30	1.356(20)
O12-C32	1.236(17)	C31-C32	1.440(20)

Table 18. (Continued)

Atoms	Angle, Degrees	Atoms	Angle, Degrees
O3-Fe1-O4	88.68(40)	O7-C15-C16	116.02(147)
O3-Fe1-O5	76.02(24)	O7-C15-C20	123.09(154)
O3-Fe1-O ¹ 4	91.32(40)	C15-C20-C21	124.56(156)
O3-Fe1-O ¹ 5	103.98(24)	C16-C15-C20	120.84(162)
O4-Fe1-O5	88.77(36)	C16-C17-C18	119.25(184)
O4-Fe1-O ¹ 5	91.23(36)	C17-C18-C19	120.21(187)
O7-Fe2-O8	163.21(47)	C18-C19-C20	123.43(167)
O10-Fe2-O11	161.41(47)	C19-C20-C15	115.30(158)
O7-Fe2-N13	85.15(49)	C20-C21-N13	123.90(156)
O8-Fe2-N13	78.50(45)	C21-N13-Fe2	129.30(109)
O10-Fe2-N14	86.00(48)	C21-N13-C22	115.08(127)
O11-Fe2-N14	75.64(49)	C22-N13-Fe2	115.32(93)
O8-C23-O9	128.25(148)	C22-C23-O8	115.94(150)
O11-C32-O12	125.76(155)	C22-C23-O9	115.81(140)
O8-Fe2-O10	87.58(45)	O10-C24-C25	118.49(142)
O7-Fe2-O11	93.65(46)	O10-C24-C29	123.61(136)
O7-Fe2-O10	93.60(46)	C24-C25-C26	119.79(163)
N13-Fe2-O11	90.60(46)	C24-C29-C28	118.25(144)
N13-Fe2-O10	107.06(48)	C24-C29-C30	120.63(165)
N14-Fe2-O7	104.08(47)	C25-C26-C27	118.99(163)
N14-Fe2-O8	92.72(46)	C26-C27-C28	125.82(186)
Fe2-O7-C15	133.14(99)	C28-C29-C30	212.08(162)
Fe2-O8-C23	121.09(108)	C29-C30-N14	130.18(165)
Fe2-O10-C24	129.13(97)	C30-N14-Fe2	123.58(142)
Fe2-O11-C32	119.48(99)	C31-N14-C31	123.42(149)
		C31-N14-Fe2	112.94(101)
		C31-C32-O11	116.74(149)
		C31-C32-O12	117.21(154)
		O8-Fe2-O11	90.38(46)

the carboxyl oxygens of the same ligand, and the carboxyl oxygens are directed toward the central iron(III). From construction of a three-dimensional model, it was found that each SALGLY ligand was close to planar. This is probably due to the delocalized π -system that is present on the phenolic and carboxy portions of the ligand.

The closest approach of the iron(II) to an iron(III) is 5.61 \AA , but a hydrogen bond between a water oxygen, 05, that is bonded to the central iron(II) and one of the non-coordinated carboxy oxygens, 08, (oxygen-oxygen distance of 2.76 \AA) joins the iron(II) complex to the iron(III) complexes on either side of the inversion center. In addition, another hydrogen bond between one of the water oxygens, 03, and the second non-coordinated carboxy oxygen, 012, of the next molecule (oxygen-oxygen distance 2.80 \AA) connects the complexes into infinite chains as is shown in the packing diagram, Figure 7. These hydrogen bonds are considerably longer than those found by Helm in the corresponding cobalt complex. The long O-O distance indicate fairly weak hydrogen bonding and these bonds would not be expected to exist to any great extent in solution. Although the oxygen of the water of hydration is in an area within the unit cell such that hydrogen bonding might be expected, the closest approach to any other oxygen is 2.91 \AA . Therefore, no significant hydrogen bonding occurs with the water of hydration.

Although the cobalt and iron compounds have identical formulas, structurally the cobalt complex consists of a trimeric unit, whereas the iron complexes are held together by hydrogen bonding to form infinite

chains. The manganese compound was investigated by Helm and found to have the same formula as both the cobalt and iron complexes and was isomorphous with the iron complex.

Both the cobalt complex and $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{SALGLY})_2]_2 \cdot 2\text{H}_2\text{O}$ are of particular importance due to their relationship to the system used as a model for vitamin B6 reactions (89) and for amine oxidase reactions (90). Although the Schiff base ligands derived from salicylaldehyde and amino acids are not catalysts for these reactions, they are structurally similar to the pyridoxal phosphate complexes which are catalytically active. The structure of a manganese(II) complex of the imine of pyridoxal and valine has been reported (91) and the metal ion has an octahedral stereochemistry with hydrogen bonding occurring in the solid state; other workers (90) have postulated that the active catalyst contains manganese(III) and some results indicate that both divalent and trivalent metal ions are involved in the reaction.

An Iron(III) Complex of
bis {(2-phenylsalicylimine)} disulfide

The Schiff base ligand, $\text{SAL}_2\text{DIAPSH}_2$, is formed by adding a solution of salicylaldehyde to a solution of 2,2'-diaminodiphenyldisulfide in the ratio of 2:1. A black crystalline product was obtained by adding the solution of SAL_2DIAPS to a ferric chloride solution in the presence of lithium methoxide as base. Analyses are consistent with an iron(III) complex of the Schiff base ligand formed by the condensation of both the amine groups with salicylaldehyde. The complex consists of an iron(III) ion, the dianion of SAL_2DIAPS , and a chloride ion, i.e. $\text{Fe}(\text{SAL}_2\text{DIAPS})\text{Cl}$.

The formula and the temperature independent magnetic moment of 5.90 B.M. are consistent with a high-spin octahedral iron(III) complex.

An X-ray structure determination revealed a distorted octahedral configuration for the iron(III) with the chloride (Cl2), one sulfur of the disulfide linkage (S3), the two phenolic oxygens (O5 and O6), and the two azomethine nitrogens (N7 and N8) bonded to the iron(III) ion. The second sulfur of the disulfide linkage (S4) is 3.79 Å away from the iron(III) and makes an Fe1-S3-S4 angle of 111.5° and an S3-S4-C30 angle of 104.2°. Ligand coordination of SAL₂DIAPS is very similar to that found for the disulfide complex, chloro(bis-{2-[(2-pyridylmethyl)amino]ethyl}disulfide) nickel(II) Perchlorate, hereafter Ni(PAD)Cl (92).

Because of the complexity of SAL₂DIAPS the numbering schemes for the individual chelate rings and the six atoms coordinated to the iron(III) are shown using a regular octahedron in Figure 8. A perspective drawing of the entire structure is given in Figure 9. The iron-chlorine distance of 2.31 Å is similar to the nickel-chlorine distance of 2.39 Å found in Ni(PAD)Cl, but is somewhat longer than the iron-chlorine distances of 2.20 Å and 2.23 Å in Fe(SALPA)Cl and Fe(SALPA)Cl · $\frac{1}{2}$ TOL. In addition, the iron-sulfur distance of 2.54 Å is very similar to the nickel-sulfur distance of 2.47 Å in Ni(PAD)Cl. The azomethine nitrogen-iron distances are 2.17 Å and 2.20 Å as compared to 2.12 Å and 2.06 Å in Fe(SALPA)Cl and Fe(SALPA)Cl · $\frac{1}{2}$ TOL, while the phenolic oxygen-iron distances are 1.87 Å and 1.91 Å as compared to 1.87 Å and 1.85 Å in Fe(SALPA)Cl and Fe(SALPA)Cl · $\frac{1}{2}$ TOL, respectively. A complete listing of the bond distances and angles for Fe(SAL₂DIAPS)Cl is given in Table 19.

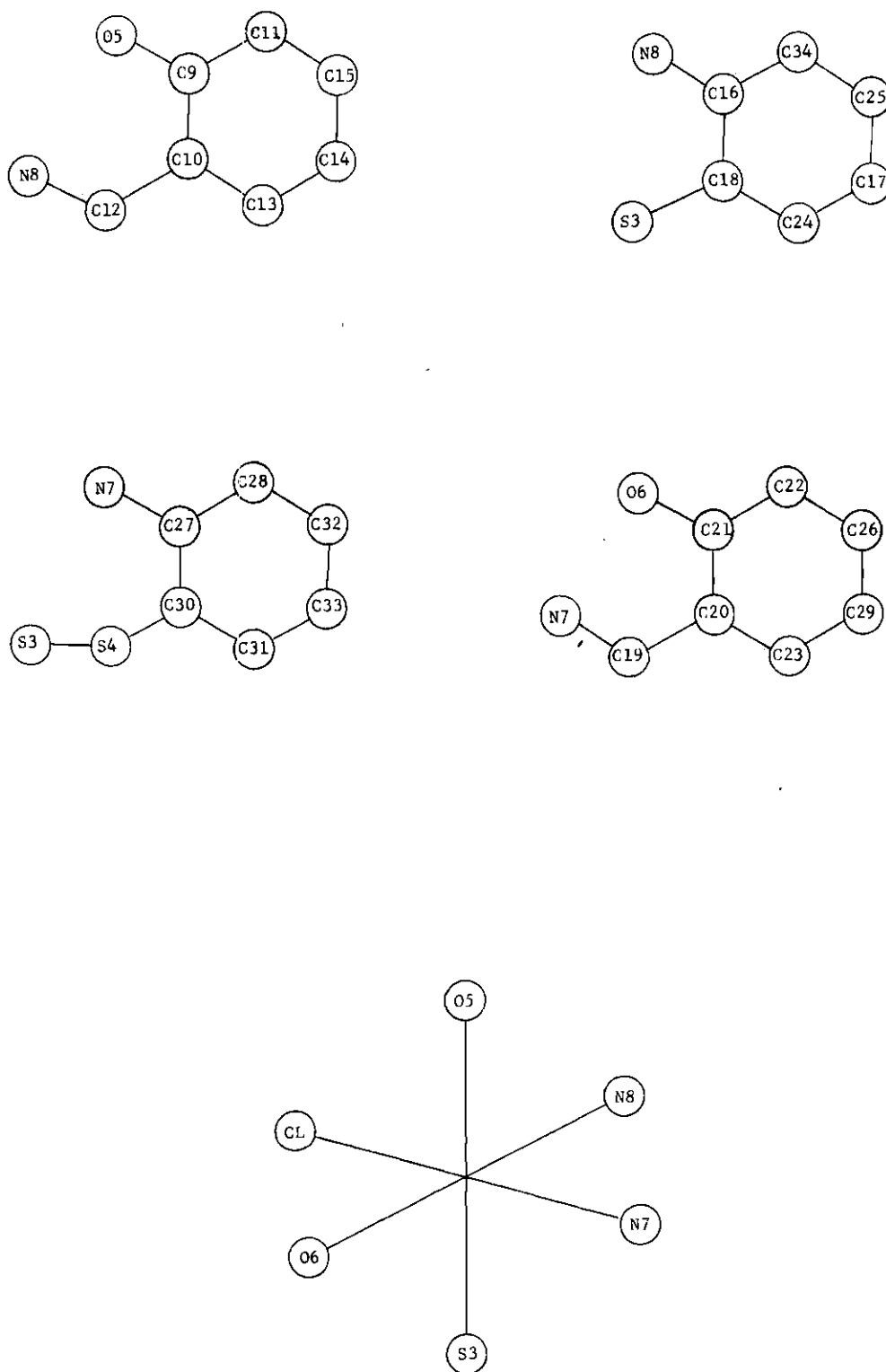


Figure 8. Schematic Drawings of Ligand SAL₂DIAPS and Idealized Octahedron of Complex Fe(SAL₂DIAPS)Cl

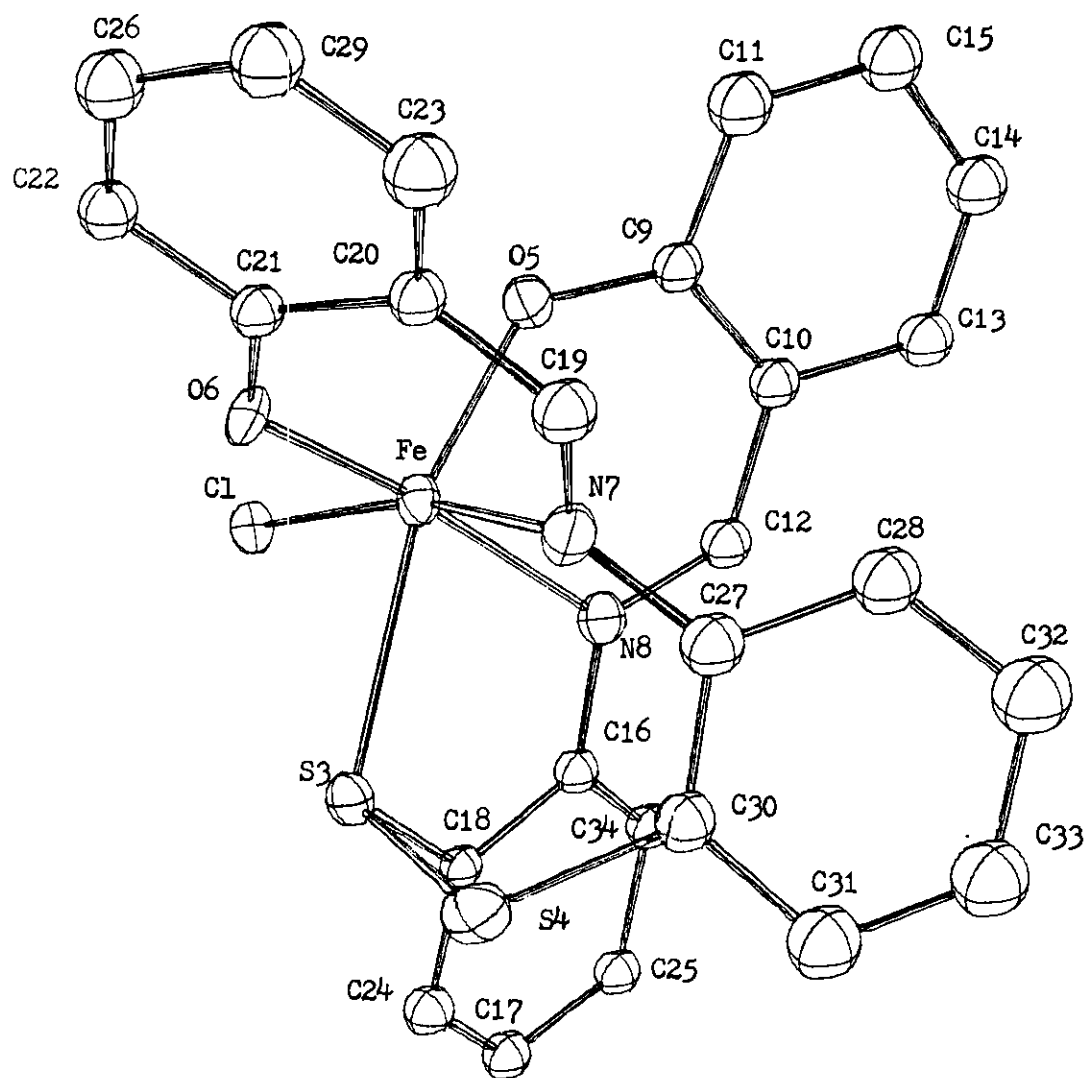


Figure 9. A Perspective Drawing of the Structure of $\text{Fe}(\text{SAL}_2\text{DIAPS})\text{Cl}$

Table 19. Bond Distances and Angles Fe(SAL₂DIAPS)Cl

Atoms	Distance, Å ^o	Atoms	Distance, Å ^o
Cl2-Fe1	2.314(4)	C17-C25	1.359(16)
S3-Fe1	1.536(4)	C25-C34	1.427(16)
O5-Fe1	1.871(8)	S3-S4	2.046(5)
O6-Fe1	1.909(7)	S4-C30	1.765(14)
N7-Fe1	2.166(12)	N7-C27	1.400(19)
N8-Fe1	2.204(10)	C27-C28	1.420(21)
O5-C9	1.316(13)	C27-C30	1.391(21)
N8-C12	1.291(14)	C28-C32	1.422(25)
C9-C10	1.439(17)	C32-C33	1.445(27)
C9-C11	1.409(20)	C33-C31	1.363(25)
C10-C13	1.435(16)	C31-C30	1.423(23)
C11-C15	1.423(21)	O6-C21	1.336(14)
C13-C14	1.359(20)	N7-C19	1.368(19)
C14-C15	1.444(22)	C19-C20	1.397(20)
S3-C18	1.768(11)	C20-C21	1.437(18)
N8-C16	1.422(15)	C21-C22	1.394(17)
C16-C18	1.404(13)	C22-C26	1.402(19)
C16-C34	1.369(15)	C26-C29	1.373(21)
C18-C24	1.396(16)	C29-C23	1.378(22)
C17-C24	1.362(17)	C23-C20	1.365(21)

Table 19. (Continued)

Atoms	Angle, Degrees	Atoms	Angle, Degrees
CL2-Fe1-S3	83.04(13)	C18-C24-C17	120.15(108)
CL2-Fe1-O5	105.38(30)	C24-C17-C25	120.65(119)
CL2-Fe1-O6	94.06(28)	C17-C25-C34	119.78(109)
CL2-Fe1-N7	165.73(33)	C25-C34-C16	119.97(96)
CL2-Fe1-N8	88.76(29)	C34-C16-C18	118.70(99)
S3-Fe1-O5	163.94(29)	Fe1-S3-S4	111.54(18)
S3-Fe1-O6	95.04(29)	Fe1-N7-C27	121.79(94)
S3-Fe1-N7	82.91(33)	S3-S4-C30	104.15(51)
S3-Fe1-N8	77.82(28)	N7-C27-C28	121.54(140)
O5-Fe1-O6	97.92(39)	N7-C27-C30	119.97(133)
O5-Fe1-N7	88.86(41)	C27-C28-C32	121.26(161)
O5-Fe1-N8	88.56(37)	C28-C32-C33	116.38(183)
O6-Fe1-N7	84.69(39)	C32-C33-C31	123.50(194)
O6-Fe1-N8	171.97(39)	C33-C31-C30	117.58(169)
N7-Fe1-N8	90.73(42)	C31-C30-C27	122.64(140)
Fe1-O5-C9	133.26(81)	C31-C30-S4	115.51(116)
O5-C9-C11	119.30(118)	C27-C30-S4	121.53(114)
O5-C9-C10	121.83(105)	C28-C27-C30	118.30(143)
C11-C9-C10	118.75(110)	Fe1-N7-C19	120.34(106)
C9-C11-C15	120.65(148)	Fe1-O6-C21	129.81(73)
C11-C15-C14	118.13(152)	O6-C21-C20	121.73(110)
C15-C14-C13	122.86(142)	O6-C21-C22	118.97(110)
C13-C10-C9	120.94(114)	N7-C19-C20	123.69(141)
C12-N8-Fe1	120.24(88)	C19-C20-C21	124.49(121)
Fe1-S3-C18	98.05(36)	C19-C20-C23	118.08(133)
Fe1-N8-C16	119.90(95)	C20-C21-C22	119.29(111)
N8-C16-C18	118.37(130)	C21-C22-C26	119.40(119)
N8-C16-C34	121.92(140)	C22-C26-C29	122.21(144)
S3-C18-C24	119.21(78)	C26-C29-C23	116.66(150)
S3-C18-C16	120.42(82)	C29-C23-C20	125.38(152)
C16-C18-C24	120.37(100)	C23-C20-C21	116.97(151)

The angles between the trans atoms Cl2-Fel-N7, SE-Fel-05, and 06-Fel-N8 of 165.73, 163.94°, and 171.97° show the amount of distortion from octahedral coordination. As can be seen in Figure 9, the pentadentate SAL₂DIAPS wraps around the iron(III) in such a fashion that the phenolic oxygens are cis and the 05-Fel-06 angle is 97.92°. This angle probably is due to the fact that the oxygens are not part of a chelate ring. As can be seen in Table 19, all those angles within chelate rings are considerably less than 90°. Also the section of the ligand system formed from chelate ring number one (a six-membered ring) and chelate ring two (a five-membered ring) is essentially planar, whereas the section composed of the chelate rings three and four shows considerable twist in the connecting atoms and, as a result, deviate significantly from planarity.

CHAPTER IV

CONCLUSIONS

Prior to this research project, numerous polynuclear Schiff base complexes had been prepared and investigated. In particular, copper(II) complexes with oxygen bridges had been considered and mechanisms for the spin exchange within the low moment compounds have been given. Investigations revealed that Cu(EIA) was tetrameric with tetrahedral coordination about the bridging oxygens, a distorted five-coordinate arrangement about copper, and that it had a normal magnetic moment. In addition it was found that Cu(PIA) (17) was dimeric with three-coordinate bridging oxygens, planar coordination of the copper ion, and that it had a subnormal magnetic moment. The difference in magnetic moments was attributed to the difference in coordination of the bridging oxygen. In the planar three-coordinate arrangement, one orbital of the oxygen is available for delocalized π -bonding, whereas in the case of four-coordinate oxygens this orbital is filled and as a result magnetic coupling cannot occur. However, the possibility that the difference in the magnetic properties was related to the difference in the coordination about the metal could not be ruled out.

The complex Cu(SALPAH)Cl provided a polynuclear complex in which the copper is five-coordinate and has a subnormal magnetic moment. As a result, the consideration of coordination of the metal ion can be eliminated as a factor affecting the magnetic behavior of the complex.

As in all other cases of oxygen-bridged copper complexes with subnormal moments, the bridging oxygens in $\text{Cu}(\text{SALPAH})\text{Cl}$ were three-coordinate and planar. Thus, this adds further support to the suggestion that the planar coordination of the bridging oxygen is the important structural feature, which is consistent with a π -mechanism for spin exchange.

In order to investigate the mechanism of magnetic coupling in polynuclear complexes of metal ions other than copper, the complex $\text{Fe}(\text{SALPA})\text{Cl}$ was prepared, its magnetic moment was found to be 4.23 B.M., and its structure was determined. The subnormal moment indicated exchange by some means. Since the ligand was the same as in $\text{Cu}(\text{SALPAH})\text{Cl}$ except for being the dianion, a dimeric oxygen-bridged structure was reasonable. It was found that the iron was five-coordinate, but square pyramidal with the iron(III) displaced out of the base. As was predicted on the basis of the subnormal moment, the bridging oxygen was again three-coordinate and planar. The complete data set collected on the solvated form of this complex, $\text{Fe}(\text{SALPA})\text{Cl} \cdot \frac{1}{2}\text{TOL}$ shows the same molecular structure with only minor differences in bond angles and bond distances.

The complex $\text{Fe}(\text{SALETA})\text{Cl}$ had been prepared and the magnetic properties investigated by West (86). An interesting feature was that the complex showed a subnormal magnetic moment. This is unusual in light of what was observed with $\text{Cu}(\text{EIA})$ and $\text{Cu}(\text{PIA})$. With EIA, copper formed a "cubane" complex with a normal moment, but the addition of a single methylene in the amino-alcohol chain of the imine, i.e., PIA, yielded a "dimeric" complex with a subnormal moment. However, it appears

that iron(III) forms only dimeric complexes with the analogous SALPA and SALETA. This probably is due to the ability of iron to form square pyramidal complexes with the metal ion displaced from the base and as a result can accommodate the smaller chelate ring of the SALETA ligand while still maintaining a planar M_2O_2 four-membered ring. Further investigation is being done to elucidate this apparent difference in behavior of iron(III) from that of copper(II).

A number of first-row transition metal ion complexes of the Schiff base ligand SALGLY were erroneously reported as polynuclear complexes with subnormal magnetic moments. X-ray structure determinations and magnetic studies revealed a new type of mixed oxidation state polynuclear compounds of the general formulation $[M(II)(H_2O)]_6$ $[M(III)(SALGLY)_2]_2 \cdot 2H_2O$. These ionic complexes are held together by hydrogen bonding and have no apparent magnetic interaction between the metal ions. The general stereochemistry of all the metal ions in the complexes is distorted octahedral. In the cases where the metal ions were either iron or manganese, an infinite chain held together by hydrogen bonds exists in the solid state, but Helm found in the case of cobalt ions, trimeric units in the solid state. These complexes are of particular importance due to their relationship to the system used as a model system for vitamin B6 reactions.

The pentadentate Schiff base ligand SAL_2DIAPS produced a distorted octahedral iron complex, $Fe(SAL_2DIAPS)Cl$, in which one sulfur of the disulfide linkage bonds to the metal ion. This structure is of particular interest in that it is the first Schiff base complex reported

which contains a disulfide linkage and is one of the few structures reported as having a disulfide linkage. In addition the framework of the ligand, SAL_2DIAPS , is such that it closely approximates the biologically important amino acid cystine. As a result, the complex may have potential value as a model system for biological systems.

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