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A STUDY OF TRANSITION METAL CUBANE-TYPE COMPLEXES:
METAL IONS IN MIXED OXIDATION STATES

A THESIS

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The Faculty of the Division of Graduate
Studies and Research

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A STUDY OF TRANSITION METAL CUBANE-TYPE COMPLEXES:

METAL IONS IN MIXED OXIDATION STATES


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SUMMARY

Bis- μ -acetato-tetrakis- $[\mu_3$ -methoxo-2,4-pentanedionato-cobalt(II, III)], $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$, has been prepared by the hydrogen peroxide oxidation of a mixture of cobalt(II) acetate, 2,4-pentanedione, and potassium hydroxide in methanol.

The preparation, magnetic properties, spectral properties, and crystal and molecular structure of the cubane-type complex have been investigated. This is the first cubane-type complex found to have metal ions in different oxidation states.

The complex crystallizes in the triclinic space group, $P\bar{1}$. The structure contains a tetrahedron of cobalt atoms with a methoxide oxygen over each face of the tetrahedron. The acetate groups bridge the top and bottom faces of the cube. The octahedral coordination of the four cobalt atoms is completed by 2,4-pentanedionato chelates and the bridging acetates. That the cobalt-oxygen distances for one pair of cobalt atoms are consistently shorter by about 0.2 Å than those of the other pair indicates that the former are the cobalt(III) ions. Unlike the cobalt(II) cubane-type complex, $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$, which has several geometrical isomers, there is only one possible geometrical configuration for this complex because of the bridging acetates.

The complex is paramagnetic, and the room temperature magnetic moment is consistent with the presence of two octahedrally coordinated cobalt(II) ions and two diamagnetic cobalt(III) ions in the complex. Low

temperature (300° - 77° K) magnetic studies revealed that the complex exhibits antiferromagnetic behavior.

Spectral studies of the complex revealed a band in the visible region of the electronic spectrum which probably results from separate absorptions by the octahedrally coordinated cobalt(II) and cobalt(III) ions in the complex.

CHAPTER I

INTRODUCTION

First row transition metal ions have been found to complex with many organic ligands to give polynuclear complexes; these complexes have exhibited interesting structural features and unusual spectral, magnetic, and chemical properties. The factors favoring the formation of polynuclear rather than mononuclear complexes are not clearly understood nor are the factors determining the structures and the relationship between the structures and the properties of these complexes.

The magnetic properties of polynuclear complexes are of particular interest because several types of magnetic interactions are possible. In some of these complexes where the arrangement and type of bridging allow two or more metal ions to approach each other closely enough for direct overlap of metal orbitals, metal ions with unpaired electrons in these orbitals could experience a total or partial pairing of their electron spins. Where metal-metal separations are large enough to deem direct overlap insignificant, multicentered overlap between orbitals on the metal ions and orbitals on the bridging groups could result in a total or partial pairing of electron spins between metal ions.

The spectral properties of these complexes are also of interest since polynuclear complexes often exhibit high symmetry and a coordination at the metal ions which is unusual and rigid; the spectra of these complexes thus provide good examples for studies of the effects of different

ligands and different geometrical arrangements of ligands on the electronic structure of the metal ions.

Polynuclear complexes have been found in a variety of structures. Examples of some of the types of structures found are μ_4 -oxo (1-4) (I), μ_3 -oxo (5-7) (II), μ_2 -oxo (8) (III), cyclic (9) (IV), CdCl_2 -type (10-12) (V), rutile-type (13-15) (VI), stacked-dimer (16,17) (VII), planar dimer (18,19) (VIII), non-planar dimer (20) (IX), and cubane-type (21-42) (X). (Roman numerals in parentheses refer to the diagrams in Figure 1.) Other structures that are not readily placed in a category have also been observed (43). Some of these structures have been observed only for certain types of metal ions and/or bridging groups; the stability of some structures is dependent on the relative sizes of the metal ions and bridging groups. One type of structure which does not seem to be restricted by relative sizes nor by the type of metal ions and/or bridging groups is the cubane-type structure.

Cubane-type structures have been found for a number of different metal ions and different bridging groups (21-42); however, relatively few examples with first-row transition metal ions have been found (23-26,42). For many years a cubane-type structure has been recognized (26) for compounds of the general formula, $[\text{Cu}(\text{R}_3\text{Y})\text{X}]_4$ (where X represents a halide ion; Y represents a Group V element; and R represents an alkyl or aryl group); however, there have been relatively few studies of these compounds. Just recently the observation was made that two iron-sulfur cubane-type units are present in the structure of the ferredoxin protein (44). The cubane-type structure (X, Figure 1) can be described as a tetrahedron of metal atoms, M, with bridging atoms, B, above each face of the tetra-

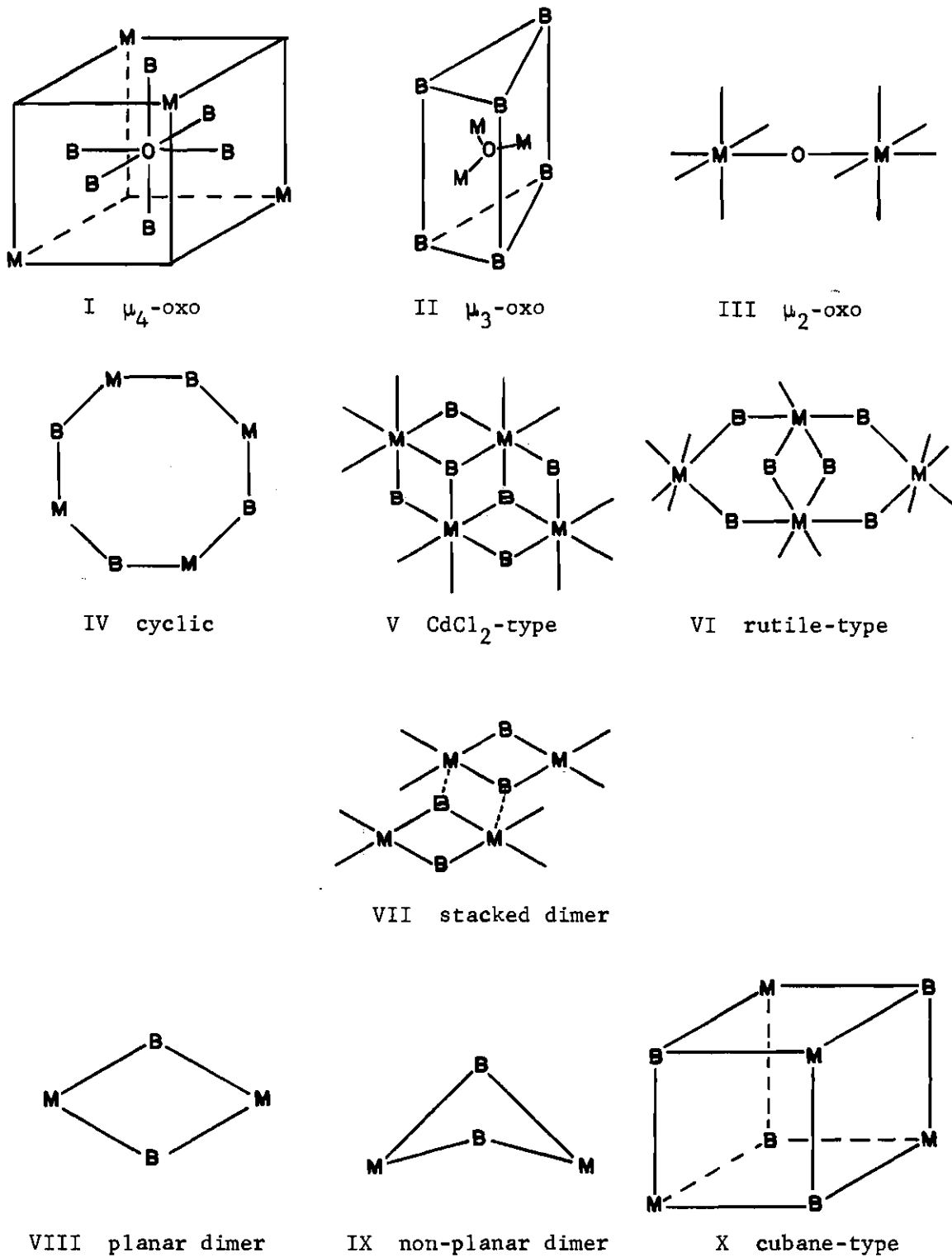


Figure 1. Examples of Some Structures Found for Polynuclear Complexes

hedron. The cubane can also be thought of as two interpenetrating tetrahedra, one of metal atoms and the other of bridging atoms. The coordination observed for the bridging atoms in the cubane-type structure has been such that the bridging atom seems to be sp^3 -hybridized. In most complexes the bridging atom has four other atoms bonded to it; however, there are some complexes in which the bridging atom has only three atoms bonded to it and has a lone pair of electrons in the fourth position. This structure has been observed for metal atoms with various coordination numbers; some examples of these coordination numbers are: four was found in the $[\text{Cu}(\text{R}_3\text{Y})\text{X}]_4$ complexes (26); five was found in $[\text{Cu}(\text{EIA})]_4$ (24); and six was found in $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$ (25).

Several years ago, a series of compounds with the formula $[\text{M}(\text{AA})(\text{CH}_3\text{O})(\text{ROH})]_x$ (where M represents Co(II), Ni(II), or Mg(II); AA represents the anion of a β -dicarbonyl compound; and R represents CH_3) was reported (21,45). Recent work (25) has indicated cubane-type structures for the compounds in which M represents Co(II) or Ni(II), AA represents 2,4-pentanedionato, and R represents CH_3 . A similar compound where R represents H was also reported (46). A compound in which M represents Ni(II), AA represents salicylaldehydato, and R represents C_2H_5 was reported (23) and shown to have a cubane-type structure. The bridging atoms in these structures are methoxide oxygens. The octahedral coordination of each metal atom is completed by a β -dicarbonyl chelate and a coordinated alcohol for $\text{R} = \text{CH}_3$ or C_2H_5 or water for $\text{R} = \text{H}$. Although a number of isomeric complexes are possible depending upon the relative orientation of the chelate planes, the complexes studied have had S_4 symmetry, either rigorously as the crystal site symmetry or accidentally.

Although the copper(II) complexes of the formula $[\text{Cu}(\text{AA})(\text{CH}_3\text{O})]_x$ were found (47) to have $x = 2$ and, therefore, were not cubane-type complexes, a five coordinate cubane-type structure was observed for the copper(II) complex of the Schiff's base of 2,4-pentanedione and 2-aminoethanol (24).

In the cubane-type structure paramagnetic metal atoms can exhibit interesting magnetic behavior. These metal atoms may interact magnetically such that the dipole of one atom is influenced by the magnetic dipole of another. In cubane-type structures this magnetic interaction or "exchange" phenomenon is usually an indirect interaction through a bridging atom or group since the metal-metal distances are too large for significant direct interaction. $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$ exhibits ferromagnetic behavior (25) and $[\text{Cu}(\text{EIA})]_4$ exhibits antiferromagnetic behavior (48). The cubane-type complexes, $[\text{M}(\text{sal})(\text{CH}_3\text{O})(\text{ROH})]_4$ (where M represents Ni(II) or Co(II), sal represents salicylaldehydato, and R represents CH_3 or C_2H_5), have also been found to exhibit ferromagnetic behavior (23,49). Although there has been some low temperature work (50) on the cubane-type complex $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$, a meaningful interpretation of its magnetic behavior has not yet been obtained; a room temperature determination indicated a magnetic moment of 5.1 B.M. (51).

A ferromagnetic interaction results when the magnetic moments of the metal atoms are aligned parallel so as to reinforce one another; an antiferromagnetic interaction results when the moments are aligned antiparallel so as to cancel. Both interactions are temperature dependent; increasing the temperature can cause sufficient randomness in the orientations of the moments such that the tendency towards alignment is minimal

and simple paramagnetism is observed. Ferro- and antiferromagnetic complexes have characteristic temperatures--Curie temperature and Néel temperature, respectively--above which they exhibit simple paramagnetism. Below the Curie temperature parallel alignment is significant, and the magnetic susceptibility of a ferromagnetic complex increases much more rapidly with decreasing temperature; below the Néel temperature antiparallel alignment is significant, and the magnetic susceptibility of an antiferromagnetic complex decreases with decreasing temperature (52,53). Although the $[\text{Cu}(\text{EIA})]_4$ complex exhibits a net antiferromagnetic interaction, the magnetic behavior is actually more complex in that both ferro- and antiferromagnetic couplings are observed in the tetramer (48).

Cubane-type structures of transition metal polynuclear complexes discussed thus far have been those involving divalent metal atoms. At the time this study was started, there had not been reported any cubane-type structures containing trivalent transition metal atoms. Considering the chemistry of some of the trivalent metal atoms (52) and the cubane-type complexes previously discussed, the possibility existed of preparing some interesting compounds by the partial or complete oxidation of divalent metal complexes. Since (1) cobalt(II) cubanes were known, (2) cobalt(II) is readily oxidized to cobalt(III), and (3) the relative stability of cobalt(III) is greatly enhanced in the presence of complexing agents such as NH_3 , CN^- , ethylenediamine, and 2,4-pentanedione (52), the preparation of cobalt complexes was attempted first.

The objective was to study the oxidation of the cobalt(II) cubane-type complexes. The study was to include the use of various oxidizing

agents and chelating ligands and the characterization of any new products resulting from oxidation of cobalt(II) complexes. Characterization included determination of spectral and magnetic properties and structure elucidation. The possibility existed that these oxidations could result in complete oxidation to a cobalt(III) complex or in partial oxidation to a complex containing both cobalt(II) and cobalt(III).

Polynuclear complexes with metal ions in mixed oxidation states have been made and investigated. Several years ago a polynuclear complex of cobalt and 2-aminoethanol was reported (54); the complex contained a trinuclear cation formulated as a central cobalt(II) atom coordinated to two tris(2-aminoethoxido)cobalt(III) complexes. A structure with octahedral coordination of the central cobalt(II) atom through face-sharing of oxygens with the cobalt(III) octahedra was proposed. Also reported were analogous trinuclear complexes, $[M(\text{Co}(\text{chelate})_3)_2]^{M+}$, with 2-aminoethanethiolate as the chelate ligand and with cobalt(III), zinc(II), and nickel(II) as the central metal, M (55,56). A more recent study (57,58) reported the preparation of the acetate salt of the trinuclear cation, $[\text{Co}(\text{Co}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3)_2]^{2+}$. As previously proposed, the trimeric cation was found to consist of two tris(2-aminoethoxido)cobalt(III) complexes, each sharing three oxygens with a central cobalt(II) atom; however, the coordination of the central cobalt(II) atom was found to be trigonal prismatic. The Co-O distances for the Co(II) were found to be 0.12 - 0.14 Å longer than for the Co(III)'s. The O-Co-O angles were 79° for the Co(II) and 85° for the Co(III)'s. The magnetic moment given was 4.05 B.M. per trimer which is reasonable for three unpaired electrons. Several dinuclear

complexes with cobalt(II) and cobalt(III) have been reported, one with 2-aminoethanol (59) and one with 2,2'-iminodi(ethanol) (60). The ferredoxin protein was just recently reported (44) to contain Fe(II) and Fe(III) in cubane-type structures. (The protein has been observed to undergo a two-electron transfer; however, it is not clear whether one cubane-type unit undergoes the two-electron transfer or two cubane-type units undergo a one-electron transfer each.)

One of the problems in working with mixed oxidation states is the identifying of the respective oxidation states. Since cobalt(II) and cobalt(III) are known to have different spectral and magnetic properties, determination of the spectral and magnetic properties of a complex should facilitate the identification of the oxidation states in the complex. A spectral study (60) of the dinuclear cobalt complexes with 2-2'-iminodi(ethanol) confirmed the existence of cobalt(III); the reported presence of cobalt(II) was confirmed by a spectral study of decomposition products of the complex in hydrochloric acid. A magnetic study of the dinuclear complex would have helped in verifying the existence of cobalt(II) in the complex.

Cobalt(II), a d^7 ion, occurs in octahedral coordination as well as trigonal prismatic, tetrahedral, square planar, and five-coordinate; however, cobalt(III) a d^6 ion, usually occurs in octahedral coordination. The cobalt cubanes referenced previously have shown octahedral coordination of the cobalt.

Octahedral cobalt(II) complexes are usually high-spin with three unpaired electrons; however, there are complexes, for example,

$[\text{Co}(\text{NO}_2)_6]^{4-}$, and $[\text{Co}(\text{diarsine})_3]^{2+}$, which are low-spin with only one unpaired electron. High-spin complexes exhibit magnetic moments that range from 4.7 - 5.2 B.M. Full orbital angular momentum contribution, $\mu_{S+L} = [4S(S+1) + L(L+1)]^{\frac{1}{2}}$, produces a moment of 5.2 B.M.; the "spin-only" moment, $\mu_S = [4S(S+1)]^{\frac{1}{2}}$, would be 3.87 B.M. The observed moments indicate that there is little quenching of the orbital angular momentum by the ligand field (52).

The ground state for an octahedral cobalt(II) ion may be ${}^4T_{1g} \text{ -- } (T_{2g})^5(e_g)^2$ for a high spin complex or ${}^2E_g \text{ -- } (t_{2g})^6(e_g)$ for a low-spin complex. It has been predicted (61) that an octahedral high-spin cobalt(II) ion should have three spin-allowed d-d transitions, those from the ground state, ${}^4T_{1g}(F)$, to each of the excited states, ${}^4T_{2g}$, ${}^4A_{2g}$, and ${}^4T_{1g}(P)$. A reported spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex contained three maxima corresponding to calculated values; the maximal values of molar extinction coefficients, for the most intense bands did not exceed $10 \text{ M}^{-1} \text{ cm}^{-1}$ (62).

Octahedral cobalt(III) complexes are usually diamagnetic; however, a few paramagnetic complexes have been reported, for example, $[\text{CoF}_6]^{3-}$ and $\text{CoF}_3(\text{H}_2\text{O})_3$ (63).

The ground state for a free cobalt(III) ion would be ${}^5T_2 \text{ -- } (t_{2g})^4(e_g)^2$. Except in a very weak field, the ground state of an octahedral cobalt(III) ion is ${}^1A_{1g} \text{ -- } (t_{2g})^6$. The ${}^1A_{1g}$ state, originating in the high energy singlet state, 1I , drops rapidly and crosses the ${}^5T_{2g}$ at a very low value of Δ . Most of the known cobalt(III) complexes, as stated earlier, have no unpaired electrons and, thus, have an ${}^1A_{1g}$ ground state. These complexes should have two spin-allowed transitions, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and

${}^1A_{1g} \rightarrow {}^1T_{2g}$; additionally, some singlet-triplet transitions could occur (52). The spectrum of $[\text{Co}(\text{ethylenediamine})_3]^{3+}$ contains two strong bands with maxima at 340 nm ($\epsilon = 72 \text{ M}^{-1} \text{ cm}^{-1}$) and 467 nm ($\epsilon = 85 \text{ M}^{-1} \text{ cm}^{-1}$) which correspond to the two transitions, ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and ${}^1A_{1g} \rightarrow {}^1T_{1g}$, respectively (64).

A visible spectrum of the cobalt cubane-type complex, $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{CH}_3\text{OH})_4]$, contained a maximum at 525 nm and a shoulder at 498 nm; the molar extinction coefficient of the band at 525 nm was approximately $19 \text{ M}^{-1} \text{ cm}^{-1}$ (51).

Absorption in the ultraviolet region is characteristic of the ligand and is not indicative of the oxidation state of the metal ions in a complex. The spectrum of the cobalt(II) cubane-type complex (51) contained a maximum at 296 nm which had a molar extinction coefficient equal to approximately half of that of the cobalt(II) acetylacetonate at 292 nm ($\epsilon = 16,200 \text{ M}^{-1} \text{ cm}^{-1}$). The spectrum of the cobalt(II) acetylacetonate contained a band at 258 nm ($\epsilon = 34,000 \text{ M}^{-1} \text{ cm}^{-1}$) (65).

CHAPTER II

INSTRUMENTATION

Analytical Study

Analysis for cobalt was performed using a photometric titrator constructed by Sawyer (66). An interference filter (λ max, 546 nm) was used in the titrator. Titration of the standard into the sample cell was accomplished with a 10 ml microburet.

Magnetic Study

The Faraday method (67) was used to determine the magnetic susceptibilities at various temperatures. In this method, the force developed by a small sample suspended in a magnetic field of constant dH/dx is measured. An Alpha Scientific Laboratories Model 9500 Electromagnet fitted with Heyding pole tips was used to develop the magnetic field. The electromagnet was powered by an Alpha Model 40-50A current regulated power supply coupled with an Alpha Model 110 Regulator. The power supply was capable of supplying current from 0-50 amps, thus providing fields of different strengths. Force on the sample was measured using a Cahn RG Automatic Electrobalance coupled to a Minneapolis-Honeywell galvanometer (sensitivity of 0.0006 $\mu\text{a}/\text{mm}$). The galvanometer was used as a "null meter." The weighing mechanism was installed in a glass vacuum bottle fitted with a 16 mm diameter hangdown tube. A vacuum of 0.3 torr was maintained during measurements. The sample was contained in a small glass

bucket suspended inside the hangdown tube by a very fine, braided, nylon thread. For low temperature work, the hangdown tube was suspended in a Dewar jacket shaped to fit between the pole faces. Measurements of magnetic susceptibilities were made at room temperature (298°K), dry ice/acetone temperature (193°K), and liquid nitrogen temperature (77°K).

Spectral Studies

Infrared Spectrum

A Perkin-Elmer 457 Grating Infrared Spectrophotometer was used to obtain the infrared spectrum. A potassium bromide pellet was used as the medium for obtaining the spectrum.

Ultraviolet and Visible Spectra

The ultraviolet and visible spectra were obtained with a Cary Model 14 Recording Spectrophotometer. The matched cell sets used were of the following path lengths: 5.005 cm, 2.500 cm, 1.006 cm, and 0.100 cm. Both methanol and methylene chloride were used as solvents.

Mass Spectrum

The mass spectrum was obtained with a Varian M-66 Mass Spectrometer under the following operational conditions: Electron energy--70 eV, electron current--50 A, probe temperature--150-230°C, and pressure of 8×10^{-6} torr.

Crystallographic Study

Initial alignment, orientation, and determination of the reciprocal cell data were accomplished with a Mark II Precession Camera and a Picker X-Ray Generator with a Dunlee molybdenum fine-focus x-ray tube.

Collection of intensity data for structure elucidation was accomplished with a Picker Four Circle Automated Diffractometer coupled with an IBM 026 Key punch. Molybdenum $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) was also used in collecting intensity data. For all x-ray work, the single crystal, cemented to a glass fiber, was mounted on a STOE Eucentric Goniometer Head, 63.97 mm, with locks. The Burroughs 5500 and Univac 1108 computers were used for all crystallographic calculations.

CHAPTER III

EXPERIMENTAL

Preparation of ComplexPreparation of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

Cobalt(II) acetate tetrahydrate (0.02 mole) was dissolved in 400 ml of methanol, heating only to dissolve the material. The cobalt(II) acetate was cooled to room temperature (25°C), and a solution of 2,4-pentanedione (0.02 mole) in 25 ml of methanol was added with stirring. To this solution was added, dropwise, potassium hydroxide (0.03 mole) in 25 ml of methanol. Stirring of the resulting solution was continued for about 15 minutes at room temperature; then 25 drops of hydrogen peroxide (30 percent) was added. The flask containing the solution was then stoppered and allowed to stand. Overnight, dark brown, plate-like crystals had begun to form. The crystals were filtered, washed with small amounts of methanol and diethyl ether, and dried in vacuum at 100°C for several hours. The compound can be recrystallized from anhydrous diethyl ether using a Soxhlet Extractor apparatus.

An attempt was made to prepare the chromium, nickel, and manganese analogs of this cobalt(II,III) cubane complex by similar procedures; similar compounds were not obtained--only metal hydroxy/methoxy compounds.

In an attempt to determine if the cubane is formed prior to oxidation or after oxidation, a sample of $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$ prepared

by Kaplan (51) was dissolved in methanol without any acetate. A small quantity of hydrogen peroxide (30 percent) was added with stirring. After the solution had stood for several days, small, dark, four-cornered, star-shaped crystals had begun to form on the sides of the flask. Whether or not this was a cubane-type compound was not known at the time of this writing.

Analyses

For the cobalt analysis, a weighed sample was heated to 2000°C in an induction furnace for several hours. The residue was fused with potassium pyrosulfate; the resulting cobalt salt was quantitatively dissolved in a small volume of deionized water, and the pH was adjusted to about four with concentrated ammonium hydroxide. The sample solution was diluted to a known volume. The cobalt content was then determined by an EDTA titration (68) using the photometric titrator described previously. A copper(II) standard was used in the titration.

The carbon and hydrogen analyses were performed by Atlantic Micro-lab, Inc., Atlanta, Georgia.

The results of the analyses are given in Table 1.

Table 1. Analytical Data for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

% Cobalt		% Carbon		% Hydrogen	
Calcd.	Found	Calcd.	Found	Calcd.	Found
26.97	26.80	38.44	38.42	5.31	5.42

Magnetic Study

Faraday Method

In general, when a quantity of material, dm , is placed in an inhomogeneous magnetic field of value, H , it experiences a force, df , along the field gradient, dH/dx . The force can be expressed as follows:

$$dF = \chi \cdot dm \cdot H \cdot dH/dx$$

In the Faraday method, specially shaped magnet poles develop a sufficient region of constant force such that a small sample experiences a constant dH/dx (67). The above equation can be rewritten

$$F = \chi \cdot m K \quad \text{or} \quad K = F / (m \cdot \chi)$$

where $K = (H \cdot dH/dx)$ and is constant for a given field strength.

Instrument Operation Procedure

The electrobalance was initially calibrated for a 0-10 mg range with the empty glass bucket suspended in the hangdown tube and the electromagnet turned off. The initial electrobalance settings were as follows:

Mass Dial Range (MDR) -- 10 mg	Factor -- 1
Mass Dial (MD) -- 0.0000	Filter -- 0
Recorder Range -- (initial setting)	

The weight of the empty bucket was coarsely counterbalanced with tare weights and a calibrating weight equal to one-half MDR (5 mg) placed on the counterbalance pan. Fine adjustment to a zero null point on the galvanometer was obtained with the Set 0/10 control. The recorder range control was adjusted concurrently from a setting of 20 (least sensitive) to

a setting of 0.1 (most sensitive) in order to obtain the most sensitive null point. A null point was considered reached when the hairline stabilized within two small scale divisions on either side of zero on the galvanometer. The 5 mg calibrating weight was removed from the counterbalance pan, and the mass dial was set at 0.5000. A null reading was obtained by adjusting the Set 5 control concurrently with the Recorder Range control. This sequence was repeated until there was no change required for the Set 0/10 and Set 5 controls. At this stage, a 10 mg range had been defined with the midpoint located precisely, and the two controls were locked.

After calibrating the electrobalance, the diamagnetic corrections for the empty glass bucket were determined at different current settings for the electromagnet. The 5 mg calibrating weight was removed from the counterbalance pan, and the mass dial was set to 0.5000. Prior to energizing the electromagnet, its height was adjusted to that position, previously determined, that placed the suspended bucket between the pole faces in a region of constant force. After energizing the electromagnet, mass readings were made at the following current dial settings: 0, 3, 4, 5, 6, 7, 8, 9, 10. A mass reading was obtained by adjusting the mass dial to obtain a null point for each current setting. The diamagnetic corrections were obtained at three temperatures (298°K, 77°K, and 193°K) by this method. The recorder range control had to be in the "Z" position when weights or sample were added or removed and when current settings were changed.

The standard used in this study was mercury tetrathiocyanatocobaltate, $\text{HgCo}(\text{CNS})_4$, with a gram susceptibility of 16.44×10^{-6} at 20° C

(69). A sample of the standard (50.32 mg) was placed in the bucket. The 5 mg calibrating weight was placed on the counterbalance pan and the mass dial was set to 0.0000. Tare weights were then added to the pan until a zero null point was obtained. The procedure for obtaining mass dial readings at the current settings was repeated at the three temperatures. The use of the 5 mg calibrating weight was continued throughout to facilitate recalibration of the electrobalance at any time.

The standard was removed from the bucket which was then cleaned in nitric acid, rinsed, and dried. A sample (49.79 mg) of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ was placed in the bucket, and the weight of the sample was counterbalanced as previously done with the standard. Again, mass dial readings were made by the same procedure used for the empty bucket and the standard. It should be noted that readings at 77°K were made only at current settings of 0, 3, 4, 5, because the mass change exceeded the 10 mg range, and extending the range would have resulted in reduced sensitivity of measurements.

Calculations

The calculations used for determining the magnetic moments at the three temperatures and the abbreviations used in the calculations are given below.

J = current setting

MDR = mass dial range mg

$\Delta r_B(J)$ = mass dial reading at J current minus mass dial reading at zero current for the empty bucket, expressed as decimal fractions

$\Delta MB(J)$ = apparent mass change at J current for empty bucket, mg

$\Delta r_{ST}(J)$ = mass dial reading at J current minus mass dial reading at zero current for standard, expressed as decimal fraction

$\Delta MST(J)$ = apparent mass change at J current for standard, mg

$\Delta r_{SAM}(J)$ = mass dial reading at J current minus mass dial reading at zero current for sample, expressed as decimal fraction

$\Delta MSAM(J)$ = apparent mass change at J current for sample, mg

MST = mass standard used in bucket, g

MSAM = mass of sample used in bucket, g

$K(J)$ = proportionality constant at J current

χ_g^* = gram susceptibility of standard

$\chi_g(J)$ = gram susceptibility of sample at J current

DIAMAG = summation of atomic diamagnetic corrections for sample

MW = molecular weight of sample

$\chi_M^{corr}(J)$ = corrected molar susceptibility for sample at J current

T = absolute temperature at which measurements were made

$\mu_{eff}(J)$ = effective magnetic moment per cobalt tetramer at J current

μ_{eff}^* = effective magnetic moment per cobalt(II) at J current.

The gram susceptibilities for the standard were calculated for the three temperatures using the following expression (69):

$$\chi_g^* = 4981.32 \times 10^{-6} (T + 10)^{-1} .$$

The values calculated were 16.17×10^{-6} , 24.54×10^{-6} , and 57.26×10^{-6} for 298°K, 193°K, and 77°K, respectively. These values were used to calculate values for the $K(J)$ using the following equations:

$$\Delta MB(J) = \Delta rB(J) \times MDR$$

$$\Delta MST(J) = (\Delta rST(J) \times MDR) + \Delta MB(J)$$

$$K(J) = [10^{-3} \times \Delta MST(J)] / (MST \times \chi_g^*)$$

The magnetic susceptibilities and magnetic moments of the sample were calculated from the following equations:

$$\Delta MSAM(J) = (\Delta rSAM(J) \times MDR) + \Delta MB(J)$$

$$\chi_g(J) = [10^{-3} \times \Delta MSAM(J)] / [MSAM \times K(J)]$$

$$\chi_M^{\text{corr}}(J) = [\chi_g(J) \times MW] + \text{DIAMAG}$$

$$\mu_{\text{eff}}(J) = 2.84[\chi_M^{\text{corr}}(J) \times T]^{\frac{1}{2}}$$

$$\mu_{\text{eff}}^*(J) = 2.84\{[\chi_M^{\text{corr}}(J)/2] \times T\}^{\frac{1}{2}}$$

Magnetic Data

The sample of complex used in the magnetic study was crystalline material isolated from the preparation solution. The magnetic data obtained are summarized in the tables below.

Table 2. Magnetic Data for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ at 298°K

Current	$\chi_g \times 10^6$	$\chi_M^{\text{corr}} \times 10^6$	$\mu_{\text{eff}}, \text{B.M.}$	$\mu_{\text{eff}}^*, \text{B.M.}$
3	23.185	20665	7.048	4.984
4	23.177	20658	7.046	4.983
5	23.225	20700	7.054	4.989
6	23.191	20670	7.048	4.984
7	23.202	20680	7.050	4.986
8	23.195	20674	7.049	4.985
9	23.197	20676	7.050	4.986
10	23.136	20622	7.040	4.979
Average $\mu_{\text{eff}}^* = 4.984$				

Table 3. Magnetic Data for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ at 193°K

Current	$\chi_g \times 10^6$	$\chi_M^{\text{corr}} \times 10^6$	$\mu_{\text{eff}}, \text{B.M.}$	$\mu_{\text{eff}}^*, \text{B.M.}$
3	32.381	28703	6.684	4.727
4	32.319	28649	6.678	4.723
5	32.215	28558	6.667	4.715
6	32.161	28511	6.662	4.711
7	32.201	28546	6.666	4.714
8	32.194	28540	6.665	4.714
9	32.229	28570	6.669	4.716
10	32.128	28482	6.659	4.709
Average $\mu_{\text{eff}}^* = 4.716$				

Table 4. Magnetic Data for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ at 77°K

Current	$\chi_g \times 10^6$	$\chi_M^{\text{corr}} \times 10^6$	μ_{eff} , B.M.	μ_{eff}^* , B.M.
3	78.532	69305	6.561	4.640
4	77.788	68392	6.517	4.609
5	77.679	68297	6.513	4.606
				Average $\mu_{\text{eff}}^* = 4.618$

Spectral Studies

Infrared Spectrum

The infrared spectrum of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ was obtained with sample of the complex made into a potassium bromide pellet. The absorption peak of polystyrene at 1603 cm^{-1} was used to calibrate the spectrum. Major absorption peaks of the spectrum are given in the table below.

Table 5. Infrared Absorption Peaks for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

cm^{-1}	Relative Intensity*	cm^{-1}	Relative Intensity	cm^{-1}	Relative Intensity
2920	m	1260	m	665	m
2820	w	1190	m	585	m
1580	s,b	1015	s	550	m
1510	s,b	920	m	490	m
1380 -	s,b	770	m	475	m
1415		710	m	425	m
1285	m				

* s--strong, m--medium, w--weak, b--broad

Ultraviolet and Visible Spectra

The ultraviolet and visible spectra were determined with the complex dissolved in methanol and in methylene chloride. The complex was stable at room temperature in both solvents for several days. The spectra in methanol given in Figures 2 and 3 were found to be identical to the spectra in methylene chloride.

Mass Spectrum

The mass spectrum of the complex was determined on a crystalline sample isolated from the preparation solution. The m/e values given are for those ions with a relative abundance greater than 10 percent of the most abundant ion ($m/e = 43$). The relative abundances, expressed as percents, are indicated in parentheses: 481(21), 257(14), 242(12), 188(30), 158(17), 124(14), 122(12), 96(26), 60(23), 58(66), 53(21), 45(19), 44(72), 43(100), 42(16), 39(14), 32(16), 31(19), 29(16), 28(12), 27(14), 18(46), 17(19), 15(40).

Crystallographic Study

Calculations

Computations were carried out on the Burroughs B-5500 computer and the Univac 1108 computer. Programs employed included modified versions of F. L. Carter's program for calculating diffractometer setting (70), Zalkin's FORDAP Fourier summation program (71), Busing-Martin-Levy's XFLS (72) and ORFFE (73), Johnson's ORTEP thermal ellipsoid plotting program (74), and several locally written programs for data reduction and least-squares plane calculations.

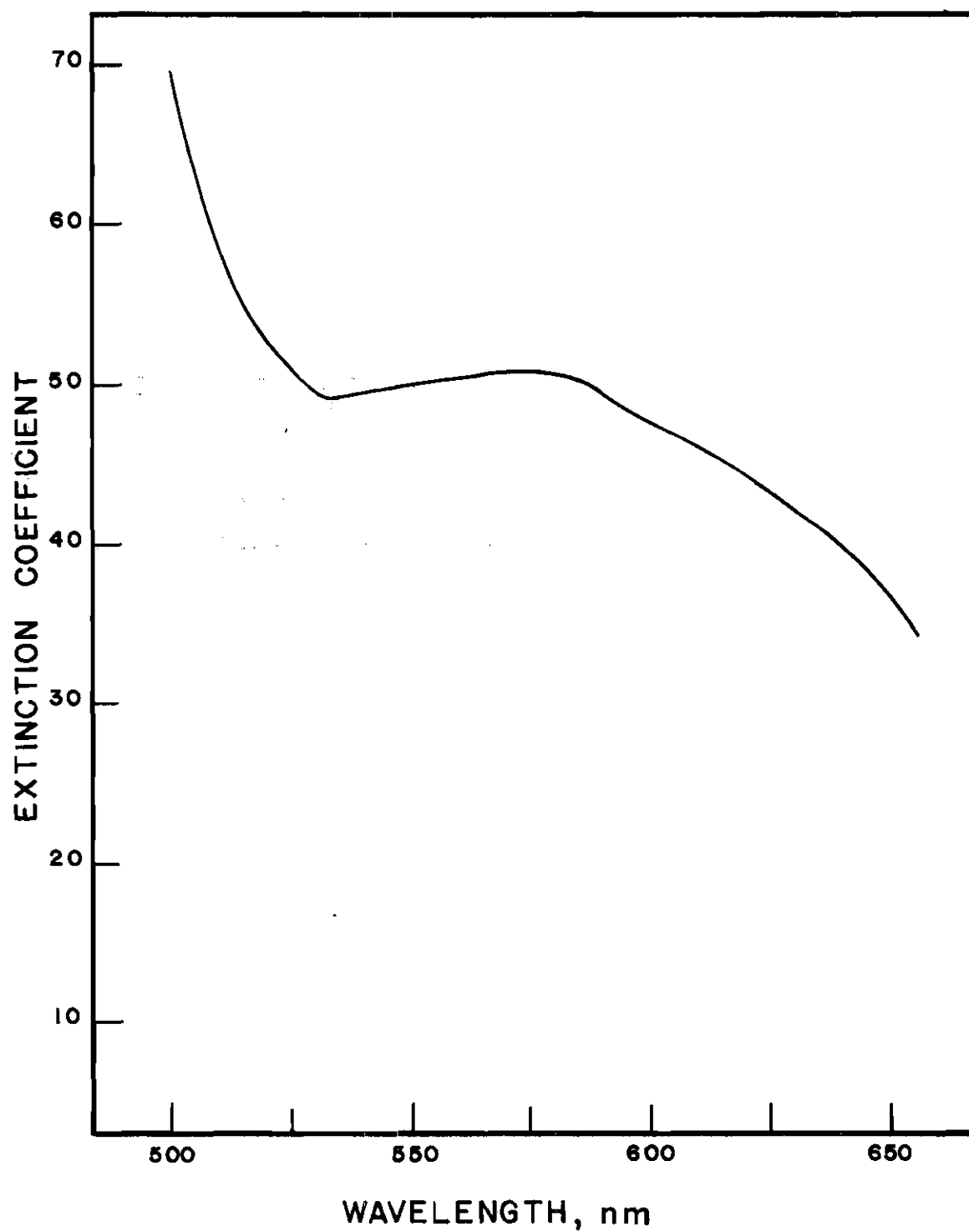


Figure 2. Visible Spectrum of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ in Methanol

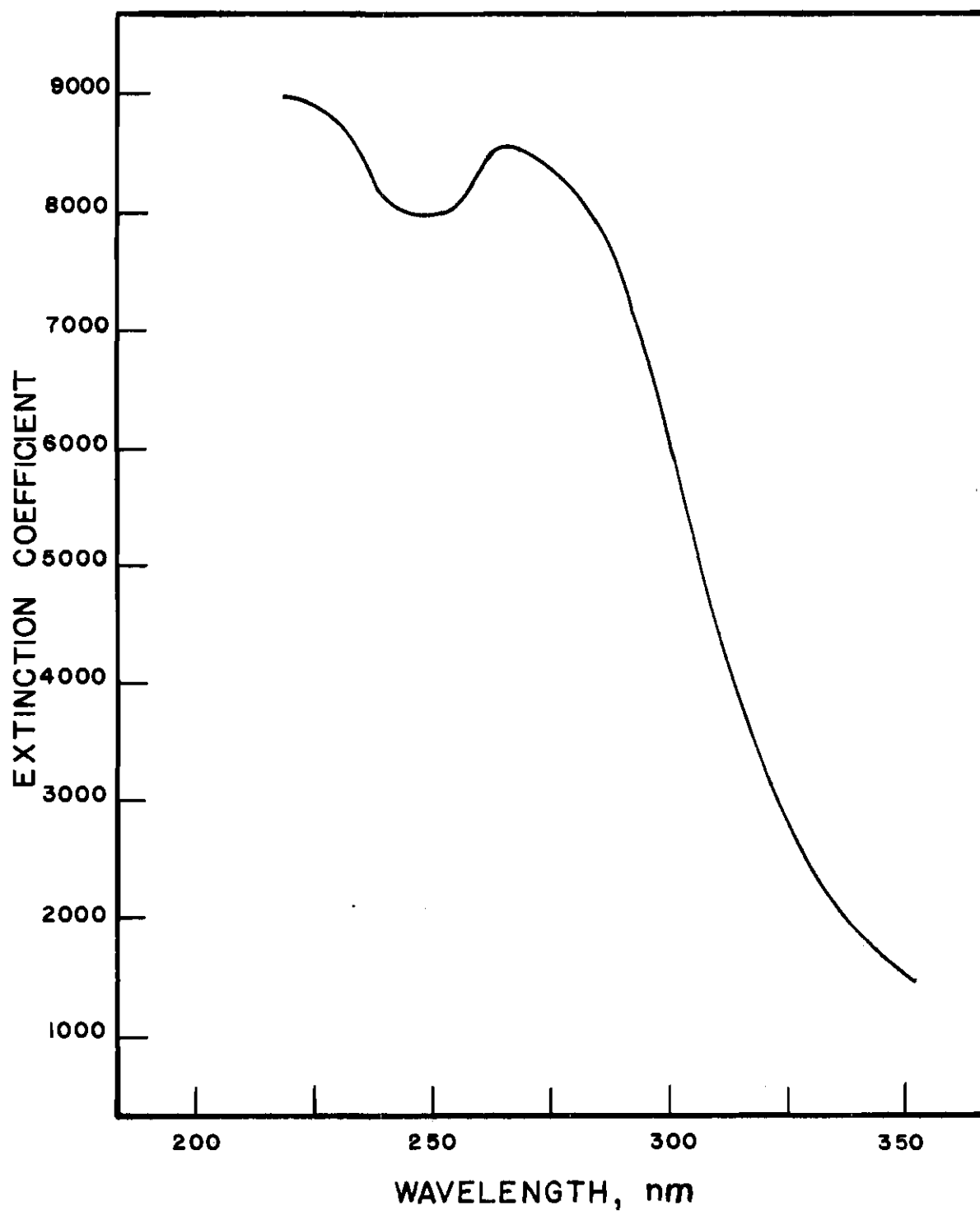


Figure 3. Ultraviolet Spectrum of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ in Methanol

Solution of the Structure of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_2(\text{C}_2\text{H}_3\text{O}_2)_2]$

Crystals isolated from the initial preparation were of sufficient size and quality for x-ray work without recrystallization. For the space group determination, a dark brown, plate-like crystal with dimensions $0.1 \times 0.2 \times 0.5$ mm was mounted on a glass rod along the long dimension. When mounted on the precession camera, the a^* axis was coincident with the camera spindle axis. Precession photographs, using zirconium-filtered molybdenum $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$), indicated a triclinic unit cell; $P\bar{1}$, No. 2 (75), was assumed to be the space group, and the successful refinement of the structure confirmed that assumption.

The same crystal and goniometer head were then transferred to the automated Picker four-circle diffractometer. Inasmuch as alignment on the diffractometer was more critical than on the precession camera, the crystal was realigned according to published instructions (76). After the first day of working at realigning the crystal, the x-ray tube burned out; a Dunlee experimental, fine-focus x-ray tube arrived two months later. After installing and aligning the new tube and completing realignment of the crystal, the four angles (θ , χ , ω and 2θ) which define the position of the crystal and counter to record a reflection in reciprocal space were determined for 20 reflections. Using the 20 reflections, refined unit cell parameters and the angle settings for collecting intensity data were calculated by a least-squares procedure (70). The cell parameters calculated from the diffractometer data were $a = 10.88 (1) \text{ \AA}$, $b = 22.51 (3) \text{ \AA}$, $c = 12.76 (1) \text{ \AA}$, $\alpha = 110.22 (8)^\circ$, $\beta = 123.34 (7)^\circ$, $\gamma = 108.92 (7)^\circ$, and $V = 1848.5 \text{ \AA}^3$ (25°C , Mo radiation). The calculated density of 1.57 g-cm^{-3}

for two molecules per unit cell agreed well with the observed density of $1.56 (1) \text{ g-cm}^{-3}$ determined by the flotation method using hexane and carbon tetrachloride.

The x-ray intensity measurements were made, with molybdenum radiation, on the same crystal used for the unit cell determination. The intensities were measured with a scintillation counter mounted 21 cm from the crystal; the intensities were collected by the θ - 2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1° per minute. A symmetrical scan of 2° was taken about the calculated position for each reflection; stationary background counts of 20 seconds were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts per second. The pulse height analyzer was set for approximately a 90 percent window, centered on the molybdenum $K\alpha$ peak. A strip recorder monitored the scan of each peak, and the scans were visually examined for erratic background and for the inclusion of $K\beta$ peaks. A standard reflection (220) was scanned every 70 reflections to check for instrument or crystal variation; no significant variation in the number of counts for this reflection was observed during the entire data collection period. Data were collected for 2370 calculated positions in the hemisphere for a positive value and equivalent reflections were averaged (HKO is equivalent to $\bar{H}\bar{K}\bar{O}$). The limits set in the Carter program were H from -16 to +16, K from -7 to +7, and L from zero to +10. This essentially collected all possible data within the Ewald sphere. Corrected intensities (I) were obtained by subtracting

three times the total measured background from the total integrated peak count (CT),

$$I = CT - 0.5(t_c/t_b)(bgd1 + bgd2)$$

where t_c is the scan time and t_b is the counting time of each background (either bgd1 or bgd2). The corrected intensities were assigned standard deviations according to the formula

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(bgd1 + bgd2) + (pI)^2]^{1/2}.$$

A total of 1166 reflections was accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.33 with $p = 0.03$. The intensities were corrected for lorentz and polarization effects; no corrections were made for absorption effects. The calculated linear absorption coefficient, μ , was 19 cm^{-1} , based on values of the atomic absorption coefficients given in the International Tables for X-ray Crystallography (75). The following formula was used to calculate μ :

$$\mu = \frac{10}{V} \times N \times \sum(\mu_a \times A)$$

where V = volume of the unit cell, N = number of molecules per unit cell, μ_a = atomic absorption coefficient, and A = number of a type atoms in the molecule.

The four cobalt atoms and sixteen oxygen atoms were located from a three dimensional Patterson synthesis. Four cycles of full-matrix least-squares refinement using the four cobalt atoms and the four bridging oxygen atoms resulted in a conventional R_1 value $(\sum ||F_o| - |F_c|| / \sum |F_o|)$ of

0.389; the remaining oxygen atoms were introduced and four cycles of least-squares refinement produced an R_1 value of 0.321. From an electron density map phased on the four cobalt and sixteen oxygen atoms, thirteen carbon atoms were located; from the two succeeding electron density maps, the remaining fifteen carbon atoms were located. A weighting scheme based on counting statistics ($w = 4I/\sigma^2(I)$) was introduced, and least-squares refinement of a scale factor, coordinates of each atom, and individual isotropic temperature factors (192 variable parameters) was continued until no parameter varied by more than 18 percent of its estimated standard deviation; R_1 and R_2 ($R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$) converged to values of 0.068 and 0.061, respectively. The final difference Fourier had no positive maxima greater than $0.34 \text{ e}/\text{\AA}^3$.

In the structure factor calculations, the scattering factors tabulated by Ibers (75) were employed for all atoms.

The positional and isotropic thermal parameters derived from the last cycle of least-squares refinement are listed in Table 6. The observed and calculated structure factors for the 1166 nonzero, unique reflections are given in Table 7.

Table 6. Final Positional and Thermal Parameters
for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

Atom	x	y	z	B(\AA^2)
Co1	0.4132(3)	0.3096(2)	0.1967(3)	2.69(5)
Co2	0.0933(3)	0.1523(2)	-0.1336(3)	2.54(5)
Co3	0.0797(3)	0.2952(2)	-0.0735(3)	3.16(5)
Co4	0.0042(3)	0.2180(2)	0.0578(3)	3.40(6)
01	0.1994(16)	0.2013(11)	0.0804(15)	3.63(27)
02	0.2587(16)	0.2668(11)	-0.0276(14)	2.81(22)
03	0.2445(15)	0.3279(11)	0.1641(14)	3.29(25)
04	-0.0787(15)	0.1712(10)	-0.1669(13)	3.30(25)
05	0.6037(16)	0.4146(10)	0.2897(15)	3.91(27)
06	0.5298(16)	0.3390(10)	0.4003(15)	4.07(27)
07	0.5523(14)	0.2743(10)	0.1926(14)	2.77(23)
08	-0.0010(16)	0.1163(10)	-0.3366(14)	3.50(26)
09	-0.0646(16)	0.0463(10)	-0.2160(15)	4.23(28)
010	0.2932(15)	0.1466(10)	-0.0727(13)	3.41(25)
011	-0.1035(19)	0.3102(12)	-0.0888(17)	5.82(34)
012	-0.0658(16)	0.2506(12)	-0.3048(15)	3.84(26)
013	0.2670(16)	0.4108(11)	0.0270(16)	3.92(28)
014	-0.1612(19)	0.2517(12)	0.0060(18)	4.96(30)
015	-0.1981(17)	0.1041(11)	-0.0462(16)	4.79(31)
016	0.1165(18)	0.2630(11)	0.2817(16)	4.68(30)

Table 6. (Continued)

Atom	x	y	z	B(\AA^2)
M1C ^a	0.2319(24)	0.1581(18)	0.1396(23)	3.26(38)
M2C	0.3578(27)	0.2949(17)	-0.0713(24)	4.68(46)
M3C	0.3250(29)	0.4122(18)	0.3004(26)	5.36(49)
M4C	-0.2910(25)	0.1035(16)	-0.3303(22)	4.12(44)
R1C1 ^b	0.8865(34)	0.5552(20)	0.4861(29)	6.52(56)
R1C2	0.7621(26)	0.4802(17)	0.4510(24)	3.84(42)
R1C3	0.8102(28)	0.4778(17)	0.5728(24)	4.52(45)
R1C4	0.6987(28)	0.4135(17)	0.5480(24)	4.60(44)
R1C5	0.7514(28)	0.4156(18)	0.6898(26)	5.37(49)
R2C1	-0.2882(34)	-0.1023(20)	0.3943(29)	6.93(59)
R2C2	-0.1849(29)	-0.0248(19)	-0.3737(26)	5.07(48)
R2C3	-0.2179(29)	-0.0273(18)	-0.4932(25)	4.84(47)
R2C4	-0.1316(28)	0.0361(18)	-0.4708(24)	3.96(41)
R2C5	-0.1777(27)	0.0356(18)	-0.6154(25)	5.01(48)
R3C1	-0.2038(33)	0.2535(20)	-0.5274(29)	7.07(62)
R3C2	-0.0448(35)	0.3027(23)	-0.3355(30)	6.21(54)
R3C3	0.0930(39)	0.3863(22)	-0.2308(34)	7.35(30)
R3C4	0.2388(31)	0.4394(20)	-0.0540(29)	5.51(51)
R3C5	0.3872(40)	0.5342(23)	0.0529(35)	8.69(72)
R4C1	0.2016(36)	0.2705(21)	0.5098(32)	7.91(65)
R4C2	0.0619(32)	0.2158(20)	0.3129(27)	5.34(49)
R4C3	-0.0806(34)	0.1359(20)	0.2041(31)	6.41(56)
R4C4	-0.2056(32)	0.0848(20)	0.0325(30)	6.40(56)

Table 6. (Concluded)

Atom	x	y	z	B(\AA^2)
R4C5	-0.3640(38)	-0.0169(22)	-0.0791(33)	7.90(66)
A1C1 ^c	0.4773(22)	0.2099(16)	0.0722(21)	2.82(36)
A1C2	0.6060(26)	0.1897(17)	0.0867(23)	4.34(43)
A2C1	-0.1857(27)	0.2798(20)	-0.0555(26)	4.34(44)
A2C2	-0.3198(34)	0.3064(20)	-0.0834(30)	6.86(60)

^aM1,2,3,4 denote the methoxides.

^bR1,R2,R3,R4, denote the 2,4-pentanedionato chelate rings.

^cA1 and A2 denote the acetates.

Table 7. Observed and Calculated Structure Factors
for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
	L = 0			2	6	31	30	-2	-3	40	41	-3	3	40	34
				3	6	34	34	1	-3	69	74	-2	3	15	14
6	0	48	46	6	6	21	19	2	-3	39	45	-1	3	24	35
-7	1	31	32	-9	7	23	22	3	-3	46	46	0	3	14	15
-5	1	20	24	-7	7	31	35	4	-3	31	36	1	3	41	47
-4	1	33	35	-6	7	69	70	5	-3	31	35	2	3	25	26
-3	1	36	34	-5	7	57	55	6	-3	24	24	-7	4	19	15
-2	1	28	31	-4	7	141	136	-6	-2	31	27	-6	4	69	68
3	1	41	44	-2	7	44	46	-5	-2	17	9	-4	4	95	91
4	1	22	24	-1	7	54	55	-4	-2	16	23	-2	4	129	126
5	1	34	32	0	7	125	111	-3	-2	41	38	-1	4	14	12
7	1	19	18	1	7	27	26	-2	-2	72	69	1	4	40	43
-3	2	35	31	3	7	28	27	-1	-2	26	30	3	4	21	21
-2	2	130	130	4	7	21	21	1	-2	63	68	-9	5	18	15
1	2	52	57	5	7	28	30	2	-2	32	32	-7	5	44	47
2	2	98	105					6	-2	22	21	-6	5	53	52
6	2	25	26		L = 1			-7	-1	37	39	-5	5	82	73
-8	3	18	16					-5	-1	20	17	-4	5	160	153
-6	3	32	37	-6	-7	24	25	-4	-1	22	20	-3	5	23	21
-4	3	31	28	-4	-7	23	28	-3	-1	51	49	-2	5	36	38
-3	3	57	57	0	-7	65	66	-2	-1	13	15	-1	5	73	63
1	3	42	38	1	-7	18	6	1	-1	36	37	0	5	44	45
4	3	22	23	2	-7	38	37	2	-1	21	20	2	5	17	17
5	3	21	19	3	-7	31	31	4	-1	40	42	3	5	40	38
-7	4	18	20	4	-7	15	17	5	-1	71	73	4	5	18	15
-6	4	41	41	6	-7	61	62	-8	0	21	21	-10	6	19	16
-5	4	56	60	8	-7	33	35	-4	0	21	22	-7	6	29	26
-2	4	72	70	-4	-6	25	24	-3	0	24	22	-6	6	53	52
-1	4	37	39	-3	-6	43	45	-2	0	16	21	-5	6	65	66
0	4	53	60	-2	-6	18	18	2	0	70	64	-4	6	218	205
1	4	32	31	-1	-6	79	83	3	0	40	40	-2	6	48	46
2	4	81	76	1	-6	64	62	5	0	20	10	-1	6	75	81
3	4	33	36	2	-6	53	57	6	0	26	28	1	6	23	25
4	4	19	19	3	-6	27	21	-7	1	41	41	2	6	49	42
-9	5	18	18	4	-6	19	18	-5	1	17	19	3	6	19	18
-8	5	24	24	6	-6	26	28	-4	1	32	31	-7	7	46	46
-7	5	20	20	-7	-5	19	13	-3	1	41	43	-6	7	60	64
-6	5	53	54	-4	-5	48	47	-2	1	28	21	-5	7	174	164
-4	5	46	46	-3	-5	28	25	1	1	70	64	-4	7	171	163
-2	5	23	21	-2	-5	86	89	2	1	15	11	-3	7	41	38
-1	5	38	40	-1	-5	40	42	3	1	17	16	-2	7	25	21
0	5	63	63	2	-5	16	15	4	1	40	37	-1	7	54	56
1	5	62	60	3	-5	28	26	5	1	69	67	0	7	27	25
2	5	16	15	6	-5	42	47	-8	2	24	25	1	7	23	22
3	5	39	38	8	-5	40	40	-6	2	51	47	5	7	29	27
4	5	24	24	-2	-4	110	106	-5	2	40	38				
6	5	25	20	-1	-4	33	25	-4	2	20	10		L = 2		
-9	6	21	22	0	-4	23	25	-2	2	37	39				
-6	6	34	32	2	-4	23	18	1	2	70	60	-4	-7	58	57
-5	6	42	42	3	-4	28	26	2	2	28	25	-3	-7	37	37
-4	6	95	96	5	-4	25	26	4	2	46	42	-2	-7	184	180
-3	6	107	104	-7	-3	21	28	-6	3	50	50	-1	-7	83	82
-2	6	42	38	-4	-3	22	22	-5	3	17	9	0	-7	60	61
-1	6	54	46	-3	-3	65	69	-4	3	18	18	1	-7	21	12

Table 7. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
2	-7	37	35	-7	-1	51	52	1	4	60	62	-3	-4	39	37
3	-7	15	14	-6	-1	49	49	2	4	23	18	-2	-4	75	77
4	-7	47	49	-5	-1	87	86	-10	5	18	16	-1	-4	60	63
8	-7	30	34	-2	-1	13	8	-7	5	54	57	0	-4	56	51
-5	-6	17	24	-1	-1	111	114	-6	5	33	35	1	-4	20	16
-2	-6	14	13	0	-1	20	20	-4	5	110	105	2	-4	42	43
-1	-6	64	63	1	-1	69	68	-3	5	56	58	5	-4	32	32
0	-6	48	43	3	-1	22	24	-2	5	22	11	-8	-3	20	25
1	-6	18	11	4	-1	66	67	-1	5	44	44	-7	-3	49	52
2	-6	46	45	5	-1	78	80	2	5	23	18	-6	-3	61	62
3	-6	37	42	-8	0	29	31	-7	6	17	15	-5	-3	103	104
4	-6	37	41	-6	0	59	60	-6	6	29	30	-4	-3	37	36
5	-6	56	61	-4	0	47	45	-5	6	31	31	-3	-3	75	76
7	-6	25	23	-3	0	72	76	-4	6	106	96	-2	-3	17	6
-7	-5	24	30	-1	0	26	28	-3	6	40	39	-1	-3	74	73
-4	-5	37	38	0	0	95	90	-2	6	55	51	1	-3	46	48
-3	-5	17	22	1	0	72	72	-1	6	34	34	2	-3	26	30
-2	-5	133	142	3	0	21	24	0	6	63	66	4	-3	42	46
0	-5	51	49	4	0	79	78	1	6	55	53	-8	-2	31	29
2	-5	37	39	-8	1	28	24	2	6	34	29	-6	-2	33	39
3	-5	32	32	-5	1	36	38	4	6	19	18	-5	-2	48	51
-6	-4	27	27	-4	1	32	28	-8	7	16	9	-4	-2	22	23
-4	-4	38	39	-3	1	76	79	-7	7	20	19	-3	-2	49	45
-3	-4	19	12	0	1	26	22	-5	7	201	185	-2	-2	19	7
-2	-4	24	27	1	1	38	38	-4	7	44	47	-1	-2	34	36
-1	-4	61	65	2	1	32	30	-3	7	49	47	1	-2	118	119
0	-4	62	63	4	1	60	58	1	7	69	66	2	-2	34	32
1	-4	50	48	5	1	35	36					3	-2	20	21
2	-4	24	22	-8	2	19	20					4	-2	39	42
-7	-3	30	33	-6	2	88	84			L= 3		5	-2	19	19
-6	-3	17	18	-5	2	15	19	-3	-7	36	37	-8	-1	24	20
-5	-3	55	57	-4	2	15	11	-2	-7	150	152	-7	-1	22	21
-4	-3	14	11	-3	2	49	49	-1	-7	59	64	-6	-1	104	104
-3	-3	14	15	-2	2	38	47	0	-7	75	82	-5	-1	110	106
-2	-3	63	57	-1	2	38	43	1	-7	31	30	-4	-1	61	59
-1	-3	95	102	1	2	41	41	3	-7	19	15	-3	-1	14	19
0	-3	63	75	2	2	27	26	4	-7	70	71	-2	-1	12	7
1	-3	28	30	3	2	53	53	6	-7	25	26	-1	-1	27	19
2	-3	37	33	4	2	54	49	-3	-6	63	63	0	-1	69	72
3	-3	38	38	-8	3	21	17	-2	-6	85	88	1	-1	51	53
4	-3	29	30	-7	3	54	53	0	-6	75	71	4	-1	62	66
5	-3	54	57	-6	3	25	21	1	-6	68	69	5	-1	29	30
-8	-2	21	16	-5	3	31	28	2	-6	43	44	6	-1	26	25
-5	-2	24	26	-4	3	21	24	3	-6	64	70	-8	0	24	22
-4	-2	45	46	-3	3	29	27	5	-6	20	18	-7	0	47	44
-3	-2	33	30	-2	3	24	18	-7	-5	22	21	-6	0	74	75
-2	-2	73	74	-1	3	78	71	-5	-5	26	31	-5	0	16	18
-1	-2	82	85	2	3	34	30	-3	-5	69	65	-4	0	15	13
0	-2	12	19	3	3	19	22	-2	-5	31	36	-2	0	57	55
1	-2	52	49	-6	4	46	45	0	-5	65	70	1	0	48	48
2	-2	44	46	-5	4	18	20	2	-5	33	34	3	0	62	62
3	-2	35	34	-4	4	149	146	5	-5	19	20	4	0	48	46
4	-2	35	38	-1	4	76	66	-5	-4	36	38	5	0	21	17
-8	-1	18	22	0	4	73	75	-4	-4	69	70	-8	1	37	33

Table 7. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-7	1	17	20	2	6	22	24	4	-3	41	40	-2	4	46	44
-6	1	54	55	-7	7	48	49	6	-3	20	23	-1	4	47	49
-5	1	28	23	-5	7	74	68	-7	-2	76	77	0	4	132	130
-4	1	63	60	-4	7	28	26	-6	-2	75	76	1	4	20	17
-3	1	64	63	-2	7	19	23	-3	-2	53	46	2	4	30	32
-2	1	43	40	-1	7	42	39	-2	-2	85	80	-9	5	32	31
-1	1	46	43	1	7	27	26	-1	-2	100	100	-8	5	28	27
0	1	41	45	3	7	25	22	0	-2	84	90	-7	5	84	83
3	1	20	15					1	-2	23	24	-6	5	29	29
4	1	24	27					2	-2	42	39	-4	5	32	32
-7	2	29	29			L = 4		3	-2	33	29	-3	5	39	39
-6	2	22	16	-6	-7	17	17	-6	-1	110	107	-2	5	22	19
-3	2	69	72	-4	-7	46	47	-5	-1	33	33	-1	5	52	51
-2	2	79	69	-3	-7	49	52	-4	-1	38	38	1	5	19	19
-1	2	35	39	-1	-7	41	41	-3	-1	36	37	-10	6	42	42
0	2	35	43	0	-7	51	55	-2	-1	84	77	-8	6	26	29
1	2	61	59	2	-7	56	56	-1	-1	60	64	-6	6	55	57
3	2	49	48	6	-7	26	29	0	-1	106	101	-5	6	16	17
-8	3	29	24	-7	-6	19	24	4	-1	18	14	-4	6	16	21
-7	3	28	26	-5	-6	19	21	-9	0	21	16	-3	6	21	24
-6	3	19	14	-3	-6	53	50	-7	0	69	65	-2	6	24	21
-5	3	67	63	-2	-6	57	61	-5	0	31	33	-1	6	65	64
-4	3	45	44	-1	-6	52	49	-3	0	51	46	0	6	121	125
-3	3	34	32	0	-6	86	94	-1	0	27	35	2	6	24	27
-1	3	43	43	1	-6	42	43	2	0	33	31	-8	7	16	20
1	3	53	48	2	-6	67	70	3	0	23	21	-7	7	72	74
-8	4	24	21	3	-6	67	70	-9	1	22	14	-6	7	18	14
-5	4	52	50	4	-6	20	23	-7	1	23	17	-4	7	36	39
-4	4	33	27	5	-6	34	41	-6	1	55	52	-3	7	18	18
-3	4	36	34	-8	-5	18	23	-5	1	14	10	-2	7	28	20
-2	4	87	91	-6	-5	31	37	-3	1	15	20	-1	7	73	69
-1	4	48	47	-5	-5	16	12	-2	1	60	64				
0	4	72	77	-3	-5	94	101	-1	1	63	61			L = 5	
1	4	64	64	-2	-5	15	9	1	1	31	27				
-11	5	22	15	-1	-5	33	33	2	1	24	20	-5	-7	29	30
-9	5	18	18	0	-5	62	62	-8	2	24	28	-4	-7	56	55
-8	5	18	10	2	-5	44	48	-7	2	37	36	-3	-7	33	30
-7	5	16	18	4	-5	27	26	-6	2	40	37	-2	-7	53	59
-6	5	24	27	-6	-4	21	20	-5	2	72	72	-1	-7	44	47
-5	5	131	119	-5	-4	40	40	-3	2	18	10	0	-7	67	67
-3	5	40	42	-3	-4	57	60	-2	2	131	127	1	-7	45	44
-1	5	22	18	-2	-4	98	92	-1	2	26	27	2	-7	27	29
1	5	89	83	-1	-4	16	14	0	2	36	39	4	-7	18	15
3	5	31	28	0	-4	108	112	-9	3	42	45	-5	-6	42	50
-11	6	19	17	1	-4	24	22	-8	3	33	31	-3	-6	32	37
-10	6	26	24	2	-4	35	31	-7	3	68	66	0	-6	80	80
-7	6	24	15	5	-4	22	18	-5	3	16	19	1	-6	17	15
-6	6	114	110	-8	-3	27	23	-3	3	54	52	2	-6	39	44
-5	6	26	23	-6	-3	89	94	1	3	45	51	4	-6	23	26
-4	6	16	15	-5	-3	79	76	3	3	26	26	-6	-5	41	41
-2	6	14	11	-4	-3	76	76	-11	4	24	21	-4	-5	42	44
-1	6	65	63	-3	-3	58	57	-10	4	40	39	-3	-5	36	36
0	6	169	169	-2	-3	18	18	-6	4	60	57	-2	-5	19	22
1	6	46	46	0	-3	71	70	-4	4	37	33	-1	-5	91	89

Table 7. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
0	-5	60	65	-5	2	22	22	-1	-7	46	45	-8	1	25	22
1	-5	16	9	-4	2	49	49	0	-7	58	55	-7	1	66	66
4	-5	18	18	-3	2	22	22	3	-7	32	30	-5	1	34	33
-7	-4	47	49	-2	2	35	30	5	-7	24	20	-4	1	18	11
-6	-4	30	31	0	2	34	34	-8	-6	23	18	-3	1	36	37
-2	-4	77	79	-10	3	18	21	-5	-6	25	23	-2	1	48	47
-1	-4	118	121	-9	3	36	36	-4	-6	21	18	-1	1	17	11
0	-4	105	101	-8	3	30	30	-3	-6	51	49	0	1	29	29
1	-4	37	35	-7	3	80	73	-1	-6	76	78	-8	2	35	33
2	-4	26	28	-5	3	55	55	-8	-5	29	31	-6	2	33	32
-8	-3	18	12	-4	3	16	10	-7	-5	17	15	-5	2	29	28
-6	-3	59	54	-3	3	46	48	-5	-5	19	18	-4	2	80	76
-4	-3	18	21	-1	3	33	27	-4	-5	20	21	-3	2	35	32
-3	-3	58	59	0	3	34	33	2	-5	33	33	-2	2	39	41
-2	-3	38	45	2	3	20	20	-8	-4	18	17	-1	2	31	26
-1	-3	84	86	-11	4	26	28	-7	-4	33	37	2	2	20	12
0	-3	42	40	-10	4	45	44	-5	-4	16	26	-11	3	31	27
1	-3	16	21	-8	4	41	42	-3	-4	55	55	-8	3	42	39
2	-3	31	33	-7	4	20	15	-2	-4	53	52	-7	3	87	82
-7	-2	79	81	-6	4	33	33	-1	-4	133	137	-6	3	71	69
-5	-2	23	22	-4	4	36	39	0	-4	34	36	-5	3	132	131
-3	-2	71	71	-1	4	32	31	1	-4	62	65	-4	3	24	21
-2	-2	65	63	0	4	48	46	2	-4	17	16	-3	3	35	35
-1	-2	209	201	2	4	24	24	-8	-3	53	55	-1	3	35	32
0	-2	88	87	-11	5	29	25	-4	-3	14	17	1	3	18	19
1	-2	52	53	-10	5	18	18	-3	-3	91	90	-11	4	26	23
2	-2	26	28	-8	5	41	37	-2	-3	183	178	-10	4	20	18
5	-2	25	22	-7	5	81	78	-1	-3	44	47	-8	4	23	25
-8	-1	40	41	-6	5	39	37	0	-3	17	18	-7	4	23	18
-6	-1	36	34	-2	5	19	16	4	-3	26	21	-6	4	34	32
-5	-1	26	23	-1	5	68	65	-9	-2	34	34	-5	4	48	48
-4	-1	46	46	1	5	24	20	-8	-2	18	22	-4	4	35	38
-3	-1	96	92	-11	6	23	21	-7	-2	18	19	-3	4	55	54
-2	-1	181	181	-10	6	27	26	-5	-2	32	35	-2	4	44	43
-1	-1	85	84	-9	6	21	19	-2	-2	25	28	-1	4	19	15
1	-1	26	25	-8	6	54	56	-1	-2	92	97	-10	5	19	17
2	-1	30	27	-7	6	17	16	0	-2	34	33	-8	5	37	34
-8	0	18	16	-6	6	37	38	1	-2	46	44	-7	5	63	62
-7	0	55	56	-5	6	20	19	-8	-1	34	35	-5	5	98	95
-6	0	22	21	-3	6	19	15	-7	-1	49	48	-4	5	31	29
-3	0	18	12	-2	6	49	46	-5	-1	20	18	-3	5	35	36
-2	0	16	9	-1	6	26	23	-4	-1	74	70	-11	6	34	32
-1	0	89	84	-8	7	30	32	-3	-1	38	37	-9	6	24	26
0	0	27	27	-7	7	31	30	-2	-1	138	138	-8	6	39	38
1	0	44	42	-5	7	27	23	-1	-1	34	33	-7	6	29	31
-9	1	25	26	-4	7	16	10	0	-1	51	51	-6	6	80	82
-7	1	94	86	-3	7	21	24	-9	0	26	26	-3	6	36	34
-5	1	22	22	-1	7	20	19	-8	0	19	18	-2	6	30	28
-4	1	56	57					-5	0	19	19	-9	7	17	13
-2	1	106	101					-4	0	28	21	-8	7	32	31
0	1	27	25					-3	0	31	27	-7	7	18	16
-10	2	23	26					-2	0	35	36	-6	7	27	21
-8	2	17	23					3	0	20	18	-5	7	19	13
-6	2	32	33					-9	1	19	10	-4	7	18	23

Table 7. (Concluded)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-8	-4	52	50	-7	1	22	23	-5	-7	26	24	-7	-1	21	16
-7	-4	85	85	-6	1	23	25	-4	-7	23	29	-5	-1	22	17
-6	-4	18	17	-4	1	45	47	-2	-7	29	28	-12	0	19	12
-5	-4	44	43	-11	2	36	35	-8	-6	40	43	-11	0	30	32
-4	-4	24	18	-10	2	32	26	-7	-6	49	52	-7	0	19	19
-3	-4	28	34	-7	2	50	48	-5	-6	19	18	-1	0	25	22
-1	-4	24	19	-5	2	24	27	-4	-6	18	20	-10	1	19	19
-8	-3	29	26	-2	2	19	22	-2	-6	22	24	-8	1	56	56
-7	-3	50	53	-1	2	42	39	-1	-6	29	26	-7	1	22	18
-5	-3	52	54	-8	3	48	51	-8	-5	31	40	-2	1	24	24
-4	-3	68	68	-6	3	20	12	-7	-5	44	43	-12	2	22	16
-2	-3	31	35	-3	3	30	32	-5	-5	30	31	-11	2	48	45
1	-3	22	14	-2	3	44	42	-4	-5	43	44	-10	2	23	21
-8	-2	45	43	-11	4	30	30	-3	-5	28	32	-9	2	46	43
-7	-2	25	35	-10	4	21	20	-2	-5	41	45	-8	2	18	16
-6	-2	19	15	-9	4	28	26	-8	-4	62	60	-12	3	25	27
-5	-2	39	37	-7	4	39	39	-5	-4	26	25	-8	3	43	46
-3	-2	22	22	-6	4	22	22	-2	-4	34	38	-6	3	28	27
-8	-1	22	20	-12	5	19	20	0	-4	19	15	-2	3	26	26
-7	-1	27	23	-7	5	20	18	-7	-3	19	14	-11	4	24	20
-5	-1	29	35	-5	5	18	20	-5	-3	43	46	-10	4	21	15
-10	0	19	24	-4	5	23	22	-4	-3	31	36	-9	4	44	47
-8	0	18	14	-9	6	27	23	-3	-3	37	41	-7	4	19	15
-7	0	19	21	-8	7	22	23	-2	-3	29	30	-3	4	23	18
-6	0	17	16	-7	7	50	51	-8	-2	35	35	-12	5	21	17
-5	0	25	21	-5	7	19	17	-6	-2	21	22	-7	5	34	33
-3	0	20	23					-4	-2	22	19	-11	7	21	15
-1	0	22	18			L=10		-3	-2	20	21	-8	7	22	21
-10	1	19	29					-10	-1	25	29	-7	7	19	18
-8	1	18	23	-7	-7	46	49	-8	-1	29	30	-5	7	29	31

CHAPTER IV

DISCUSSION OF RESULTS

The preparation used initially, with the exception of the hydrogen peroxide, was similar to that used in the preparation of the cobalt(II) complex, $[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)(\text{CH}_3\text{O})(\text{CH}_3\text{OH})]_4$. The stoichiometry of the initial preparation included a ratio of potassium hydroxide to cobalt salt of 2:1, however, further attempts to get better crystalline product in the preparation resulted in a ratio of potassium hydroxide to cobalt salt of 3:2. In attempting to oxidize all of the cobalt(II) to cobalt(III) and obtain a cobalt(III) complex, a large excess of hydrogen peroxide was initially used; later work with the preparation revealed that using a stoichiometric quantity or a large excess of hydrogen peroxide resulted in the same product being formed, although the yield was less with the smaller quantity of hydrogen peroxide.

Elemental analyses of the crystalline product indicated an empirical composition of $\text{CoC}_7\text{H}_{11.5}\text{O}_4$. Similarities in the IR spectra of this product and the cobalt(II) cubane-type complex (51) suggest the presence of a 2,4-pentanedionato group and a methoxide group. Assuming the presence of these two groups and disallowing the possibility of a peroxy group because of the excess carbon and lack of excess oxygen, the remaining carbon, oxygen, and 1 1/2 hydrogens could be explained by the presence of acetate in the product. The presence of these three groups is consistent with the

initial x-ray data obtained in the unit cell determination if it is assumed that in the unit cell there are two tetranuclear cubane-type molecules, $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$, related by an inversion center. Comparison of the IR spectra of this product and the cobalt(II) complex revealed several bands that could be due to the presence of acetate; a band at 1580 cm^{-1} and one at 1285 cm^{-1} could be attributed to COO stretching vibrations. Previous spectral studies (77-80) have reported intense absorptions in the regions of $1560\text{-}1600\text{ cm}^{-1}$ which were attributed to stretching vibrations of the COO group. The mass spectrum of this product also contains evidence for the presence of 2,4-pentanedionato and acetate groups. Table 8 contains some of the m/e values and the ions to which they could be attributed.

Table 8. Significant Fragment Ions in the Mass Spectrum of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

m/e	Ion*	m/e	Ion
481	$\text{Co}_2(\text{AA})_2(\text{CH}_3\text{O})_2\text{AcCO}_2$	58	Ac-H
257	$\text{Co}(\text{AA})_2$	44	CO_2
242	$\text{Co}(\text{AA})_2\text{-CH}_3$	43	CH_3CO
188	$\text{Co}(\text{AA})\text{+OCH}_3$	31	CH_3O
158	$\text{Co}(\text{AA})$	28	CO
96	AA-3H's	27	CH_3C
60	Ac+H	15	CH_3

* AA = 2,4-pentanedionato
Ac = acetate

Although most mass spectra contain a small peak at $m/e = 44$ due to carbon dioxide in the instrument or sample, the peak at $m/e = 44$ in this spectrum is considered significant because of its relative abundance and is attributed to CO_2 from acetate. In view of the stoichiometry, charge balance requires the presence of two divalent and two trivalent cobalt atoms per molecule; a single crystal x-ray structure determination was initiated to verify the cubane structure, the presence of cobalt in two oxidation states, and to determine the mode of coordination for the acetates.

Solution of the structure of this complex shows it to be similar to that found for tetrakis [μ_3 -methoxo-2,4-pentanedionatomethanolicobalt(II)] (25). The complex consists of octahedrally coordinated cobalt atoms and methoxide oxygens at alternate corners of a distorted cube; in addition to three μ_3 -methoxide oxygens, each cobalt atom is coordinated to a chelate 2,4-pentanedionato group and to an acetate oxygen. The acetate groups form μ_2 -bridges across the top and bottom faces of the cubane unit. Because of the two bridging acetate groups, there is only one possible geometric form. Two perspective drawings of the structure are shown in Figures 4 and 5. In Figure 5, the structure without the acetate bridges is viewed looking down the 2-fold rotation axis. Rings one and two approach somewhat of a coplanar arrangement as do rings three and four. Although the complex occupies a crystallographic site which requires no symmetry, it approaches C_{2v} symmetry; in fact, except for differences which result from differences in cobalt-oxygen distances, the complex would approach D_{2d} symmetry. (Table 9 presents selected interatomic distances and angles for the complex.) However, as seen in Table 9, all of

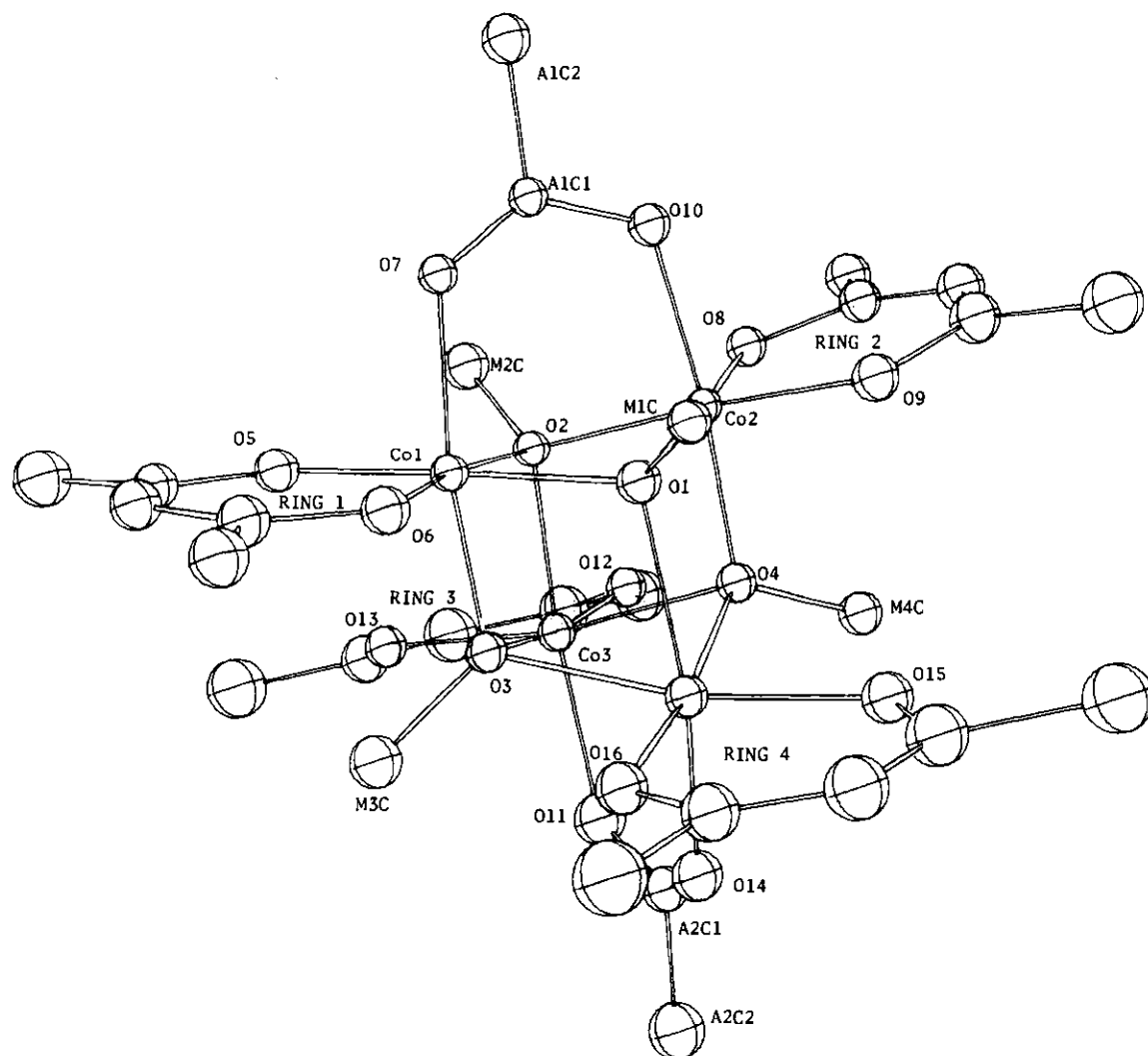


Figure 4. A Perspective Drawing of the Structure
of $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

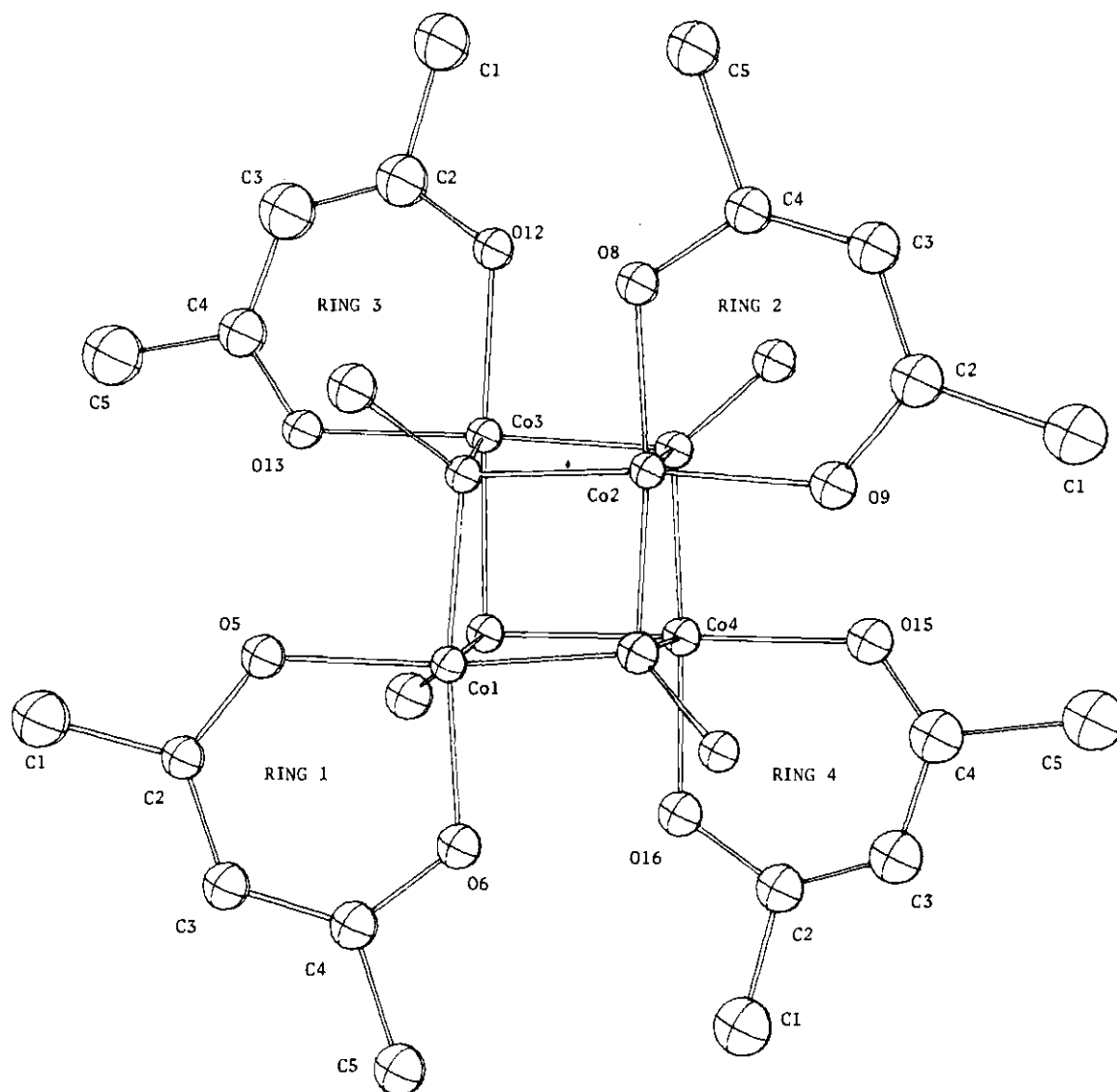


Figure 5. A Perspective Drawing of the Structure of
 $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$ without Acetates

Table 9. Interatomic Distances and Angles for
 $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

Atoms	Distance, Å	Atoms	Angle, degrees
Co1-Co2	2.825(10)	02-Co1-03	81.5(6)
Co1-Co3	3.142(7)	03-Co1-05	95.8(8)
Co1-Co4	3.170(6)	03-Co1-06	94.6(6)
Co1-01	1.89(2)	01-Co1-03	80.6(7)
Co1-02	1.92(1)	02-Co1-07	90.9(6)
Co1-03	1.87(2)	05-Co1-07	89.8(7)
Co1-05	1.86(2)	06-Co1-07	92.2(6)
Co1-06	1.85(1)	01-Co1-07	93.0(7)
Co1-07	1.94(2)	02-Co1-05	92.1(7)
Co2-Co3	3.114(7)	05-Co1-06	95.3(7)
Co2-Co4	3.183(4)	01-Co1-06	90.5(7)
Co2-01	1.91(1)	01-Co1-02	81.7(7)
Co2-02	1.90(2)	02-Co2-04	82.6(7)
Co2-04	1.91(2)	04-Co2-08	95.1(6)
Co2-08	1.87(1)	04-Co2-09	94.0(7)
Co2-09	1.83(2)	01-Co2-04	82.1(6)
Co2-010	1.93(1)	02-Co2-010	92.0(7)
Co3-Co4	3.017(6)	08-Co2-010	89.6(6)
Co3-02	2.09(2)	09-Co2-010	90.9(7)
Co3-03	2.14(1)	01-Co2-010	92.7(6)
Co3-04	2.12(2)	02-Co2-08	91.5(7)

Table 9. (Continued)

Atoms	Distance, Å	Atoms	Angle, degrees
Co3-011	2.04(2)	08-Co2-09	94.9(7)
Co3-012	2.00(2)	01-Co2-09	91.4(7)
Co3-013	1.99(2)	01-Co2-02	82.1(7)
Co4-01	2.16(2)	02-Co3-03	71.7(5)
Co4-03	2.09(2)	02-Co3-013	96.1(7)
Co4-04	2.14(1)	02-Co3-012	98.8(6)
Co4-014	2.04(2)	02-Co3-04	73.4(6)
Co4-015	1.99(2)	03-Co3-011	95.6(6)
Co4-016	2.01(2)	011-Co3-013	94.6(8)
01-M1C	1.44(3)	011-Co3-012	92.9(6)
02-M2C	1.53(2)	04-Co3-011	95.7(7)
03-M3C	1.54(3)	03-Co3-013	93.5(7)
04-M4C	1.49(2)	012-Co3-013	91.5(8)
R1C2-05	1.32(2)	03-Co3-04	83.0(7)
R1C4-06	1.32(2)	04-Co3-012	90.5(7)
R1C1-R1C2	1.49(4)	01-Co4-03	69.8(7)
R1C2-R1C3	1.37(3)	01-Co4-04	71.2(6)
R1C3-R1C4	1.34(3)	01-Co4-015	98.2(8)
R1C4-R1C5	1.54(3)	01-Co4-016	100.2(6)
R2C2-09	1.36(2)	03-Co4-014	95.7(8)
R2C4-08	1.32(3)	04-Co4-014	94.3(6)
R2C1-R2C2	1.57(4)	014-Co4-015	95.8(8)

Table 9. (Continued)

Atoms	Distance, Å	Atoms	Angle, degrees
R2C2-R2C3	1.34(3)	014-Co4-016	93.9(7)
R2C3-R2C4	1.25(4)	03-Co4-016	92.7(6)
R2C4-R2C5	1.62(3)	015-Co4-016	89.9(7)
R3C2-012	1.35(4)	03-Co4-04	83.6(5)
R3C4-013	1.35(3)	04-Co4-015	92.2(6)
R3C1-R3C2	1.56(3)	Co1-01-Co2	96.1(8)
R3C2-R3C3	1.34(4)	Co1-01-Co4	102.8(10)
R3C3-R3C4	1.42(3)	Co2-01-Co4	103.0(8)
R3C4-R3C5	1.53(4)	Co1-02-Co2	95.2(8)
R4C2-016	1.34(3)	Co1-02-Co3	103.1(6)
R4C4-015	1.25(3)	Co2-02-Co3	102.5(5)
R4C1-R4C2	1.61(3)	Co1-03-Co3	103.2(6)
R4C2-R4C3	1.29(4)	Co1-03-Co4	106.2(10)
R4C3-R4C4	1.39(3)	Co3-03-Co4	90.9(5)
R4C4-R4C5	1.65(4)	Co2-04-Co3	101.1(5)
A1C1-07	1.20(2)	Co2-04-Co4	103.4(6)
A1C1-010	1.31(2)	Co3-04-Co4	90.0(5)
A1C1-A1C2	1.54(3)	Co1-01-M1C	120.0(11)
A2C1-011	1.29(3)	Co2-01-M1C	117.1(16)
A2C1-014	1.14(4)	Co4-01-M1C	114.8(11)
A2C1-A2C2	1.66(4)	Co1-02-M2C	120.1(10)

* * * * *

Table 9. (Continued)

Atoms	Angle, degrees	Atoms	Angle, degrees
Co2-02-M2C	120.9(14)	Co3-012-R3C2	120.7(17)
Co3-02-M2C	111.9(15)	Co3-013-R3C4	126.1(14)
Co1-03-M3C	120.2(11)	012-R3C2-R3C1	111.8(27)
Co3-03-M3C	113.8(16)	012-R3C2-R3C3	130.7(26)
Co4-03-M3C	117.8(11)	013-R3C4-R3C3	123.6(31)
Co2-04-M4C	118.4(14)	013-R3C4-R3C5	117.4(23)
Co3-04-M4C	121.4(16)	R3C1-R3C2-R3C3	117.3(35)
Co4-04-M4C	117.7(10)	R3C2-R3C3-R3C4	123.5(34)
Co1-05-R1C2	125.8(16)	R3C3-R3C4-R3C5	118.8(34)
Co1-06-R1C4	124.2(16)	Co4-016-R4C2	124.6(15)
05-R1C2-R1C1	113.2(21)	Co4-015-R4C4	125.0(16)
05-R1C2-R1C3	123.0(25)	016-R4C2-R4C1	111.6(24)
06-R1C4-R1C3	125.5(21)	016-R4C2-R4C3	126.4(23)
06-R1C4-R1C5	110.1(22)	015-R4C4-R4C3	128.5(29)
R1C1-R1C2-R1C3	123.8(20)	015-R4C4-R4C5	114.9(22)
R1C2-R1C3-R1C4	125.9(20)	R4C1-R4C2-R4C3	122.0(30)
R1C3-R1C4-R1C5	124.4(20)	R4C2-R4C3-R4C4	124.9(31)
Co2-08-R2C4	121.7(17)	R4C3-R4C4-R4C5	115.9(29)
Co2-09-R2C2	123.7(16)	Co1-07-A1C1	124.0(12)
09-R2C2-R2C1	108.6(20)	Co2-010-A1C1	121.5(16)
09-R2C2-R2C3	125.1(30)	07-A1C1-010	130.3(20)

Table 9. (Concluded)

Atoms	Angle, degrees	Atoms	Angle, degrees
08-R2C4-R2C3	130.4(22)	07-A1C1-A1C2	118.5(16)
08-R2C4-R2C5	104.2(24)	010-A1C1-A1C2	110.9(20)
R2C1-R2C2-R2C3	126.2(24)	Co3-O11-A2C1	122.0(22)
R2C2-R2C3-R2C4	123.9(26)	Co4-O14-A2C1	126.5(17)
R2C3-R2C4-R2C5	125.1(22)	011-A2C1-O14	132.8(27)
		011-A2C1-A2C2	105.9(29)
		014-A2C1-A2C3	120.3(22)

the cobalt-oxygen distances for the upper two cobalt atoms (1.83-1.94 Å) are shorter than those of the lower two cobalt atoms (1.99-2.16 Å); since stoichiometry and charge balance require two divalent and two trivalent cobalt atoms per molecule, it would appear that the upper two cobalt atoms, Co1 and Co2, are trivalent and the lower two cobalt atoms, Co3 and Co4, are divalent. The difference in bond lengths for these cobalt-oxygen bonds (0.16-0.22 Å) is comparable to the 0.15 Å difference found for the cobalt(II)- and cobalt(III)-nitrogen distances in the hexammine complexes (81) and for the 0.13 Å difference found for the cobalt(II)- and cobalt(III)-nitrogen distances in the trinuclear complex $[\text{Co}_3(\text{OCH}_2\text{CH}_2\text{NH}_2)_6]^{3+}$ (58).

The distortion of the cubane unit is most apparent in the four-membered cobalt-oxygen rings which form the top and bottom of the cube. The four-membered rings are considerably bent; the bending of each ring can be thought of as a folding along the oxygen-oxygen axis so that all of the cobalt atoms move away from the center of the cube. As seen in Table 10, the dihedral angles between the O-Co-O planes of these rings are 21.9° for the upper or cobalt(III) ring and 36.3° for the lower cobalt(II) ring. The differences in the cobalt-oxygen-cobalt angles in the two four-membered rings, 90.0° and 90.9° in the cobalt(II) ring and 95.2° and 96.1° in the cobalt(III) ring, help indicate the difference in the size of the two rings. The least-squares planes, given in Table 11, of the rings also are indicative of distortions in the rings.

The distortion of the octahedral coordination of the metal atom is reflected in the oxygen-cobalt-oxygen angles. The angles at the cobalt(III)'s vary from 80.6° to 95.8° while the angles at the cobalt(II)'s

vary from 71.2° to 100.2° ; the greater distortion at the cobalt(II)'s is consistent with the smaller crystal field stabilization of the divalent d^7 ions relative to the trivalent d^6 ions.

Table 10. Dihedral Angles Between Planes Each Defined by Three Atoms for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

Atoms of First Plane	Atoms of Second Plane	Angle, degrees
01-Co1-02	01-Co2-02	21.92(90)
03-Co3-04	03-Co4-04	36.34(80)

The bond distances and bond angles for the 2,4-pentanedionato groups are included in Table 9, and the least-squares planes of the rings and deviations of the individual atoms from these planes are included in Table 11; these groups do not show any unusual features when compared to 2,4-pentanedionato groups from other structures.

The two cobalt-oxygen distances for each acetate are equivalent to within the estimated standard deviations; however, there is a considerable difference between the two carbon-oxygen distances of each acetate. Similar differences in the carbon-oxygen distances in bridging acetates have been found in other structures (82,83). Although the carbon-carbon distances are equivalent within the sum of their estimated standard

Table 11. Equations of Least-Squares Atomic Planes and Distances of Atoms (Å) from These Planes for $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$

(a) Equation of the Plane Including (Co2, O1, O2):

$$0.899X - 0.266Y + 0.347Z + 0.676 = 0$$

Atom	Distance from Plane, Å
Co1	0.528
Co2	0.000
O1	0.000
O2	0.000
O3	-1.281

(b) Equation of the Plane Including (Co4, O3, O4):

$$0.705X - 0.583Y + 0.404Z + 3.749 = 0$$

Atom	Distance from Plane, Å
Co3	-0.885
Co4	0.000
O3	0.000
O4	0.000
O6	2.190

(c) Equation of the Best Least-Squares Plane of Ring 1 (O5, O6, R1C2, R1C3, R1C4):

$$0.907X - 0.398Y + 0.138Z + 1.415 = 0$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Co1	0.071	R1C1	-0.066
O1	0.038	R1C2	-0.026
O2	0.045	R1C3	0.024
O5	0.012	R1C4	-0.013
O6	0.004	R1C5	-0.064
O7	1.994		

Table 11. (Concluded)

- (d) Equation of the Best Least-Squares Plane of Ring 2
(08, 09, R2C2, R2C3, R2C4):

$$0.901X - 0.271Y + 0.339Z + 0.739 = 0$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Co2	0.054	R2C1	0.010
01	0.036	R2C2	0.023
02	0.036	R2C3	-0.015
08	0.006	R2C4	-0.001
09	-0.011	R2C5	-0.140
010	1.953		

- (e) Equation of the Best Least-Squares Plane of Ring 3
(012, 013, R3C2, R3C3, R3C4):

$$0.996X - 0.084Y + 0.023Z + 1.017 = 0$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Co3	-0.316	R3C1	-0.055
03	-0.373	R3C2	-0.029
04	-0.301	R3C3	0.026
011	-2.338	R3C4	-0.024
012	0.018	R3C5	0.032
013	0.012		

- (f) Equation of the Best Least-Squares Plane of Ring 4
(015, 016, R4C2, R4C3, R4C4):

$$0.910X - 0.333Y + 0.246Z + 3.273 = 0$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Co4	0.151	R4C1	0.059
03	0.709	R4C2	0.006
04	0.632	R4C3	0.017
014	-1.796	R4C4	-0.027
015	0.018	R4C5	0.134
016	-0.010		

deviations, one of the acetate carbon-carbon distances is extremely long. Attempts to find better positions for the atoms in this region resulted in refinement to the same final positions. Although the solution of the structure substantiated the proposed stoichiometry for the complex and gave further evidence that the complex contained cobalt atoms of different oxidation states, the magnetic behavior of the complex at various temperatures and its electronic spectral properties were studied to obtain additional information as to the nature of the cobalt atoms.

The complex was found to be paramagnetic with a magnetic moment of 3.6 B.M. per cobalt atom at room temperature. Assuming that there are two divalent and two trivalent cobalt atoms per molecule and that the trivalent cobalt atoms are diamagnetic, the room temperature magnetic moment per cobalt(II), 4.98 B.M., is in the normal range, 4.7 - 5.2 B.M. (52), for a high-spin octahedrally coordinated cobalt(II). The magnetic moment is temperature dependent, decreasing to a value of 4.62 B.M. per cobalt(II) at 77°K; the cobalt(II)'s, thus, show antiferromagnetic coupling in contrast to the ferromagnetic coupling exhibited by the nickel(II) cubane-type complexes (25,49). This difference is not surprising, however, when one considers: (1) the change in electronic structure in going from d^8 nickel(II) to d^7 cobalt(II) and (2) the additional bridging by the acetates in the present structure. The change from d^8 to d^7 provides a vacancy in the t_{2g} orbitals and the acetate provides a π -pathway for an indirect exchange interaction; since the half-filled t_{2g} orbital can be oriented in such a way as to overlap with the acetate π -system, an antiferromagnetic coupling is possible. Consistent with the proposed indirect exchange in the cobalt-cobalt distance for the two cobalt(II)'s, 3.02 Å,

deeming a direct metal-metal interaction improbable.

The visible region of the electronic spectrum of the complex contains a maximum at 573 nm with a molar extinction coefficient of $50.9 \text{ M}^{-1} \text{ cm}^{-1}$. This observed band is probably a result of separate absorptions by the octahedrally coordinated cobalt(II) and cobalt(III) ions in the complex. The ultraviolet region contains a maximum at 267 nm with a molar extinction coefficient of $8552 \text{ M}^{-1} \text{ cm}^{-1}$ per cobalt. The ultraviolet spectrum of cobalt bisacetylacetonate contains a band at 292 nm with a molar extinction coefficient of about $8100 \text{ M}^{-1} \text{ cm}^{-1}$ per acetylacetonate; likewise, the spectrum of cobalt trisacetylacetonate contains a band at 258 nm with a molar extinction coefficient of about $11,000 \text{ M}^{-1} \text{ cm}^{-1}$ per acetylacetonate (65). Noting the similarities in the spectra of the cobalt(II, III) complex and the acetylacetonates, the one band found here might be attributed to two separate bands overlapping. It should also be noted that the spectrum of cobaltous acetate contains a band in the region of 330 nm (84). Therefore, the band in this spectrum could be due to absorption by the 2,4-pentanedionate groups and by the acetates.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The complex reported in this thesis, $[\text{Co}_4(\text{C}_5\text{H}_7\text{O}_2)_4(\text{CH}_3\text{O})_4(\text{C}_2\text{H}_3\text{O}_2)_2]$, is the first example of a cubane-type complex which contains metal ions in different oxidation states. Prepared by the hydrogen peroxide oxidation of a mixture of cobalt(II) acetate, 2,4-pentanedione, and potassium hydroxide in methanol, the compound has been characterized by elemental analyses, spectral and magnetic studies, and by a complete structural determination. All of the results obtained are consistent with a complex containing two divalent and two trivalent cobalt atoms.

Elucidation of the structure by a single crystal x-ray method revealed that it is very similar to that of the cobalt(II) cubane-type complex. The structure contains a tetrahedron of cobalt atoms with methoxide oxygens located over each face of the tetrahedron. The top and bottom faces of the cube thus formed are bridged by the two acetate groups. The somewhat distorted octahedral coordination of each cobalt atom is completed by a 2,4-pentanedionato chelate and an oxygen of a bridging acetate. Unlike the cobalt(II) cubane-type complex with coordinating methanols and the analogous complex with coordinating waters, only one geometrical configuration is possible due to the bridging acetates.

The room temperature magnetic moment is consistent with the presence of two octahedral cobalt(II) atoms and two diamagnetic cobalt(III)

atoms. The complex exhibits antiferromagnetic coupling in the temperature range 330° - 77° K, and interaction through the bridging acetate is proposed. Additional magnetic studies should be done at lower temperatures to further characterize the magnetic behavior.

An absorption band in the visible region of the electronic spectrum is observed; however, this band is probably a resultant band produced by two separate bands due to absorptions by the octahedrally coordinated cobalt(II) and cobalt(III) atoms in the complex.

It is probable that similar complexes of other transition metal ions could be prepared with the use of different oxidizing agents and/or ligands which are similar to those in this complex.

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*The abbreviations used herein conform to those adopted by the IUPAC and AIP as described in the List of Periodicals, Chemical Abstracts, 55, 1J (1961) and later supplements.

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