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POLYNUCLEAR COMPLEXES OF COBALT(II)-COBALT(III)
WITH 2, 2'-DIHYDROXYDIETHYLAMINE

A THESIS

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POLYNUCLEAR COMPLEXES OF COBALT(II)-COBALT(III)

WITH 2, 2'-DIHYDROXYDIETHYLAMINE

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GLOSSARY OF TERMS

acac	acetylacetonate
B. M.	Bohr Magneton
DETA	2, 2'-dihydroxy diethyl amine
META	2-aminoethanol
X_g	gram susceptibility
$X_{\text{molar}}^{\text{corrected}}$	molar susceptibility corrected for diamagnetism
μ_{eff}	effective magnetic momentum
EDTA	ethylene diaminetetraacetic acid
PAN	1-(2- pyridylaza)-2-naphtol
λ	wave length
(META ₃ -H)	three META groups with one proton removed
(DETA-H)	one DETA group with one proton removed

SUMMARY

Crystals of a new compound, $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$, were prepared from sodium triscarbonatocobaltate(III) trishydrate and 2,2'-dihydroxy-diethylamine, and an attempt was made to solve the structure of this compound by single-crystal x-ray diffraction.

To determine the oxidation states of the cobalt atoms, the magnetic moment was determined and the visible spectrum was studied; from these studies it was found that Co(II) and Co(III) occur in a 2 to 1 ratio in this compound. From carbon, nitrogen, and hydrogen analyses, it was difficult to determine the number of carbonate ions because of the large molecular weight of the compound. From a carbonate analysis the compound was found to contain three carbonate ions per six cobalt atoms. To distinguish between hydroxide ions, coordinated waters, and waters of crystallization, thermogravimetric analysis was performed and four hydroxy ions, four coordinated waters and eight waters of crystallization were identified. A crystallographic study revealed a tetrameric unit of cobalt atoms which has the same structure as the titanium alkoxides. Because of twinning, disordering, or poor data, the remaining two cobalt atoms were not located.

CHAPTER I

INTRODUCTION

In previous studies, mononuclear and polynuclear complexes of cobalt with 2-aminoethanol and 2,2'-dihydroxydiethylamine were prepared by Hieber and Levy (1, 2) and by Brintzinger and Hesse (3). $\text{Co}(\text{META})_3\text{X}_2$, $\text{Co}(\text{META}_3\text{-H})\text{X}$, $\text{Co}_2(\text{META}_6\text{-H})\text{X}_3$ (where X = Cl, Br, I) and $\text{Co}_3(\text{META}_6\text{-4H})\text{X}_2$ (where X = Cl, Br) were prepared from anhydrous cobalt(II) halides and 2-aminoethanol, mixed in a 1 to 3 ratio, in absolute ethanol. The cobalt atoms of these complexes were reported as cobalt(II) (1). The red crystals which were obtained from 2,2'-dihydroxydiethylamine and cobalt halides were reported as $\text{Co}(\text{DETA})(\text{OH})\text{X}$ or $\text{Co}(\text{DETA-H})(\text{H}_2\text{O})\text{X}$ (where X = Cl, Br, I), while the green crystals which were also obtained were reported as $\text{Co}_2(\text{DETA}_3\text{-3H})\text{X}$ (Fig. 1). Compounds with the formula $\text{Co}_2(\text{DETA}_2\text{-3H})(\text{H}_2\text{O})_4\text{X}$ were obtained by adding water to $\text{Co}_2(\text{DETA}_3\text{-3H})\text{X}$ and the color of these crystals were also reported as green. When $\text{Co}_2(\text{DETA}_2\text{-3H})(\text{H}_2\text{O})_4\text{X}$ compounds were dried at 185 degrees, using phosphorous pentoxide as a drying agent, the color changed and rose-violet compounds were obtained; the formulas were reported as $\text{Co}_2(\text{DETA}_2\text{-3H})(\text{H}_2\text{O})\text{X}$. All of the cobalt in these 2,2'-dihydroxydiethylamine complexes was reported to be cobalt(II) (1).

$\text{Co}(\text{META}_3\text{-2H})3\text{H}_2\text{O}$ and $\text{Co}_2(\text{META}_6\text{-H})(\text{NO}_3)_3$ were prepared from various salt of cobalt(II) and 2-aminoethanol by H. Brintzinger and B. Hesse.

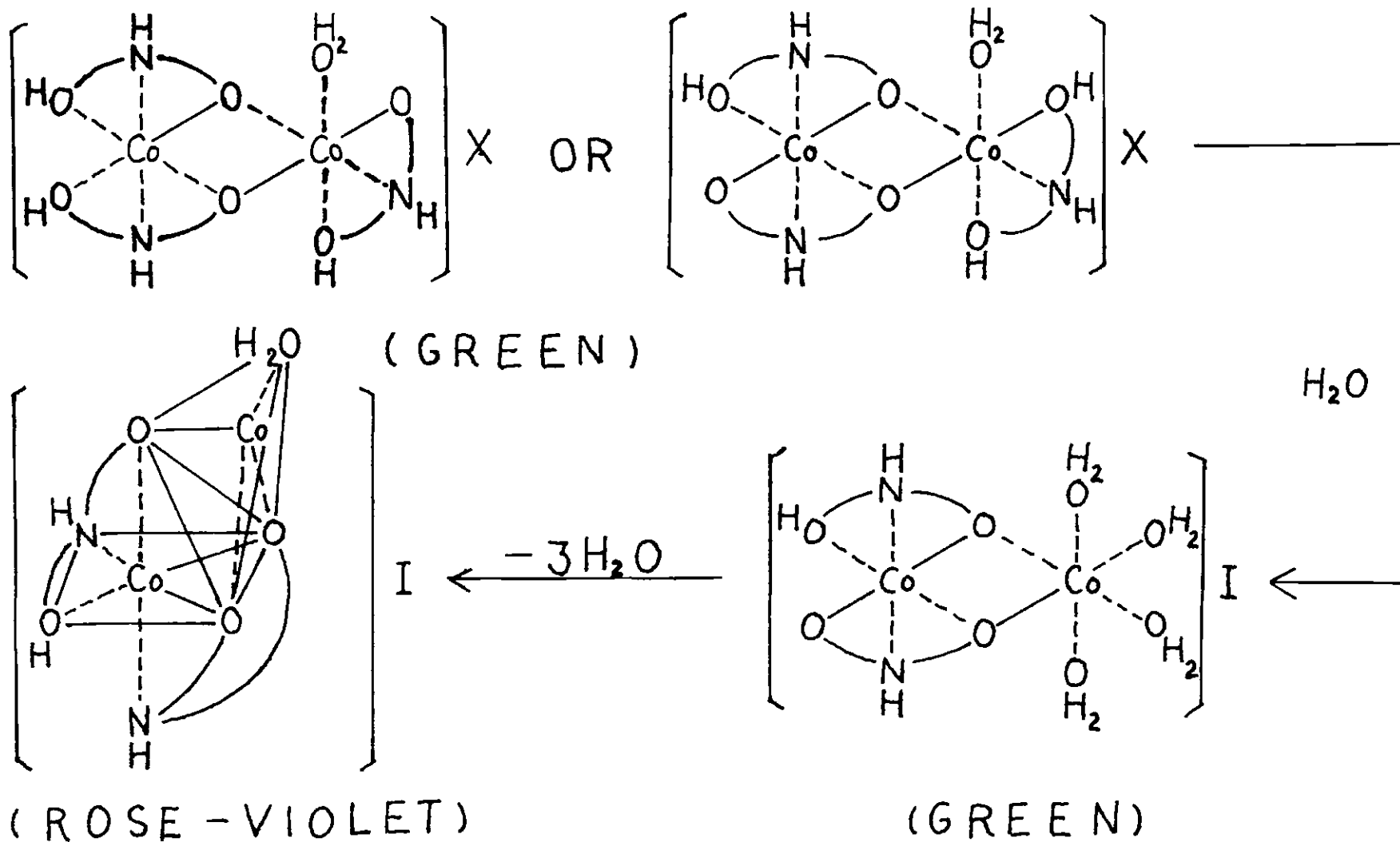


Figure 1. Structures Proposed (1, 2) for the Compounds Prepared

from Cobalt(II) Halides and DETA.

These cobalt compounds were also reported to contain only cobalt(II) (3). H. Brintzinger and B. Hesse also attempted to prepare cobalt(III) complexes by the reaction of pentammine cobalt(III)-chloride and 2-aminoethanol, but the products were again reported as cobalt(II) compounds, $\text{Co}_3(\text{META}_6-4\text{H})\text{I}_2\cdot 6\text{H}_2\text{O}$.

Later the previously described (1, 3) compounds, $\text{Co}_2(\text{META}_6-3\text{H})(\text{NO}_3)_3$ and $\text{Co}_2(\text{META}_6-3\text{H})\text{Br}_3\cdot 4\text{H}_2\text{O}$, and $\text{Co}(\text{META}_3-3\text{H})$ were prepared by Joneda and Kida (4) by the reaction of cobalt(III) pentammines with 2-aminoethanol; no reference was made to the earlier published work. They concluded that the cobalt in these compounds was cobalt(III).

In a later investigation, the trinuclear complexes were again prepared by V. V. Udovenko and A. N. Gerasenkova and were shown, by potentiometric titrations, to contain both cobalt(II) and cobalt(III). $\text{Co}_3(\text{META}_6-6\text{H})\text{SO}_4\cdot 12\text{H}_2\text{O}$ was prepared by the reaction of carbonatotetramine cobalt(III) sulfate with 2-aminoethanol. In the structure proposed, 2-aminoethanol anions formed chelates with cobalt(III) ions, the center cobalt atom of the trimer was cobalt(II), and oxygen faces were shared between the cobalt(II) ion and the cobalt(III) trischelates.

Dinuclear and trinuclear complexes which contain cobalt in different valence states were prepared from diaquotetrammine cobalt(III) sulfate. It was reported that 2-aminoethanol has a reducing action toward cobalt(III) only at high temperature such as when the reaction is proceeding at the temperature of a boiling water bath (6).

The structure of a trinuclear cobalt complex of 2-aminoethanol was reported by J. A. Bertrand, J. A. Kelley and E. G. Vassian (22). Dark red

crystals of $\text{Co}_3(\text{META}_6-6\text{H})(\text{acetate})_2$, which were crystallized from methanol as the anhydrous salt, were monoclinic and belonged to space group C2, the density calculated from precession photographs was 1.68 g/cm^3 , assuming two molecules per unit cell. A conventional R value of 11% was obtained with all reflections weighted at unity. The trimer consisted of two tris(2-aminoethoxido)cobalt(III) complexes, each sharing three oxygens with a central cobalt(II). The two-fold site symmetry related the two tris-chelates and required that the two be the same optical configuration. The coordination of the central cobalt(II) (Fig. 2) was unusual with the oxygens arranged at the corners of an almost perfect trigonal prism with cobalt-oxygen distances of 2.03, 2.03 and $2.05 \overset{\circ}{\text{A}}$.

The preparation and crystal structure of $\text{CoNi}(\text{META}_6-3\text{H})\text{I}_2$, a hydrogen bonded dinuclear complex, was reported by J. A. Bertrand, W. J. Howard and A. R. Kalyanaraman (23). The magnetic moment of this compound was 3.12 B.M. and indicated a paramagnetic nickel(II) ion and a diamagnetic cobalt(III) ion. The cobalt(III) and nickel(II) ions were disordered in an 8-fold set of positions. Due to disorder, two sets of oxygen and nitrogen positions were located, and occupancy factors of 0.5 were used for these oxygen and nitrogen atoms. The disorder in the oxygen and nitrogen positions resulted from the difference in size of the two metal ions. One set of metal-oxygen and metal-nitrogen distances (1.93 and $2.06 \overset{\circ}{\text{A}}$ respectively) was identical to that found for the tris-(2-aminoethoxido)cobalt(III) unit of $(\text{Co}_3(\text{META}_6-6\text{H}))^{2+}$, the other set of metal-oxygen and metal-nitrogen distances (2.08 and $2.15 \overset{\circ}{\text{A}}$ respectively) were reasonable values for a nickel(II) chelate. The solved structure of the cation is shown in Figure 3. The

two tris-chelates are joined face-to-face by hydrogen bonding as indicated by three equivalent oxygen-oxygen distances of 2.51 \AA ; this oxygen-oxygen distance indicates very strong bonding between the two tris-chelates. The two tris-chelates are of opposite optical configurations because of the inversion center between the two. The six oxygen atoms of a dimeric unit form a distorted octahedron about the inversion center.

Dinuclear cobalt complexes of 2, 2'-dihydroxydiethylamine containing different oxidation states were reported by V. N. Evreev and G. A. Kotlyar (7). $\text{Co}_2(\text{DETA}_3-4\text{H})\text{X}$ (where X is Cl, Br, or I) were prepared from hexaquocobalt (II) chloride and an excess of 2, 2'-dihydroxydiethylamine by passing air through a methanol solution. It was reported that $\text{Co}_2(\text{DETA}_3-4\text{H})\text{X}$ contained cobalt in different oxidation states, namely one cobalt(III) and one cobalt(II) per molecule. The compounds of the formula $\text{Co}_2(\text{DETA}_3-4\text{H})\text{X}$ are stable in air, but lose water at 100°C and decompose at $200\text{--}220^\circ\text{C}$ without melting. The crystals are insoluble in organic solvents but soluble in water. Crystals of $\text{Co}_2(\text{DETA}_3-4\text{H})(\text{H}_2\text{O})\text{X}$ were dissolved in water and from this solution crystals of $\text{Co}_2(\text{DETA}_2-4\text{H})\text{X}(\text{H}_2\text{O})_4$ were obtained. The reaction which occurs and proposed structures for both compounds are indicated in Figure 1. The structure proposed for $\text{Co}_2(\text{DETA}_2-4\text{H})\text{X}(\text{H}_2\text{O})_4$ contains a cobalt(III) octahedrally surrounded by two ligands and joined to cobalt(II) by sharing two oxygen atoms of each 2, 2'-dihydroxydiethylamine; four of the octahedral positions of cobalt(II) are occupied by water molecules.

The structures proposed for the 2, 2'-dihydroxydiethylamine complexes have assumed bridging by the alkoxide oxygen; since most of the complexes

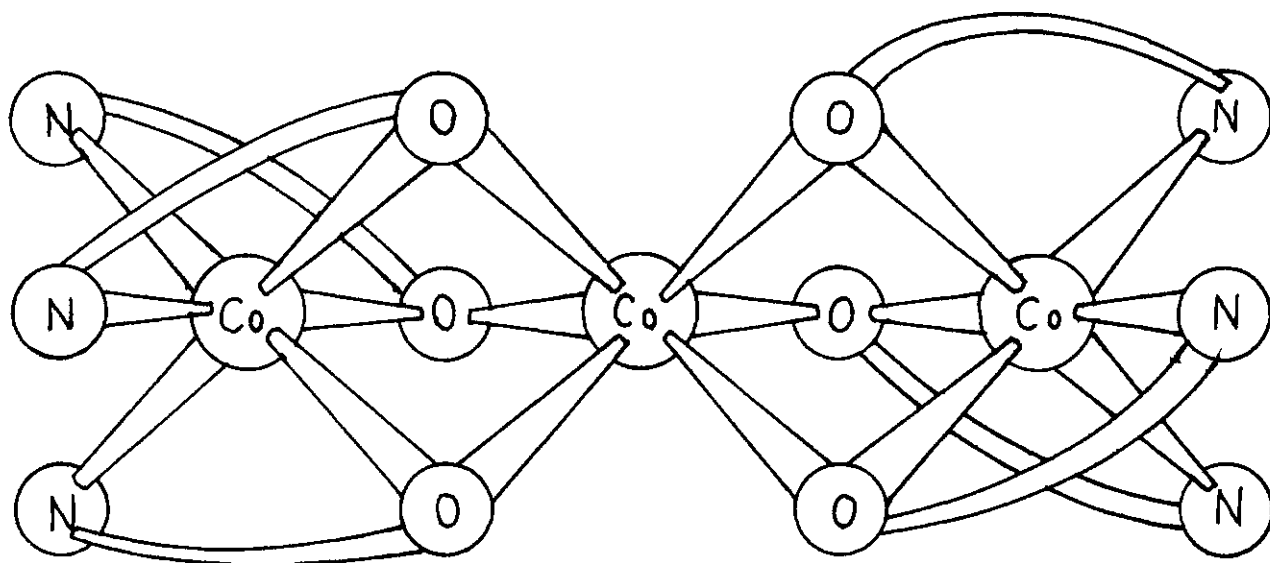


Figure 2. Structure of $\text{Co}_3(\text{META}_6-6\text{H})^{2+}$.

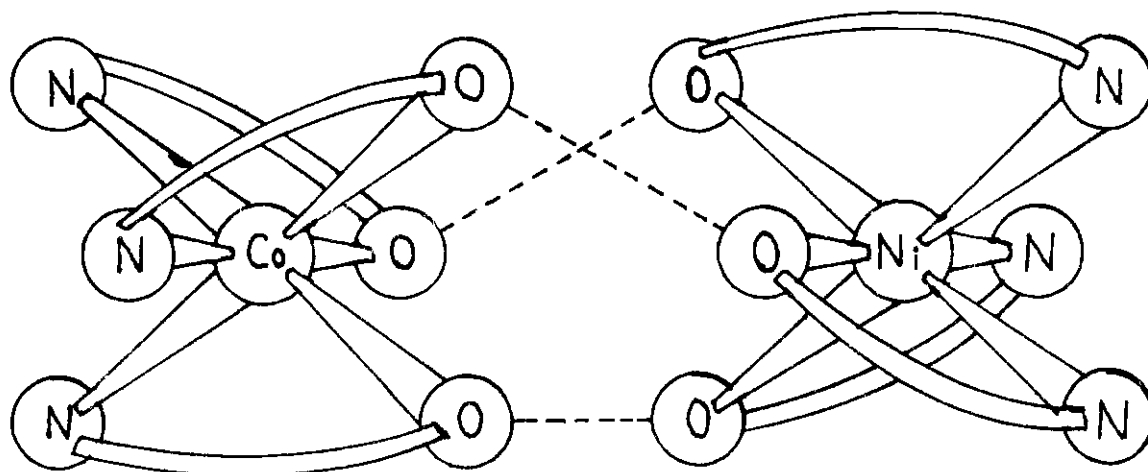


Figure 3. Structure of $\text{CoNi}(\text{META}_6-3\text{H})\text{I}_2$.

contain water, there is the possibility of an alternate formulation as hydroxides with the other proton of the water on the alcohol oxygen. Several types of structures have been found for bridging alkoxides and for bridging hydroxides.

A cubane-type structure for a cobalt alkoxide complex, $\text{Co}_4(\text{OCH}_3)_4(\text{acac})_4(\text{CH}_3\text{OH})_4$, was reported by J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and A. C. Sherwood (24). The red crystals were prepared from cobalt(II) acetylacetonate by the addition of potassium hydroxide in refluxing methanol. The crystals belong to the space group $C2/c$ and the calculated density from X-ray study is 1.43 g/cm^3 assuming four molecules per unit cell. From the magnetic susceptibility of the compound, all of the cobalt atoms in this compound are cobalt(II). The structure is shown in Figure 4.

Several titanium alkoxide structures with bridging alkoxide groups have been reported (8, 9, 10, 27). A crystallographic study of $\text{Ti}_4(\text{OC}_2\text{H}_5)_{16}$ was reported by J. A. Ibers (8). The crystals of this compound belong to space group $C2/c$ with $16 \text{ Ti}(\text{OC}_2\text{H}_5)_4$ in the unit cell. The reported structure of the tetramer is shown in Figure 5. This compound contains three types of oxygen: two oxygen atoms bridge groups of three titanium atoms at an average distance of 2.23 \AA ; four oxygen atoms bridge pairs of titanium atoms at an average distance of 2.03 \AA ; the remaining ten oxygen atoms are terminal with an average Ti-O distance of 1.77 \AA (8).

Later the crystal structure of monomethyl triethyl titanate was investigated by R. D. Witters and C. N. Caughlan (10). The crystal of monomethyl triethyl titanate was assumed to belong to the space group $P\bar{1}$. The space group was

changed to P1 and a discrepancy index of 13.6% was reached. This crystal has the same basic tetramer structure as $\text{Ti}_4(\text{OC}_2\text{H}_5)_{16}$ (Fig. 5).

The structure of titanium tetramethoxide was reported by D. A. Wright and D. A. Williams (27). The crystals of this compound belong to space group $\text{P}\bar{1}$ and the unit cell has two crystallographically independent $\text{Ti}(\text{OCH}_3)_4$ units. The reported structure of the tetramer is basically the same as the $\text{Ti}_4(\text{OC}_2\text{H}_5)_{16}$ and $\text{Ti}_4(\text{OCH}_3)_4(\text{OC}_2\text{H}_5)_{12}$ structures (Fig. 5). In general, the more titanium atoms coordinated to an oxygen atom the longer are its titanium-oxygen bonds, and for any given bridging oxygen atom the Ti(1)-O bond length is always longer than the Ti(2)-O bond (27).

A hydroxide-bridged compound, $(\text{Co}_4(\text{OH})_6(\text{NH}_3)_{12})\text{Cl}_6 \cdot 8\text{H}_2\text{O}$, was reported by I. Sotofte and E. Bang (25). The crystals belong to the space group $\text{R}\bar{3}$, and have a density of 1.80 g/cm^3 which was calculated from the X-ray data assuming 24 molecules per unit cell; six hydroxide oxygen atoms are μ_2 -oxygen and all of the 12 nitrogen atoms are terminal (Fig. 6). The cobalt-nitrogen distances are $1.99 - 2.05 \text{ \AA}$ and the cobalt-oxygen distances are $1.90 - 1.96 \text{ \AA}$.

Another bridging-hydroxide compound, $(\text{Cr}_4(\text{OH})_6(\text{NH}_3)_{12})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was reported by Bang and Narasimhayya (26). These crystals belong to the space group Pbca and have a density of 2.17 g/cm^3 for the calculated and observed density assuming four molecules per unit cell. The solved structure is shown in Figure 7. The four chromium atoms lie in a plane and form an eight-membered ring with alternating hydroxide groups which are slightly out of the plane (0.18 \AA). The μ_2 -hydroxide groups have chromium-oxygen distances of $1.94 - 1.99 \text{ \AA}$,

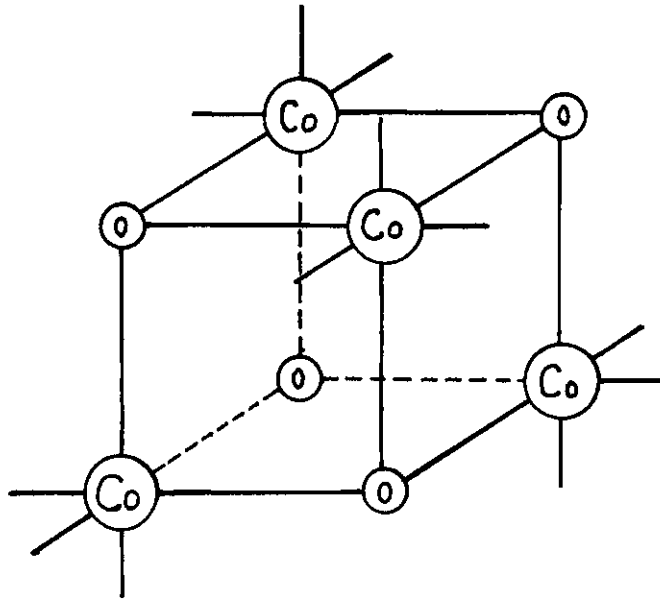


Figure 4. Structure of $\text{Co}_4(\text{OCH}_3)_4(\text{acac})_4(\text{CH}_3\text{OH})_4$.

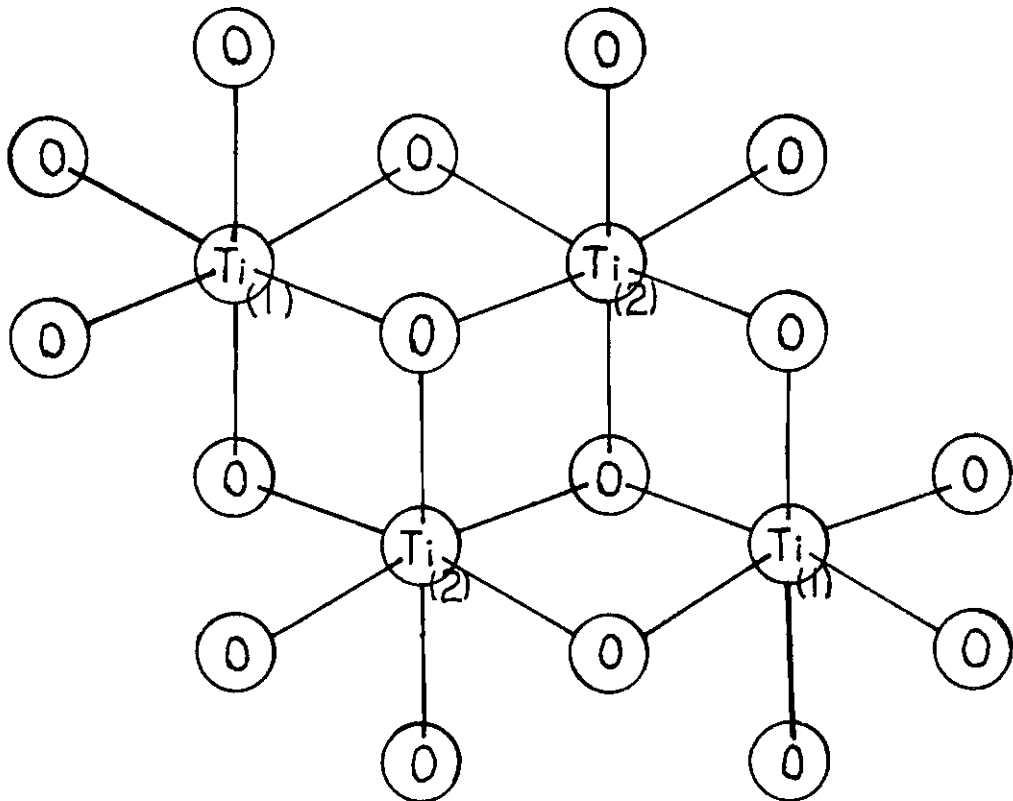


Figure 5. Structure of Titanium Alkoxide.

and the cobalt-oxygen distances are 1.90 - 1.96 Å.

Another bridging-hydroxide compound, $(\text{Cr}_4(\text{OH})_6(\text{NH}_3)_{12})\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was reported by Bang and Narasimhayya (26). These crystals belong to the space group Pbc_a and have a density of 2.17 g/cm³ for the calculated and observed density assuming 4 molecules per unit cell. The solved structure is shown in Figure 7. The four chromium atoms lie in a plane and form an eight-membered ring with alternating hydroxide groups which are slightly out of the plane (0.18 Å). The μ_2 -hydroxide groups have chromium-oxygen distances of 1.94 - 1.99 Å, the distance of the chromium 1 atoms is 2.93 Å, the distance between chromium 2 atoms is 6.62 Å; the chromium 1-nitrogen distance is 2.10 Å and the chromium 2-nitrogen distance is 2.06 - 2.13 Å. The chromium 1-oxygen-chromium 2 angles are 134° and 135°, the chromium 1-oxygen-chromium 1 angle is 96°.

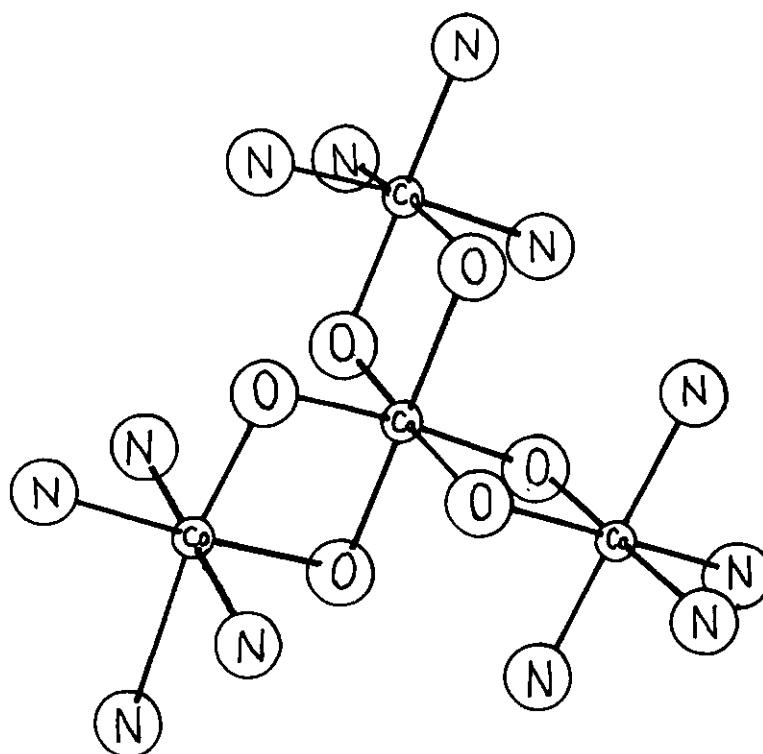


Figure 6. Structure of $(\text{Co}_4(\text{OH})_6(\text{NH}_3)_{12})\text{Cl}_6 \cdot 8\text{H}_2\text{O}$.

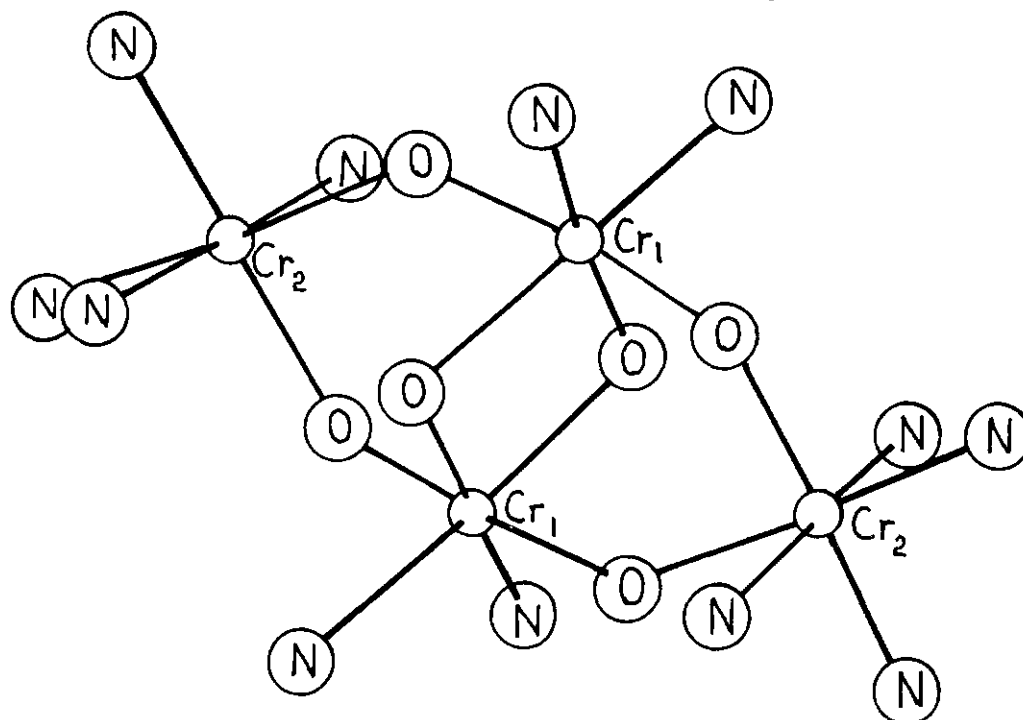


Figure 7. Structure of $(\text{Cr}_4(\text{OH})_6(\text{NH}_3)_{12})\text{Br}_2 \cdot 2\text{H}_2\text{O}$.

CHAPTER II

PREPARATION OF COMPLEXES

Preparation of Sodium Triscarbonatocobaltate(III) Trishydrate

The sodium triscarbonatocobaltate(III) trihydrate was prepared by the method of Bruer and Dinkard (11). Twenty-five milliliters of water was added to a 300 ml beaker which contained 23g of sodium bicarbonate. This mixture was cooled in an ice bath with stirring. A mixture of 14.6g of cobalt(II) nitrate hexahydrate and 10 ml of 30 per cent hydrogen peroxide was dissolved in 25 ml of water. This solution was also cooled in an ice bath. The cobalt(II)-hydrogen peroxide solution was then slowly added to the sodium bicarbonate water mixture; during the addition of the cobalt(II) solution, the temperature was not allowed to rise above five degrees. The mixture effervesced quite vigorously and turned green. Stirring was continued after the cobalt(II) solution was added until effervescence had ceased, approximately 30 minutes. The green precipitate which formed was filtered with suction, washed with water three times, washed twice with absolute ethanol to remove any unreacted cobalt(II), and then washed with diethyl ether.

The yield of olive green powder was 93% of theoretical. The sodium triscarbonatocobaltate(III) trihydrate was prepared as needed, since it slowly decomposed on standing and turned dark brown after one day.

Preparation of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$

To 7.24 grams (0.02mole) of sodium triscarbonatocobaltate(III) trihydrate, 4.21 grams(0.04moles) of 2,2'-dihydroxydiethylamine was added with 12 ml of water and the mixture was warmed on a steam bath about 1 hour. At first, the color of the mixture was dark brown, but it became dark green after 30 minutes. The solution was cooled, about 100 ml of methanol was added, and a precipitate of sodium carbonate separated. The solution was filtered by suction and was heated on a steam bath until the amount of solution was reduced to about 30 ml. Methanol was again added to the solution, the solution was then cooled, sodium carbonate was again precipitated, and the solution was filtered. This procedure was repeated four or five times until no more sodium carbonate was precipitated.

The solution was warmed on the steam bath for 48 hours and the solution was evaporated almost to dryness; a rose-violet precipitate was obtained. Methanol was added and the rose violet precipitate of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ was filtered and washed with methanol. The rose-violet precipitate was dried under vacuum at 100 degrees for twenty-four hours.

Preparation of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$

The rose-violet powder of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ was dissolved in water and a green solution was obtained. The solution was allowed to evaporate for a week, during which time a green compound crystallized. The product was filtered and washed with dry ethanol. Dark green needle-like monoclinic crystals were obtained. The same type of crystals were obtained by mixing sodium

triscarbonatocobaltate(III) trihydrate (0.01mole) and 2,2'-dihydroxydiethylamine (0.01mole) and heating on the steam bath. From this procedure, the crystals were mixed with Na_2CO_3 crystals and were difficult to purify.

Attempted Preparation of $\text{Co}_2(\text{DETA}_3-4\text{H})\text{Cl}4\text{H}_2\text{O}$

Following the published method of synthesis (7), 19.00 grams (0.08mole) of the hexaquacobalt(II) chloride was dissolved in 90 ml of methanol and was filtered. This solution was mixed with a solution of 50.40 grams (0.48mole) of 2,2'-dihydroxydiethylamine in 50 ml methanol, and a pink-colored powder precipitated. Air was passed through this mixture with stirring for 24 hours, during which time the pink precipitate redissolved and the solution turned green; this mixture was filtered.

The green precipitate was crystallized from methanol and from water but neither solution gave crystals large enough for x-ray work. The size of the crystals was 1/100-1/50 mm. Attempts were made to reduce the speed of crystal growth by adding sodium acetate or acetylacetone but the resulting crystals were still not large enough for x-ray work. With n-butanol, n-propanol, and ethanol the results were the same as with methanol and the crystals were never large enough for x-ray work. The green solid was insoluble in nonpolar solvents such as acetone, benzene, and ether.

The anion of the starting material was changed by replacing the cobalt(II) chloride with cobalt(II) acetate. Air was passed through the mixture with 2,2'-dihydroxydiethylamine for 24 hours, but only a light pink precipitate was

obtained and the color of the filtrate was red. It seemed that oxidation did not occur in this cobalt(II) acetate and 2,2'-dihydroxydiethylamin mixture.

CHAPTER III

EXPERIMENTAL TECHNIQUES AND INSTRUMENTATION

Methods of Analysis(A) Cobalt Analysis

The cobalt was determined by photometric titration (12) with copper solution and ethylenediaminetetraacetic acid (EDTA) using 1-(2-pyridylaza)-2-naphthol (PAN) as indicator. About 3.177 grams of copper metal was dissolved in nitric acid and diluted to 1000 ml to give a 0.05 N aqueous copper solution. Exactly 3.72146 grams of EDTA was dissolved in 500 ml of water and 0.0199942 N of EDTA solution was obtained.

(1) Standardization of Copper Solution with EDTA. To 6.00 ml of EDTA solution, measured by microburet, was added 5.00 ml of water and 15.00 ml of a buffer solution of pH 5. To this solution, 15.00 ml of ethanol was added quite slowly with stirring and then 3 drops of PAN indicator was added. This mixture was titrated with the copper solution and the color change at the end-point was detected by a photometer.

(2) Preparation and Titration of Cobalt Sample. About 100 mg of an accurately weighed sample was heated to 1100°C in a crucible for 10 hours. The crucible and sample were cooled to room temperature quite slowly and 1 gram of potassium pyrosulfate was added; the crucible was reheated to 600°C . The fused mixture was slowly cooled to room temperature, 2 ml of water was added, and

the mixture was heated slowly to dissolve the fused mixture. The resulting solution was diluted to 30 ml, was adjusted to pH 4 with concentrated ammonium hydroxide, and the solution was then diluted to 100 ml in volumetric flask. To 15.00 ml of this cobalt solution was added 7.5 ml of EDTA solution and 15.00 ml of buffer solution of pH 5. To this mixture 10.00 ml of ethanol was added with stirring and 3 drops of PAN indicator was added. The excess of EDTA was back titrated with the copper solution.

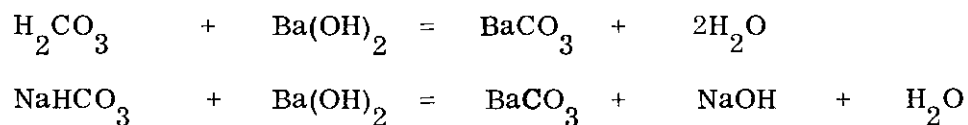
(B) Sodium Analysis

Sodium analysis was by the Flame Emission method, which is generally used in analytical laboratory (28). This method was checked by a known complex, $\text{NaCo}(\text{acac})_3$, which is similar to the complex, $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$. The $\text{NaCo}(\text{acac})_3$ was used as a standard and the analysis of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$, indicated 0.9998 sodium atom per six cobalt atoms.

(C) Carbonate Ion Analysis

Analysis of carbonate ion was by acid-base titration. An excess amount of acid was added to a weighed sample and the carbonate ion was removed as carbon dioxide under a nitrogen gas flow. The carbon dioxide was collected in a known amount of base and the excess base was back titrated by acid.

The second ionization constant of carbonic acid is so small that it cannot be determined as dibasic acid by a direct titration. However, the carbonate ion can be removed by precipitation. A measured excess of barium hydroxide was added to the solution of carbon dioxide or bicarbonate (13).



The excess is back titrated with standard acid, using phenolphthalein or thymol-blue as indicator, without filtering off the barium carbonate precipitate.

This method was checked with sodium bicarbonate and cobalt(II) carbonate. The sample solution was treated with phosphoric acid, which is a non-volatile acid, and nitrogen gas was allowed to flow for 24 hours. The result of this analysis was 97% of calculated value.

Carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Analytical results for sodium, carbon, cobalt, hydrogen, nitrogen, and oxygen are summarized in Tables 1, 2, and 3.

Table 1. Analytical Data for $\text{NaCo}_6(\text{DETA}_{10}^{-11\text{H}})(\text{CO}_3)_3$

	sodium	cobalt	carbon	hydrogen	nitrogen	oxygen*
Calculated	1.44%	22.14%	32.34%	6.25%	8.77%	29.06%
Found	1.57%	24.05%	31.66%	6.01%	9.35%	27.36%

* Oxygen percentage is by difference.

Table 2. Analytical Data for $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$

	Sodium	Cobalt	Carbon	Hydrogen	Nitrogen	Oxygen*
Calculated	1.57%	24.13%	22.13%	6.03%	5.74%	40.40%
Found	1.60%	25.71%	22.30%	5.81%	5.58%	39.00%

* Oxygen percentage is by difference.

Table 3. Analytical Data for $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3$

	Sodium	Cobalt	Carbon	Hydrogen	Nitrogen	Oxygen
Calculated	1.84%	28.28%	25.94%	5.24%	6.72%	31.99%
Found	--	--	25.64%	4.70%	6.57%	--

Thermogravimetric Analysis

About 4 mg of sample was weighed accurately on a Cahn electrobalance. The temperature was raised continuously at a constant rate and a constant nitrogen gas flow was maintained over the sample. The weight change and the change of temperature were both recorded continuously.

The analysis was done at two different rates of temperature change (Fig. 8). For the first, the rate of temperature change was 80 degrees per minute and the weight of sample was 3.722 mg. Three discontinuities were observed in the curve; approximately eight water molecules were lost around 240°C .

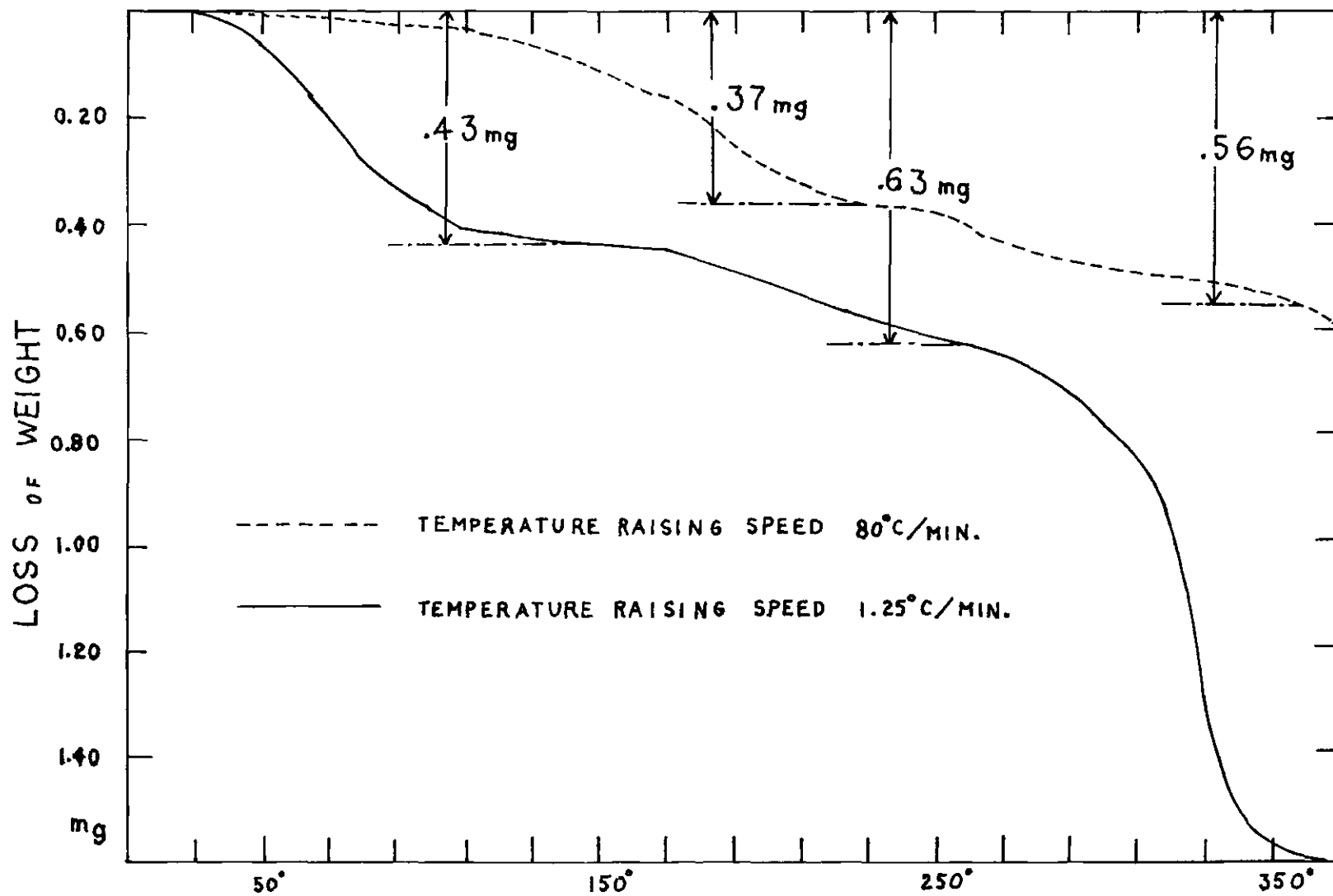


Figure 8. Thermogravimetric Analysis of $\text{NaCo}_6(\text{DETA}_{6-7\text{H}})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$.

The weight loss agrees quite well with the analytical data for $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$ and for $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3$, which was obtained from the hydrate by drying under vacuum at 100°C for 24 hours.

A distinct weight change due to loss of carbonate ions was not observed since 2,2'-dihydroxydiethylamine decomposed in the same temperature range.

Spectral Studies

Infrared spectra were obtained using potassium bromide pellets. The sample and potassium bromide were ground in an agate mortar quite finely and pressed in a metal ring. The spectra were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer. The resulting spectra are presented in Figures 10 and 11.

Visible spectra were obtained in aqueous solutions. For comparison, spectra of samples $\text{Co}(\text{acac})_3$ and hexaquocobalt(II) chloride were obtained. The relationship between absorbancy and molar absorbancy is indicated by the equation:

$$\log_{10}(I^0/I) = \epsilon \cdot \ell \cdot c$$

ϵ = constant specific for the substance (molar absorbancy)

c = concentration (moles/liter)

ℓ = thickness (centimeters)

I^0 = Incident intensity of light

I = Intensity of light after passing through the cell

The concentration of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$, $\text{CoIII}(\text{acac})_3$, and $\text{Co(II)Cl}_2 \cdot 6\text{H}_2\text{O}$ were 0.901×10^{-3} M, 2.750×10^{-3} M, and 45.64×10^{-3} M,

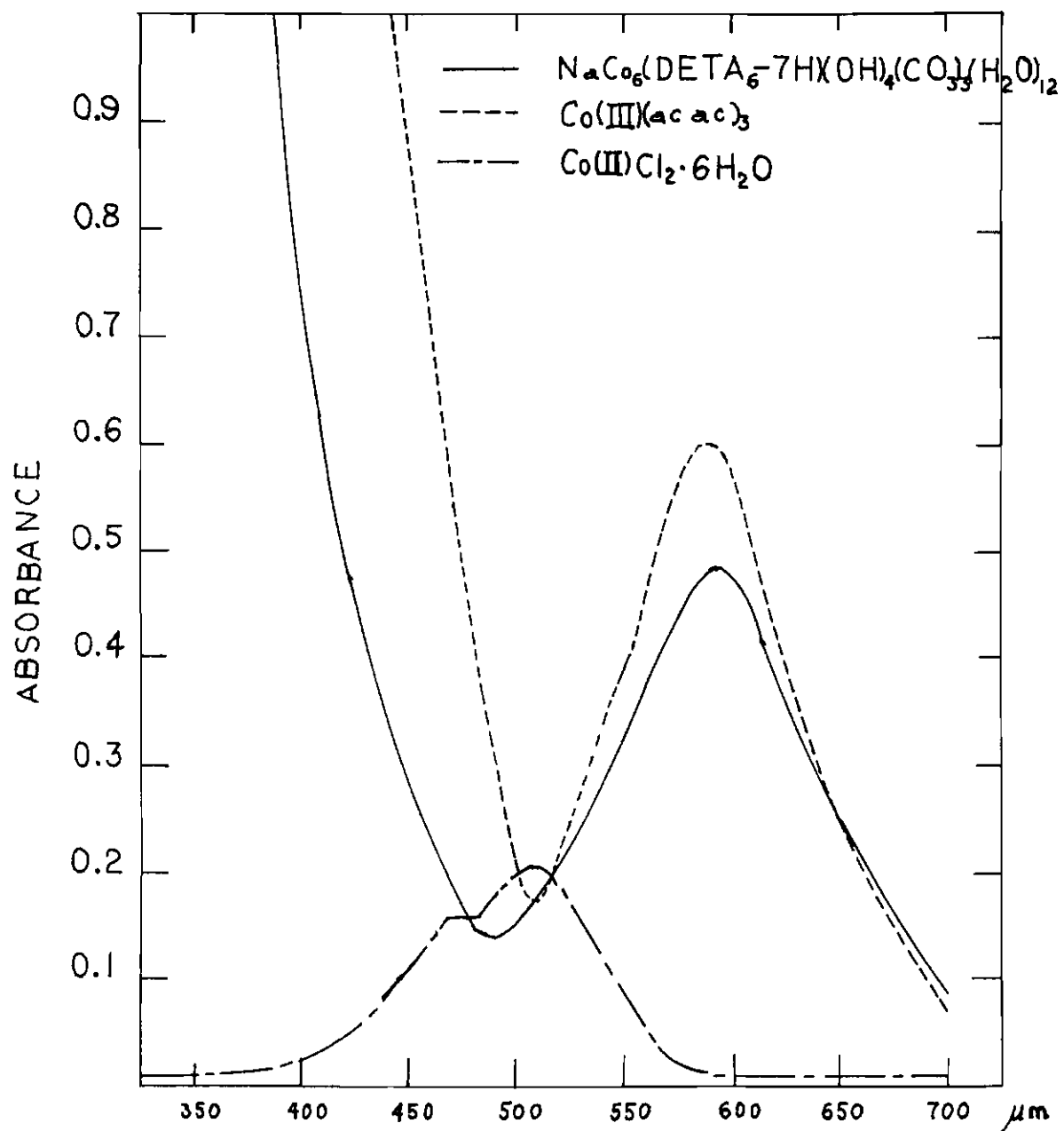


Figure 9. Visible Spectrum of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$.

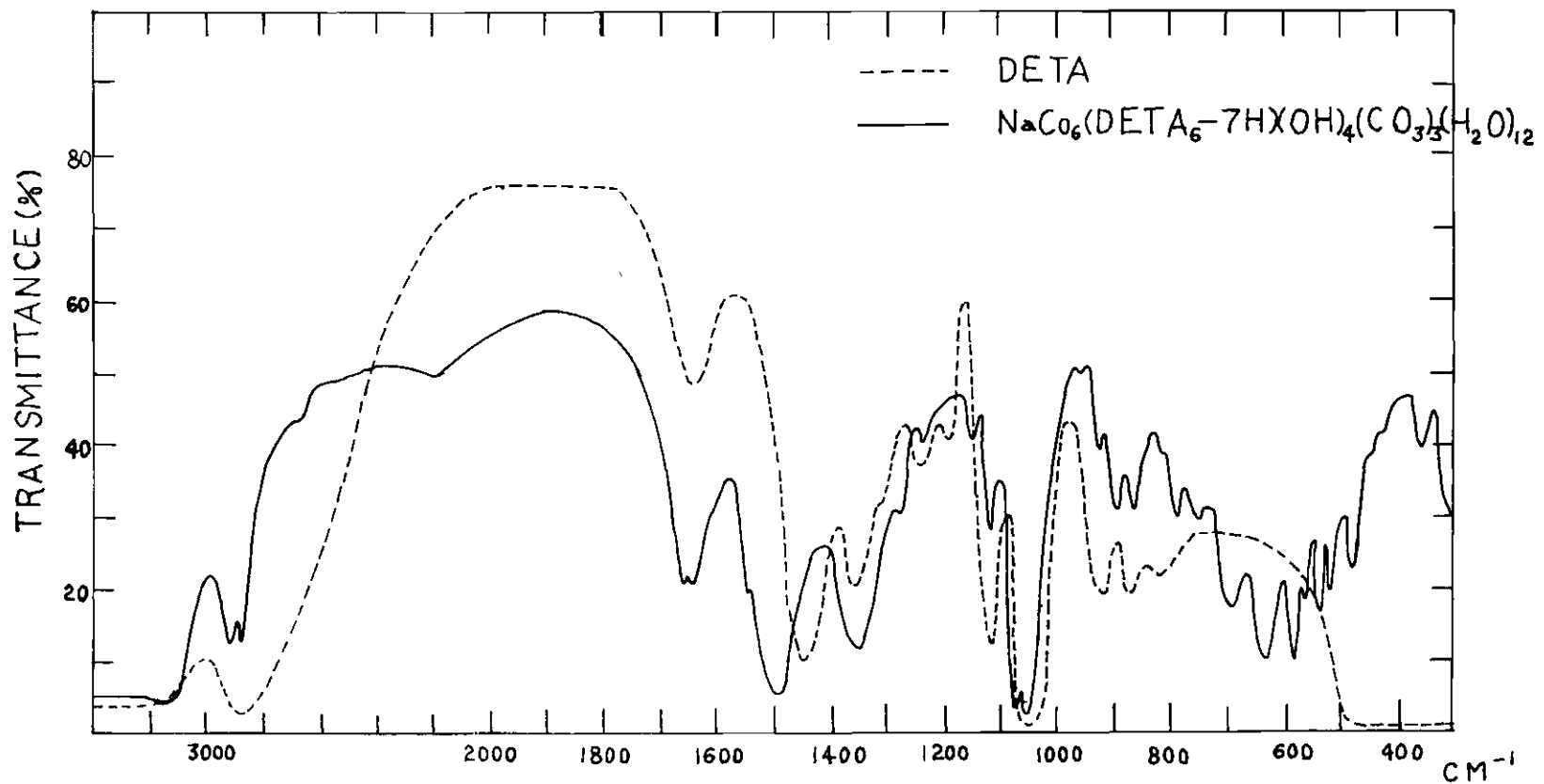


Figure 10. Infrared Spectrum of NaCo₆(DETA₆-7H)(OH)₄(CO₃)₃·12H₂O.

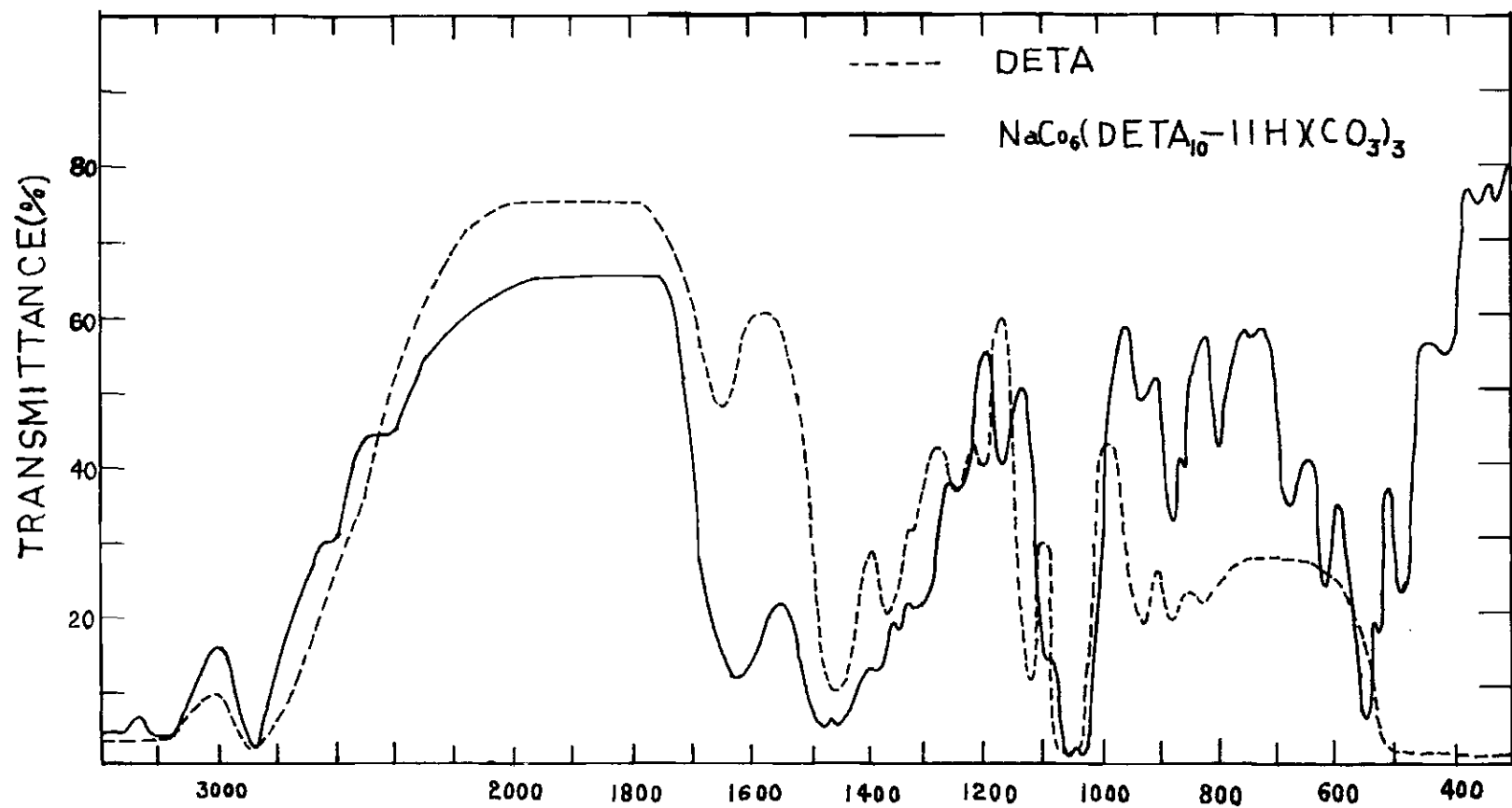


Figure 11. Infrared Spectrum of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$

respectively. The spectra are shown in Figure 9. The molar absorbandy of $\text{NaCo}_6(\text{DETA}_6^{-7}\text{H})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$ at $580\ \mu\text{m}$ was approximately twice the molar absorbandy of Co(III)(acac)_3 , at the same wave-length.

Magnetic-Moment Studies

All of the magnetic moment values were obtained from solid samples using the Faraday method. About 50 mg of each sample was weighed accurately in the small glass bucket. The $\text{Hg}(\text{Co}(\text{CNS})_4)$ complex served as a standard; it has a gram susceptibility of 16.44×10^{-6} c. g. s. units.

A Cahn No. 2000 R G Electrobalance and Alpha Scientific Laboratories electromagnet were used. The power supply was capable of supplying currents from 0.00 to 9.00 amps. Usually six readings, all at different magnetic field strengths, were recorded for each sample.

The temperature was that of the room for all readings. A correction for the diamagnetic susceptibility of each sample was made using Pascal's constants from the literature (14).

The nomenclature and procedure for obtaining the tube calibration constant at given force field strengths and the effective magnetic moments of the samples are given below.

A = weight of empty sample bucket, zero current

B = weight of empty sample bucket, at a given current

C = weight of filled sample bucket, zero current

D = weight of filled sample bucket, at a given current

S = B - A = apparent mass change for empty bucket

$F = D - C =$ apparent mass change for filled bucket

$F' = F - S =$ apparent mass change corrected for the diamagnetic
character of the sample bucket

$\gamma =$ temperature independent paramagnetism per metal ion

$\beta =$ tube calibration constant for a given field strength

$T =$ absolute temperature

Calculation of ' β ' Values Using $H_g(\text{Co}(\text{CNS})_4)$ as the Standard

$$\frac{1}{k} = \beta = \frac{16.44 \times 10^{-6} x(C-A)}{F'}$$

Calculation of Effective Magnetic Moment of Sample

$$\frac{F'}{\text{sample weight}} = X_g$$

$$X_{\text{molar}}^{\text{corrected}} = X_g (\text{molecular weight of sample}) + \text{diamagnetic corrections}$$

$$\mu_{\text{eff}} = 2.84 (X_{\text{molar}}^{\text{corrected}} \cdot T)^{\frac{1}{2}}$$

Crystallographic Studies

Calculation

All computations were carried out on a Univac 1108 computer. Modified versions of Zalkin's FORDAP Fourier summation program (15), the Busing, Martin, and Levy XFLS Least-Squares Program (16), a data reduction program (17), and a minimum function program by Bertrand were used.

Attempted Solution of the Structure of $\text{NaCo}_6(\text{DETA}_{6-7\text{H}})(\text{OH})_4(\text{CO}_3)_3(\text{H}_2\text{O})_{12}$

A green needle-like crystal with dimensions 0.10 x 0.15 x 5.00 mm was

mounted on precision camera with the long dimension, h , along the spindle axis. The 0.15 x 5.00 mm surface of the crystal is a parallelogram with an acute angle equal to approximately 60 degree.

Orientation precision photographs were taken, using zirconium filtered Mo $K\alpha$ radiation, $\lambda = 0.7106 \text{ \AA}$. The crystal was found to be monoclinic with $a = 18.42 \text{ \AA}$, $b = 21.77 \text{ \AA}$, $c = 15.75 \text{ \AA}$, and $\beta = 120^\circ$. The density calculated on the basis of eight molecules per unit cell, 1.805 g/cm^3 , agrees with the experimental value, 1.801 g/cm^3 , obtained by the flotation method using a mixture of carbon tetrachloride and 1,2-dibromoethylene.

From the symmetry observed, a zone located at a spindle setting of $155^\circ 45'$ was designated $h k 0$ and a zone located at a spindle setting of $65^\circ 50'$ was designated $h 0 l$. The absence of $h k l$ reflections with $k + l = 2n + 1$ and the absence of $h 0 l$ reflections with $l = 2n + 1$ indicated space group Cc or C2/c. The Patterson Synthesis gave some evidence that the correct space group was C2/c. Due to their different symmetries, the strongest non-origin peaks in the Patterson should occur on the line $0, y, 1/2$ for space group Cc but strong peaks of equal intensity should occur on the line $0, y, 1/2$ and $x, 0, 1/2$ for space group C2/c; the latter situation was observed in this case.

The same crystal which was used for the space group determination was mounted on the automated Picker four-circle diffractometer. The crystal was realigned on the diffractometer according to published instructions (18). The four angles (ϕ , χ , ω and 2θ) which define the position of the crystal and counter to record a reflection in reciprocal space, were determined for seventeen

reflections. From these seventeen reflections, refined unit cell parameters and angle settings for the remaining data were obtained by least-square method using the computer program written by F. Carter and modified for the Univac 1108 computer by Bertrand and Kirkwood (19). The cell parameters obtained from this first alignment with Molybdeum $K\alpha$ radiation ($\lambda = 0.7107$) are $a = 18.29 \text{ \AA}$, $b = 21.60 \text{ \AA}$, $c = 15.73 \text{ \AA}$, $\beta = 119^\circ 57'$, and unit cell volume $V = 5390 \text{ \AA}^3$. The intensities were collected by the $\theta - 2\theta$ scan technique with a take-off angle of approximately 1.6° and a scan rate of one degree per minute. A symmetrical scan of two degrees was taken about the calculated position for each reflection. When the scan was completed, stationary background counts of twenty seconds each were taken at the beginning and at the end of the scan. All reflections within the limits $-h \rightarrow h$ ($h = 16$), $0 \rightarrow k$ ($k = 22$), and $0 \rightarrow l$ ($l = 16$) were collected. The intensity value was obtained by subtracting the background from the total integrated peak count. Settings for 5458 reflections were calculated but after two weeks a standard reflection had decreased in intensity to such an extent that the collection of data was terminated after 2832 reflections. Because of the procedure of collecting low 2θ reflections first, the reflections that were not collected were all high angle, weak intensity reflections. A total of 2519 unique reflections were accepted as being statistically above background ($\sigma I/I > 0.33$) and were used in the refinement. These reflections were corrected for Lorentz and polarization effects but were not corrected for absorption. Periodic checks of standard reflection showed only slight variation during the two weeks of data collection.

A three-dimensional Patterson function was calculated using the 2519 reflections and from this Patterson function positions were obtained for cobalt atoms in two sets of general, eight fold positions. From the distances between cobalt atoms of different sets and between pairs of cobalt atoms from the same set, four molecular units each containing four cobalt atoms were observed. However, from the Patterson function the coordinates of the third set of eight cobalt atoms were not found. Using the two sets of cobalt atoms positions that were found, an electron density map was calculated and eight oxygen and nitrogen atoms were located. After several cycles of least-squares refinement of the scale factor, atomic coordinates and isotropic temperature factors, the conventional R, value $(\sum ||F_o| - |F_c|| / \sum |F_o|)$ was only 44.3%. Using the minimum function, the same peaks which were present in the electron density map were observed. At this point, there appeared to be no way to solve the complete structure from the data available and the structure refinement was not continued. The positions of atoms which were located are shown in Table 5.

Table 4. Calculated and Observed Frequencies of Co(III) Carbonato Complexes (cm^{-1}) (20)

Species	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(A_1)$	$\nu_5(B_2)$	$\nu_6(B_2)$	$\nu_7(B_2)$	$\nu_8(B_1)$
Calc. Frequency of Unidentate	1376	1069	772	303	1482	672	92	850*
Calc. Frequency of Bidentate	1595	1038	771	370	1282	669	429	834**
CaCO_3 (Calcite)		879	1429-1492	706				
CaCO_3 (aragonite)	180		1492, 1504	706, 711				
$\text{NaCo}_6(\text{DETA}_6-7\text{H})$ $(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$	over	over	780	350	over	700	--	860
$\text{NaCo}_6(\text{DETA}_{10}-11\text{H})$ $(\text{CO}_3)_3$	over	over	740	350	over	675	--	860

* observed frequency of $(\text{Co}(\text{NH}_3)_5\text{CO}_3)\text{Br}$

** observed frequency of $(\text{Co}(\text{NH}_3)_4\text{CO}_3)\text{Cl}$

over the absorbance which overlap with the absorbance of 2, 2'-dihydroxydiethylamine

CHAPTER IV

RESULTS AND CONCLUSIONS

Although 2,2'-dihydroxydiethylamine complexes containing both cobalt(II) and cobalt(III) have been prepared, crystals suitable for x-ray work have not been obtained. In order to find a new preparation for these complexes which would yield crystals, the reaction of $(\text{Co}(\text{DETA}-2\text{H})_2)^-$ with cobalt(II) was considered and attempts were made to prepare the cobalt(III) complex, $(\text{Co}(\text{DETA}-2\text{H})_2)^-$.

For this purpose, sodium triscarbonatocobaltate(III) trihydrate was prepared and was reacted with 2,2'-dihydroxydiethylamine and a rose-violet powder was obtained after the evaporation of solvent. From carbon, nitrogen, hydrogen, sodium and carbonate analyses, this compound was identified as $\text{NaCo}_6(\text{DETA}_{10}^{-11\text{H}})(\text{CO}_3)_3$. This compound was recrystallized from water and green needle-like crystals were obtained; from carbon, nitrogen, hydrogen, sodium, and carbonate analyses, these crystals were identified as $\text{NaCo}_6(\text{DETA}_6^{-x\text{H}})(\text{CO}_3)_3 \cdot 16\text{H}_2\text{O}$. It was not clear whether all of the water was present as water molecules or whether there were some hydroxide ions present. To solve this question, the crystals were dried under vacuum at 100°C for twenty-four hours and carbon, nitrogen, and hydrogen analyses were obtained for the resulting solid. From these analytical results, it was assumed that there are twelve water molecules and four hydroxide ions per formula unit. For additional support of this result, thermogravimetric analysis was done and the results of this analysis (Fig. 8) also agree

quite well with the analytical results; eight water molecules are lost at around 100°C and four water molecules are lost at 240°C. From these results, eight water molecules are probably present as waters of crystallization and four water molecules are probably present as coordinated waters. The crystals of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ decomposed at 195° - 210° C without melting.

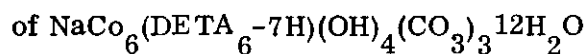
The infrared spectrum was taken to determine the nature of the carbonate. The observed frequencies of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$, $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$, and literature values for cobalt carbonate complexes are listed in Table 4. Since many absorption bands of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ and $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ overlap with the band of 2, 2'-dihydroxydiethylamine, it is not clear whether the carbonate ions are monodentate or bidentate.

The magnetic moment of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ is 4.3 B. M. per gram atom of cobalt. The calculated $\mu_{\text{S+L}}$ value of cobalt(II) is 5.40 B. M. and the observed values of cobalt(II) are in the range 4.80 B. M. to 5.20 B. M.; cobalt(III) is usually diamagnetic (21). If $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ contains two cobalt(III) ions and four cobalt(II) ions, the magnetic moment per gram atom of cobalt(II) is 5.18 B. M.; this is a reasonable value for the magnetic moment of octahedrally coordinated cobalt(II).

The magnetic moment of the complex $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ is 3.57 B. M. If it is assumed that three cobalt(II) and three cobalt(III) atoms are contained in $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$, the magnetic moment per gram atom of cobalt(II), 5.05 B. M., is reasonable.

In the visible spectrum of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$, an

Table 5. Cobalt and Oxygen Atoms' Position and Thermal Parameters



Atom	X	Y	Z	$B, \text{\AA}^2$
Co 1	0.2508	0.3222	0.4994	1.7601
Co 2	0.3191	0.2376	0.3985	0.7833
O 1	0.2292	0.3168	0.3572	3.1432
O 2	0.2567	0.1772	0.3659	1.2994
O 3	0.3400	0.2424	0.5044	4.5520
O 4	0.3409	0.2391	0.2868	5.0837
O 5	0.3323	0.3797	0.5126	1.9182
O 6	0.3998	0.1187	0.5508	1.4570
O 7	0.3966	0.3259	0.4248	1.5348
O 8	0.4257	0.1745	0.4505	3.2561

absorption band is observed at 590 nm with an extinction coefficient of $86.08 \text{ M}^{-1} \text{ cm}^{-1}$. The absorption band of Co(III)(acac)_3 is observed at 580 nm with an extinction coefficient of $218.12 \text{ M}^{-1} \text{ cm}^{-1}$; the absorption bands of hexaquacobalt(II) chloride are observed at 520 nm with extinction coefficient of $4.49 \text{ M}^{-1} \text{ cm}^{-1}$ and at 450 nm with extinction coefficient of $3.50 \text{ M}^{-1} \text{ cm}^{-1}$. The molar absorptance of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ is approximately twice that of Co(III)(acac)_3 . This is consistent with the assumption that the compound $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ contains two cobalt(III) atoms and four cobalt(II) atoms (Fig. 9).

The crystal of $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ was prepared by recrystallization of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ from water. In aqueous solution four molecules of 2,2'-dihydroxydiethylamine of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ were replaced by hydroxide ions and water molecules to give $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$. This is the same type of replacement observed for $\text{Co}_2(\text{DETA}_3-3\text{H})\text{I}(\text{H}_2\text{O})$, which gave $\text{Co}_2(\text{DETA}_2-3\text{H})\text{I}(\text{H}_2\text{O})_4$ upon treatment with water (1) (Fig. 1), and also for $\text{Co}_2(\text{DETA}_3-4\text{H})\text{X}$, which gave $\text{Co}_2(\text{DETA}_2-4\text{H})\text{X}_4\text{H}_2\text{O}$ (where X is Cl, Br, and I) (7). Compounds with the formula $\text{Co}_2(\text{DETA}_2-4\text{H})\text{XH}_2\text{O}$ also lost crystalline water at 100°C and decomposed at $200^\circ - 220^\circ \text{C}$ without melting. Quite similar behavior was observed for $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{HO})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$.

To obtain a complete structure for $\text{NaCo}_6(\text{DETA}_6-7\text{H})(\text{OH})_4(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$, an x-ray diffraction study was attempted. From the space group and density, Patterson vectors were expected for three 8-fold sets but only two sets of 8-fold

position were observed. Using these as cobalt positions, an electron density map was calculated and eight oxygen atoms which related to a cobalt tetramer were found. The remaining set of cobalt atoms was not observed in the electron density map. A minimum function calculation was made to locate the remaining cobalt position, but coordinates for additional cobalt atoms could not be found.

These problems are possibly caused by the crystal being a twinned crystal, the crystal containing disordered groups, or the collected data being poor. In the case of a twinned crystal, it is possible that only the positions of atoms consistent with the higher symmetry of the twin appear in the Patterson. In the case of disordered groups, the cobalt tetramer could be in ordered positions and the remaining cobalt atoms could occupy disordered positions; in this case, it is also possible that only the tetramer of cobalt atoms would appear in the Patterson. Although additional peaks were observed in the electron density, placing carbons in these positions did not improve the refinement significantly and no further work was done on the structure.

The portion of the structure located is similar to the titanium alkoxide structures (Fig. 5). The structure is not necessarily a tetramer since the remaining cobalt atoms may be part of the molecular unit or they may be present as separate ions. However, the similarity of the bridging arrangement to that in the titanium alkoxide structures makes a tetramer unit seem reasonable. Furthermore, if the remaining cobalt atoms were part of the same unit they should appear in the electron density since disorder or twinning effects could not affect one part of a unit without affecting the entire unit (8, 9, 10, 27).

There still remains a question as to the oxidation states of the tetrameric unit since there could be two or four cobalt(II) atoms in the tetrameric unit. To answer this question would require that all of the carbon atoms be located and that the positions of the coordinated 2, 2'-dihydroxydiethylamine be found. From the cobalt-oxygen distances, the cobalt(II) and cobalt(III) ions could then be identified. The structure of $\text{NaCo}_6(\text{DETA}_{10}-11\text{H})(\text{CO}_3)_3$ is also left as an interesting question. If this structure is solved, the relationship between these compounds and the previously reported compounds can be cleared up.

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