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The Reaction of Ethylenediamine with Cobalt (II) Perchlorate and Oxygen in Dilute Aqueous Solutions

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THE REACTION OF ETHYLENEDIAMINE WITH COBALT (II)
PERCHLORATE AND OXYGEN IN DILUTE AQUEOUS SOLUTIONS

A Thesis
Presented to
the Graduate Faculty
Central Washington State College

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Robert J. Karmy
August 1968

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ABSTRACT

Cobalt (II) perchlorate was reacted with ethylenediamine and molecular oxygen. Various mole ratios of ethylenediamine to cobalt (II) were oxygenated and studied by photometric, potentiometric, conductometric, magnetic susceptibility, freezing point depression, electron spin resonance and cobalt (II) extraction methods. The fact that the complex was brown in color, diamagnetic, contained ethylenediamine to cobalt to oxygen in a mole ratio of 4:2:1 was confirmed. The complex underwent olation to form a polymeric species with excess base. The complex could not be oxidized to a green paramagnetic complex by reacting it with sodium peroxydisulfate, potassium bromate, bromine or chlorine.

Ammonia was added to a 2:1 mole ratio solution of ethylenediamine to cobalt (II) perchlorate before oxygenation. Upon oxygenation this solution also turned brown. This ammonia-containing-complex underwent no olation reaction and was postulated by analogy to contain ammonia: ethylenediamine:cobalt:oxygen in a mole ratio of 2:4:2:1. Crystals of this ammonia-containing-complex were obtained.

ACKNOWLEDGMENTS

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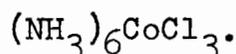
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INTRODUCTION

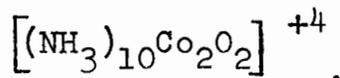
Chemical compounds are the basis of chemistry and life. The general term "chemical compounds" can be divided into two classes: (A) those compounds whose components are not capable of independent existence and function, and (B) those compounds whose components are capable of independent function and existence. It is this last group of compounds that is of interest. An example of this class of compounds is that represented by mixtures of the salts KCl , HgCl_2 and MgCl_2 . Each of these salts exists by itself and has an independent function. However, of the possible combinations of these salts, two salts, formulated originally as $2\text{KCl} \cdot \text{HgCl}_2$ and $2\text{KCl} \cdot \text{MgCl}_2$ were thought to be of the same type. It was later realized that these two salts were not of the same type (1). It was found that the former salt in solution yielded two potassium ions and a total of three ions per mole, whereas the latter salt yielded a total of seven ions per mole. It is now realized that the first salt is a complex or coordination salt expressed as $\text{K}_2(\text{HgCl}_4)$, in which the four chloride ions are firmly attached to the mercury ion, whereas the second salt is correct as written and is called a double salt. Thus again is found a division of the class of compounds that is under consideration: (A) those compounds which are strictly mixtures of their reactants and retain the identity of the reactants, and (B) those

compounds that are so called complex or coordination compounds in that the product of the combination is different from the sum of the reactants.

An important class of coordination compounds is the metal amines. In 1798 Tassaert (2) reported that ammoniacal solutions of cobalt (II) chloride allowed to stand overnight yield an orange colored crystalline product containing six molecules of ammonia and found to be



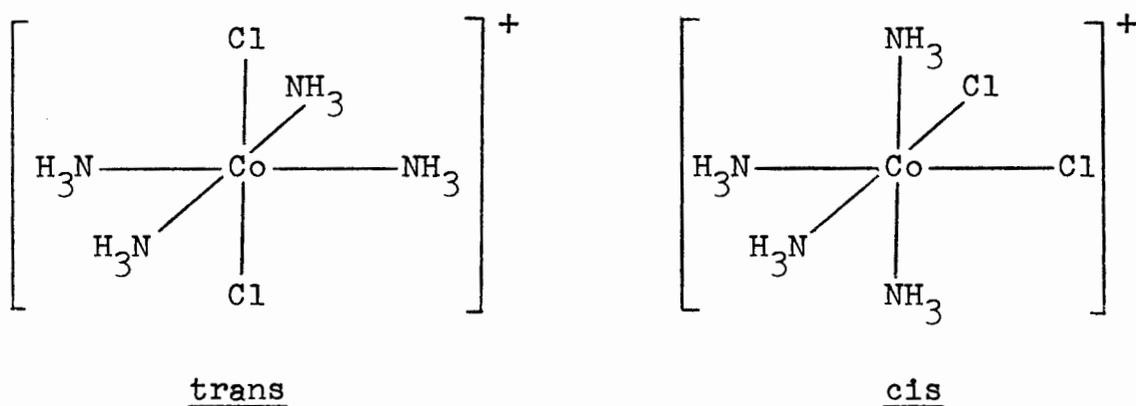
Tassaert (2) also reported that this ammoniacal solution of cobaltous chloride turned brown when exposed to air, and that when this solution was boiled, it changed to a red color. The brown species was found to be



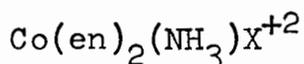
Other compounds of the cobalt(III) chloride containing fewer than six ammonia molecules per complex were also prepared as shown in Table I (3). In 1893, Werner (4) finally correctly interpreted the structure of the cobalt (III) ammine chloride compounds.

As part of the explanation for the structure of the cobalt (III) ammine compounds, Werner proposed that there were six coordination bonds directed in space which were similar to the valence requirements of the atom. However, these coordination bonds could be satisfied by either a negative or neutral group. One specification was that the

coordination bonds had to be satisfied every time before the valence requirements were satisfied. With this consideration, Werner predicted two isomers of $\text{CoCl}_3 \cdot 4\text{NH}_3$, the cis and the trans.



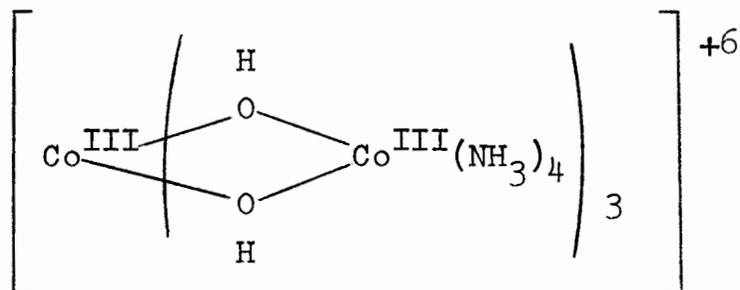
Werner's theory also predicted optical isomerism among the compounds of cobalt (III). In 1911, Werner (5) succeeded in resolving the cis form of



(X = Cl, Br en = ethylenediamine)

into dextro- and levo-rotatory forms by crystallization of the d-bromocamphorsulfonates. This seemed to be convincing proof of the correctness of Werner's theory, but there were those who tenaciously held to the idea that the optical activity was caused by the organic ethylenediamine, even though it showed no optical activity of itself. As final proof of his argument that optical activity lay in the metal

ion, Werner (6) effected the resolution of hexol, tris-tetraamminecobalt(III)- μ -diolcobalt(III) ion.



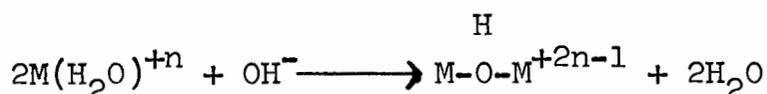
Hexol is a purely inorganic material with two forms of high rotatory power (molecular rotation = $\pm 47,600^\circ$).

TABLE I
COBALT (III) AMMINE CHLORIDES

Compound	Color	Class Name	No. of Ionic Chlorides	Werner's Formulation
CoCl ₃ 6NH ₃	orange	luteo salt	3	Co(NH ₃) ₆ ⁺³ 3Cl ⁻
CoCl ₃ 5NH ₃	purple	purpureo salt	2	Co(NH ₃) ₅ Cl ⁺ 2Cl ⁻
CoCl ₃ 4NH ₃	green	praseo salt	1	<u>trans</u> Co(NH ₃) ₄ Cl ₂ ⁺ Cl ⁻
CoCl ₃ 4NH ₃	violet	violeo salt	1	<u>cis</u> Co(NH ₃) ₄ Cl ₂ ⁺ Cl ⁻
CoCl ₃ 4NH ₃	blue green	-----	0	Co(NH ₃) ₃ Cl ₃

Polynuclear metallic ammine compounds such as the hexol studied by Werner (6), differ from the mononuclear metallic ammine compounds in that the central metal ions are

linked to each other by single atoms or groups of atoms (7). Of the possible bridging groups, some of the most common are NH_2^- , OH^- , O^- , NO_2^- , SO_4^- and O_2^- . Two metal ions may be linked together by one, two or three of these groups, all groups being either the same or different. The OH^- bridge is usually formed by olation, which seems to be a pronounced tendency of almost all hydroxo complexes (1). Olation is the name given to the formation of polynuclear complexes by the splitting out of water between hydroxo groups as indicated by the following equation.



The oxygen atom between the two metal atoms may be protonated, forming a hydroxo bridge.

Frémy, Vortmann, Jörgensen and others studied polynuclear compounds, and it was Frémy who first studied the oxidation products of the cobalt (II) amines in 1852 (8). After passing a stream of air through an ammoniacal solution of cobalt (II) nitrate, Frémy obtained some brownish-green crystals from which he determined the composition to be $\text{Co}_2\text{O}_2(\text{NH}_3)_{10}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$. The crystals were decomposed by hot water and lost an amount of oxygen equal to 5.2 per cent of the complex. Gibbs (9) extended the work of Frémy by methods very similar to those of Frémy and obtained dark olive-green prisms. However, the complex formula determined

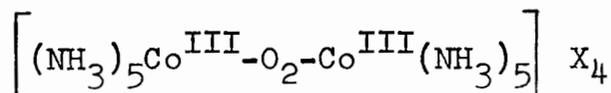
by Gibbs contained two more oxygen atoms than that determined by Frémy, and had the formula $\text{Co}_2\text{O}_4(\text{NH}_3)_{10}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$.

Seven years later in 1883, Maquenna (10) obtained a green sulfate by treating Frémy's crystals with sulfuric acid. He believed this new compound to contain the same one to one ratio of cobalt to oxygen as had been determined by Frémy, which was correct.

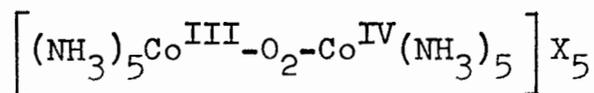
Peroxo Complexes

This new set of dark brown compounds was called the oxycobalt series, while the green complexes were called the anhydro-oxycobalt series by Vortmann (11).

Mono-bridged species. By following Frémy's work, Werner and Mylius (12) prepared several compounds of the oxycobalt series. They found that these could be converted to the green anhydro-oxycobalt series by drawing air over the dark brown oxycobalt crystals for five to six days. In keeping with Werner's theory of coordination compounds, Werner and Mylius proposed the structure of



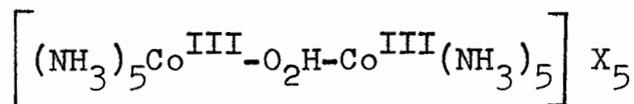
for the oxycobalt series and the structure of



for the anhydro-oxycobalt series.

Wardlaw and Percival (13) have also investigated the

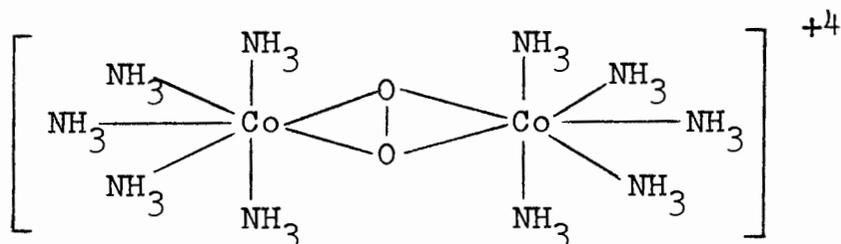
peroxo bridged polynuclear metal ammines and they agree with Werner's configuration. The concept of a cobalt ion in an oxidation state of four is subject to some controversy, and structures involving an O_2H^- such as



have been presented to overcome the idea of a tetrapositive oxidation state for one of the cobalt ions.

Malatesta (14) prepared a series of μ -peroxocobalt (III, IV) decammines and observed magnetic moments of 1.7 Bohr magnetons for these compounds. Malatesta considered this to agree with the dicobalt (III, IV) configuration, leaving no doubt with him that one cobalt atom is in a higher oxidation state than the other. This same conclusion was also supported by Jakob and Ogorzalk (15), Thompson and Wilmarth (16), Gleu and Rehm (17) and Dunitz and Orgel (18).

In 1960, Vlcek (19) suggested that the O_2 bridging group lies with its axis perpendicular to the Co-Co axis. This suggestion was born out in 1963 through crystallographic data collected by Vannerberg (20).

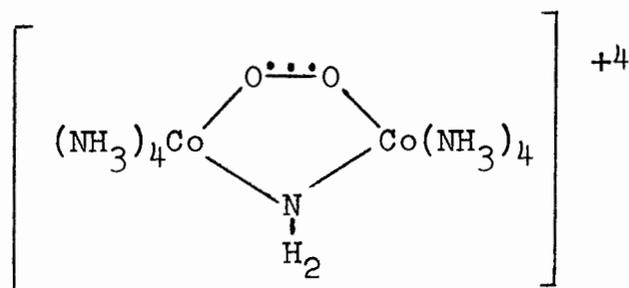


Such a description would establish the equivalence of the cobalt nuclei. Electron resonance studies (21, 22, 23, 24) confirm this conclusion and show that there is appreciable unpaired electron density at the cobalt nuclei in the mono-bridged and the di-bridged species studied. These results indicate that in the green salts the unpaired electron is in an anti-bonding molecular orbital with appreciable density on both cobalt nuclei (23). While this conclusion may depend to some extent on the ligands, it appears to hold for the mono-, di- and tri-bridged amino species of ammonia, ethylenediamine and cyanide (21, 22, 23). Fielding (26, 27) observed the absence of semiconducting properties of the complex compounds which would also seem to be in accordance with the equivalence of the cobalt atoms.

In 1965, Vannerberg (28) published a paper in which he observed that for the brown diamagnetic μ -peroxo-dicobalt tetrathiocyanate, the O-O axis was "skewed" from being perpendicular to the Co-Co axis with a O-O bond distance of 1.65 Å, as compared to a distance of 1.47 Å for the O-O distance as found in H₂O₂ (29), and 1.49 Å as in BaO₂ (30). Vannerberg still found the Co-O-O-Co group in the brown diamagnetic ion to be planar and held that this meant that the paramagnetic cation had a net valence of 7/2 for each cobalt atom, much as he had noted in 1963.

Finally, Schäfer (31) observed for the paramagnetic complex of octaammine- μ -peroxo- μ -amido-cobalt IV cation

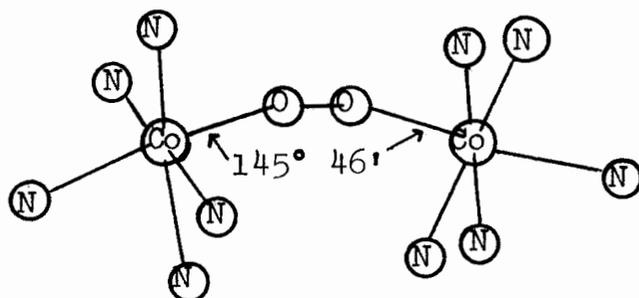
that the two bridging groups were nearly planar with the two cobalt atoms and that the O-O bond length in this paramagnetic ion was that of a typical superoxide of 1.31 Å. This would seem to indicate a structure of



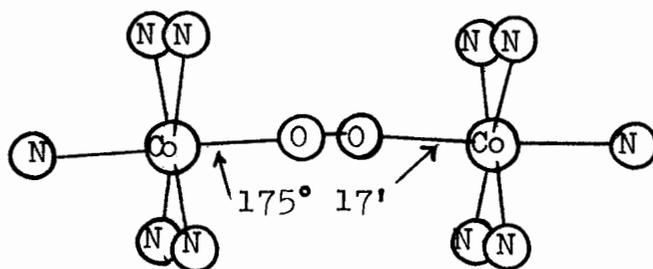
in which the O-O bond is noted as being composed of three electrons, thus forming a shorter bond as found.

After this, Schäfer (31) next considered that if one electron is added to the paramagnetic cation to form the diamagnetic cation, that the O-O bond should lengthen to about that found for the normal peroxide, and that the Co-O-O-Co group should no longer be planar, but should develop a torsion angle about the O-O bond similar to that of 90° as found in H₂O₂. In 1967 Schäfer (31) reported the structure of decammine- μ -peroxo-dicobalt disulfate tetrahydrate. When Schäfer compared the mono-bridged decaammine- μ -peroxo-dicobalt (+4) cation and the decaammine- μ peroxo-dicobalt (+5) cation, the only differences between the two that he found was that in the diamagnetic compound, the O-O bond length had lengthened from 1.31 Å of the paramagnetic compound to 1.47 Å for the true peroxo compound, which is

exactly the same as that found in H_2O_2 and that in the diamagnetic compound there now was a torsional angle of $145^\circ 46'$ versus the $175^\circ 17'$ of the paramagnetic cation.



+4 cation

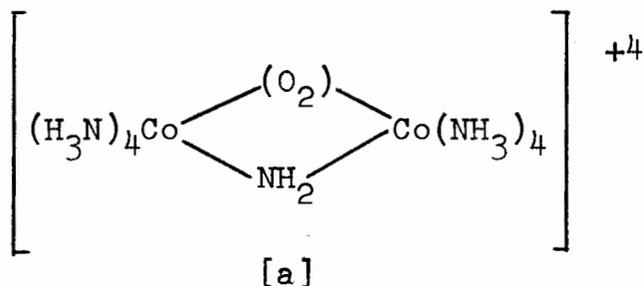


+5 cation

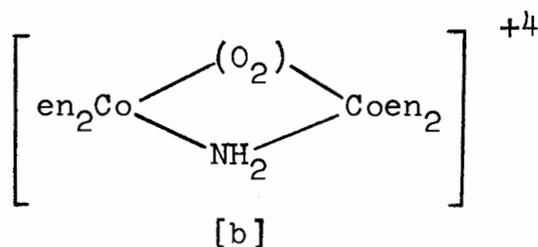
Thus, Schäfer feels that there can be no doubt that in both the paramagnetic green complexes and in the diamagnetic brown complexes the cobalt atoms are in the +3 oxidation state and never in a $+3 \frac{1}{2} \text{ -- } +3 \frac{1}{2}$ or $+3 \text{ -- } +4$ combination of oxidation states.

Di-bridged species. When an ammoniacal solution of

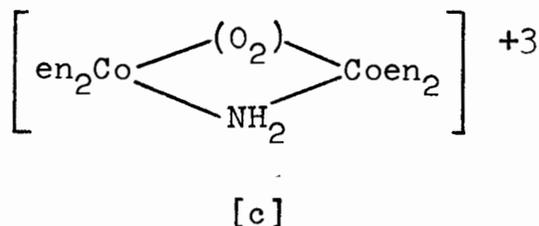
cobalt (II) sulfate is oxidized with air, a red solid is obtained which is a mixture of complex cobalt species (32) from which the green paramagnetic dibridged cation [a]



can be extracted (35, 36). The yield of the paramagnetic complex is low, but may be increased by the use of ozonized air (23). This cation may be reduced in a one-electron step to the diamagnetic complex (34). When treated with ethylenediamine the paramagnetic complex undergoes an ammonia replacement to form [b]

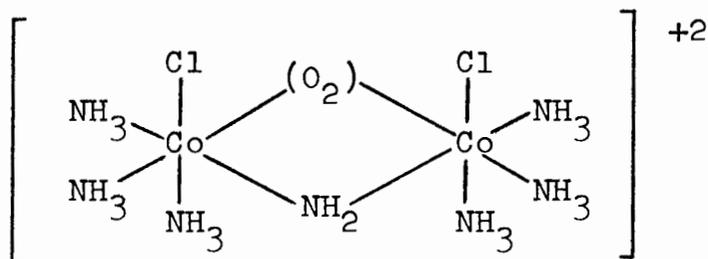


which in the presence of excess base undergoes the one-electron reduction to the diamagnetic analog [c] (37).



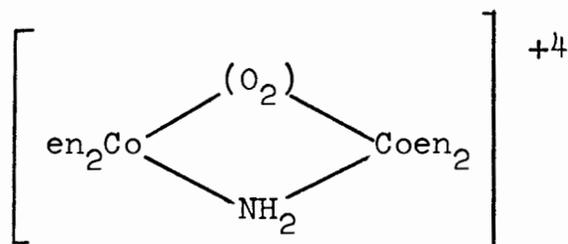
The insoluble chloride of the green paramagnetic cation formulated by Werner to be the symmetrical dichloro species

[d]



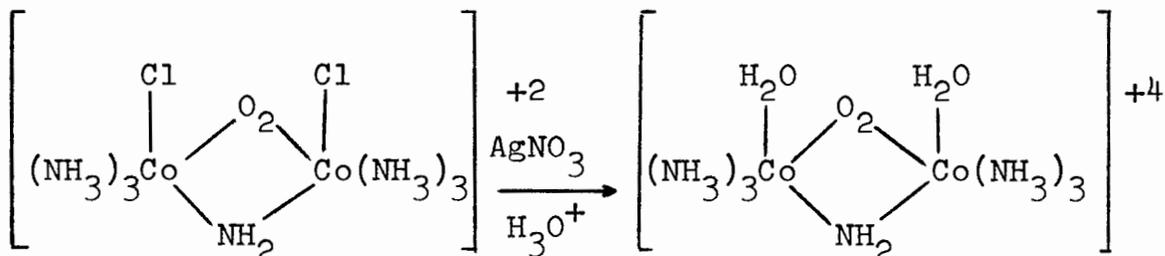
[d]

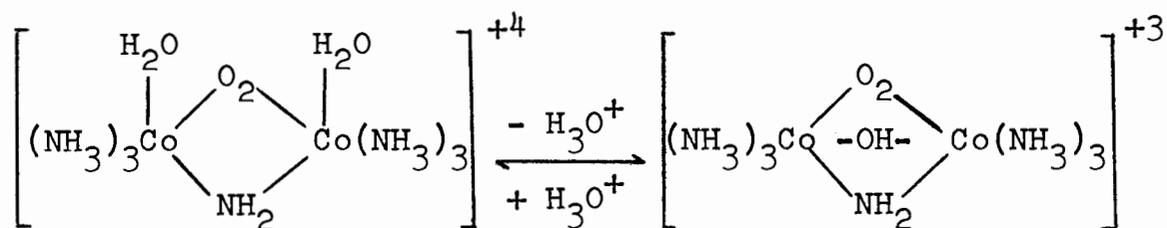
is precipitated by the action of ammonium chloride and hydrochloric acid (36) to [b].



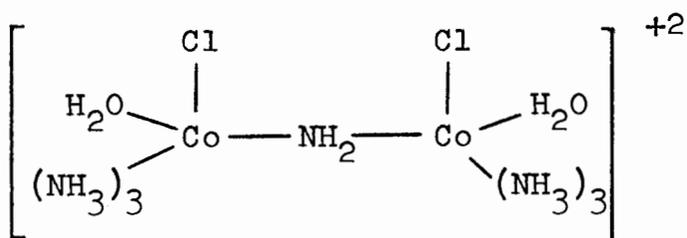
[b]

Tri-bridged species. Treatment of the symmetrical dichlorodibridged cation with acidified silver nitrate solution gives the symmetrical diaquo complex, which appears to be in equilibrium with the tri-bridged species (34).





It may also be prepared from the melanochloride (34).



Statement of Problem

The cobalt-ammonia system has been quite extensively studied (8, 9, 5, 6, 16, 28, 31). Recently, peroxide systems of cobalt and various amino acids have been reported (38, 39, 40, 41). In 1966, Bosnich, Poon and Tobe (42) reported that of the polydentate amines, the first stable peroxide system was one with 1,4,8,11-tetraazacyclotetradecane. The mono-bridged short chain bidentate amines have been studied very little because these peroxo complexes with cobalt are dark colored, relatively unstable, have half-lives on the order of only an hour or so, and have never been crystallized. Hence, no direct chemical analysis or structural techniques such as X-ray analysis has been applied.

In 1959, Warren (43) and Habib (44) reported that in preliminary studies with propylenediamine and ethylenediamine respectively, some type of brown cobalt complex was formed with oxygen in a ratio of $O_2:Co:en = 0.5:1:2$ which can go to form a complex with a 0.5:1:2.5 mole ratio. This work represents a continuing effort to elucidate the nature and some of the properties of the brown oxygen complex of cobaltous ion and ethylenediamine in dilute aqueous solutions.

MATERIALS AND METHODS

Reagents

Cobaltous perchlorate was prepared by the addition of 70% perchloric acid to cobaltous chloride. Both reagents were Mallinckrodt analytical reagent grade. The solution was boiled until copious white fumes evolved. On cooling, crystals of cobaltous perchlorate were obtained which were filtered and washed with alcohol. The cobaltous perchlorate was tested for the presence of chloride by the addition of a solution of silver nitrate to some aqueous cobaltous perchlorate. Since no precipitation of silver chloride was observed, it was assumed the cobaltous perchlorate was essentially chloride free.

Matheson Coleman and Bell 89-100% ethylenediamine was purified by fractional distillation, collecting the fraction boiling in the range of 115 to 117 degrees Centigrade. Six grams of ethylenediamine were diluted to one liter with distilled water to approximate a one-tenth molar concentration.

One-tenth molar ammonium hydroxide was prepared by diluting 6.7 milliliters of 15 molar ammonium hydroxide to one liter with distilled water.

One-tenth molar hydrochloric acid was prepared by diluting 8.3 milliliters of 12 molar hydrochloric acid to one liter with distilled water.

One-tenth molar sodium hydroxide was prepared by diluting 60 milliliters of a filtered solution of saturated sodium hydroxide at 25 degrees Centigrade to one liter.

A saturated solution of ammonium thiocyanate was prepared at 25 degrees Centigrade, filtered and the iron present removed by multiple extractions with Matheson Coleman and Bell 4-methyl-2-pentanone.

Apparatus

All beakers, burets and pipets were either Kimax or Pyrex brands.

Conductivity titrations were performed using a YSI 31 conductivity bridge by Yellow Springs Scientific Instruments and a YSI conductivity cell of cell constant $K = 1.0 \pm 1\%$. All conductivity titrations were performed in a Sargent constant temperature bath maintained at 25.0 ± 0.05 degrees Centigrade.

Potentiometric titrations were performed with a Leeds and Northrup expanded scale pH meter using a glass electrode and a saturated calomel electrode.

Spectrophotometric work was done with a Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer with hydrogen and tungsten lamps. Matched quartz cells manufactured by Beckman Instruments were used for the ultraviolet work and matched pyrex cells were used for the work in the visible range.

Freezing point depressions were observed with a ISI

Beckman thermometer.

Aeration of the solutions was performed by introducing Industrial Air Products purified oxygen into the solution through a sintered glass bubbler.

Electron spin resonance spectra were taken by Mr. Richard Janusz at Washington State University, Pullman, Washington on a Varian instrument.

Magnetic susceptibility measurements were also performed at Washington State University by Mr. Richard Janusz and the author. The equipment was designed and built at Washington State University.

Analytical Procedures

The cobaltous perchlorate solution of one-tenth molar concentration was standardized by the following spectrophotometric method. Ten milliliters of a 0.1 gram per milliliter solution of ethylenediamine-tetra-acetic acid (EDTA), five milliliters of saturated ammonium acetate to buffer the solution at pH 5 to 6, 75 milliliters of water and ten drops of ten percent hydrogen peroxide were added to five milliliter aliquots of cobaltous perchlorate. The solution was boiled for five minutes, after which two more drops of hydrogen peroxide were added. The solution was boiled another twenty-five minutes, cooled and diluted to 500 milliliters in a volumetric flask. The absorbance of the solution was determined at the observed maximum of $\lambda = 540$

millimicrons. The molar absorbtivity of the Co (III) EDTA complex was 312 liter moles⁻¹ centimeters⁻¹ at that wavelength (45). The concentration of the solution was then calculated from the equation

$$A = abc$$

where A = absorbance, a = molar absorbtivity, b = path length in centimeters and c = concentration in moles per liter. The repeatability for this determination was $\pm 0.6\%$.

The one-tenth molar solution of sodium hydroxide was standardized potentiometrically against primary standard potassium hydrogen phthalate. Differential plots were used to determine the end-point of the titration to $\pm 0.1\%$.

The one-tenth molar hydrochloric acid was standardized by potentiometric titration against the standard sodium hydroxide. Differential plots were used to determine the end-point of the titration to $\pm 0.1\%$.

The one-tenth molar solution of ethylenediamine was standardized by potentiometric titration against standard hydrochloric acid. Differential plots were used to determine the end-point of the titration to $\pm 0.1\%$.

The one-tenth molar ammonium hydroxide was standardized by potentiometric titration against standard hydrochloric acid. Differential plots were used to determine the end-point of the titration to $\pm 0.1\%$.

EXPERIMENTAL

Procedures

Spectrophotometric measurements. Various solutions containing mole ratios of ethylenediamine to cobalt ranging from 0.5:1 to 3.5:1 were prepared and oxygenated. The solutions were diluted to a cobalt concentration of about 0.0002 molar. The spectra were then taken using one centimeter quartz cells over the range in wavelength from 200 to 330 millimicrons and pyrex one centimeter cells over the range in wavelength from 330 to 650 millimicrons. The absorbances of the solutions were taken at the observed maximum of 355 millimicrons. In some solutions hydroxide ion was added after oxygenation but before dilution. In other solutions ammonium hydroxide was added before oxygenation. The reproducibility was $\pm 2\%$.

Potentiometric titrations. The pH meter was standardized with a Leeds and Northrup standard buffer of pH 6.86 at 25 degrees Centigrade. Oxygen was bubbled continuously through the solution of water and cobaltous ion and the ethylenediamine was added in one milliliter increments. After each addition, some time was allowed for the pH to reach a constant value. The reproducibility was $\pm 1.5\%$.

Conductometric titrations. A titration beaker containing a known volume of water and cobaltous ion was placed in a

constant temperature bath at 25 degrees Centigrade and allowed to come to equilibrium. The solution was then oxygenated and an increment of ethylenediamine added and allowed to continue oxygenating for one minute. At the end of this time, the oxygenation was stopped, the electrodes placed in the solution and the conductance read. The electrodes were then removed from the solution, placed in distilled water, the oxygenation started again and the next increment added. The same procedure was used for the conductometric titration of a 2:1 mole ratio solution of ethylenediamine to cobalt titrated with increments of sodium hydroxide or other reagents. The conductance was corrected to account for the increase in the volume of the solution after addition of titrant by use of the formula

$$\underline{C} = \frac{C_o (V_o + V_1)}{V_o}$$

where \underline{C} = corrected conductance, C_o = observed conductance, V_o = initial solution volume and V_1 = volume of titrant added. The reproducibility was $\pm 1\%$.

Extraction of cobalt. Uncomplexed cobalt (II) was extracted from solutions of complex containing ethylenediamine to cobalt mole ratios ranging from 0.5:1 to 2.5:1 by the following method. The solution was prepared by slow addition of ethylenediamine to a solution of cobaltous ion

with continuous oxygenation. The oxygen was bubbled for five minutes after the last increment was added. During the ethylenediamine addition and the additional five minute wait, the solution was kept in a zero degree Centigrade ice bath to cool the reaction mixture. To this cold solution was added 30 milliliters of cold saturated ammonium thiocyanate and 100 milliliters of cold 4-methyl-2-pentanone. The solutions were shaken for one minute in a separatory funnel and the lower aqueous layer drained off. To the top organic layer which was blue-colored and presumably containing thiocyanate complexes of Co (II) was added 20 milliliters of 2.5 molar hydrochloric acid and it was shaken for three minutes. The acid phase was drained off. The organic phase was repeatedly extracted until it was clear and contained no more blue color. The acid phases were all combined and neutralized with one molar sodium hydroxide to a pH of 6.5. The cobalt content was then analyzed by the procedure given for the standardization of the cobaltous perchlorate in the analytical procedures.

Freezing point determination. The freezing point depression of a solution of oxygenated ethylenediamine and cobalt of mole ratio 2:1 was determined by placing the solution in a freezing point tube, surrounding the freezing point tube with an air jacket which was in a cold bath of crushed ice and 40% ethanol. A calibrated Beckman thermometer was placed in the freezing point tube and the solution

stirred with a ring type stirrer. Readings were taken at 30 second intervals until the solution showed a minimum temperature followed by a maximum temperature, after which the readings were taken for another five minutes. The readings were plotted versus time and the plot extrapolated back to obtain the "true" freezing point. The reproducibility was $\pm 0.1\%$.

Electron spin resonance spectra. A 2:1 mole ratio of ethylenediamine to cobalt solution was made with continuous oxygenation. The solution was placed in a sample holder tube and placed in the magnetic field of the detector. The magnetic field was turned on and the frequency of the oscillating magnetic field varied over the range of the scan. It should be pointed out that due to various delays, the solution was left standing for approximately 45 minutes after the formation of the complex before the spectra were obtained.

Magnetic susceptibility measurements. The Gouy balance was calibrated by placing a one molar solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a sample container, weighing the sample and container, applying a magnetic field of 10,000 gauss, and weighing them again. The solution of the complex was made up in a 2:1 ethylenediamine to cobalt mole ratio, placed in the sample holder, weighed with no magnetic field and weighed again in the magnetic field.

Precipitation of complex. Twenty milliliters of 1.7 molar cobalt perchlorate, 2.3 milliliters of 15 molar ammonium hydroxide and 4.08 grams of 100% ethylenediamine were mixed together and oxygenated for two hours at ten degrees Centigrade. The crystals were filtered out by vacuum filtration and washed three times with cold distilled water. Air was sucked through for five minutes after which the crystals were transferred to a vacuum dessicator and stored for 12 hours at a pressure of two millimeters of mercury. The photometric spectrum of the solution from which the crystals were obtained was taken. Some of the crystals were dissolved in water and the spectrum of this solution also taken.

Attempts were made at precipitation of the ethylenediamine-cobalt-oxygen complex with no ammonia present by adding acetone, ethanol and other organic solvents to a concentrated solution of the complex, and by lowering the temperature to zero degrees Centigrade.

Oxidation studies. Solutions with an ethylenediamine to cobalt ratio of 2:1 were prepared and oxygenated. To these solutions were added various oxidants such as Br_2 , Cl_2 , sodium peroxydisulfate, potassium bromate and oxygen with a slight amount of ozone in it.

RESULTS

During the oxidation of the cobalt solution with molecular oxygen the color of the solution was observed to change from light pink to a deep red-brown.

The spectra of the pink cobalt (II) and of the dark red-brown species are noted in Figure 1. A maximum absorbance is observed for the pink solution at $\lambda = 505$ millimicrons, while the maximum absorbance for the brown complex is at 355 millimicrons. When the absorbance (355 millimicrons) of a series of solutions with varying ethylenediamine to cobalt mole ratios (0.5:1 to 3.5:1) was plotted versus mole ratio, three things were observed: (A) a linear increase in absorbance up to a mole ratio of 2.0:1; (B) a change in the slope of the line between 2.0 and 2.5; and (C) a slope of approximately zero for any mole ratio greater than 2.5:1, as shown in Figures 2 and 3. When sodium hydroxide was added to a 2:1 mole ratio solution of ethylenediamine to cobalt (Figures 2 and 4), the absorbance increased up to the addition of 0.5 moles of sodium hydroxide per mole of cobalt. The increase in absorbance was also true for a 0.5 mole ratio addition of ammonium hydroxide to the 2:1 complex. When hydrochloric acid was added to the solutions of sodium hydroxide or ammonium hydroxide, the absorbance was observed to return to the original absorbance value of the 2:1 complex of ethylenediamine and cobalt. Figure 5 shows a Beer's law

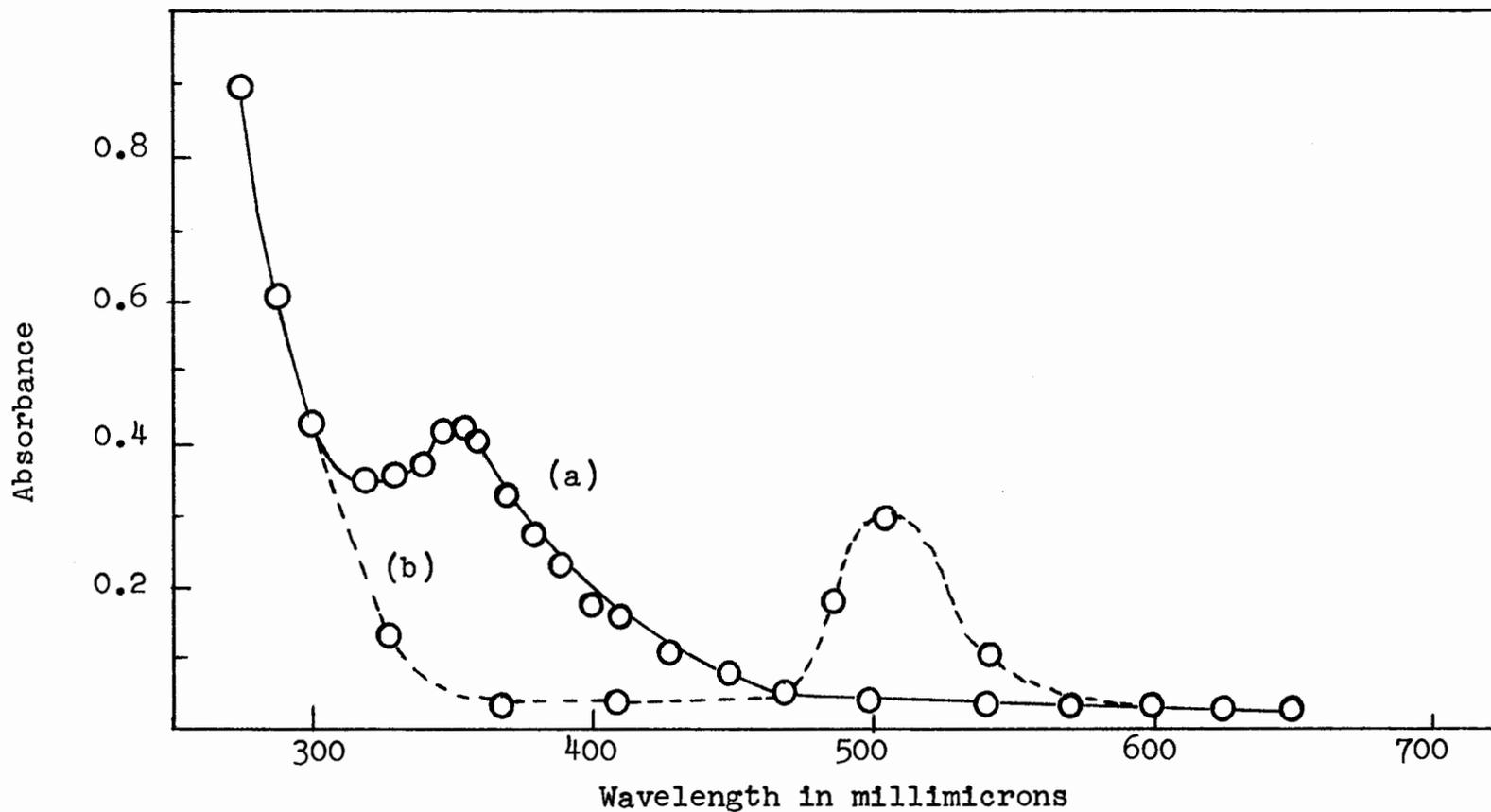


FIGURE 1

Absorption spectra of (a) μ -peroxo cobalt 2:1 mole ratio of ethylenediamine to cobalt, $[\text{Co}^{\text{III}}] = 0.0002$ moles/liter and (b) cobalt (II) ion, $[\text{Co}^{\text{II}}] = 0.005$ moles/liter.

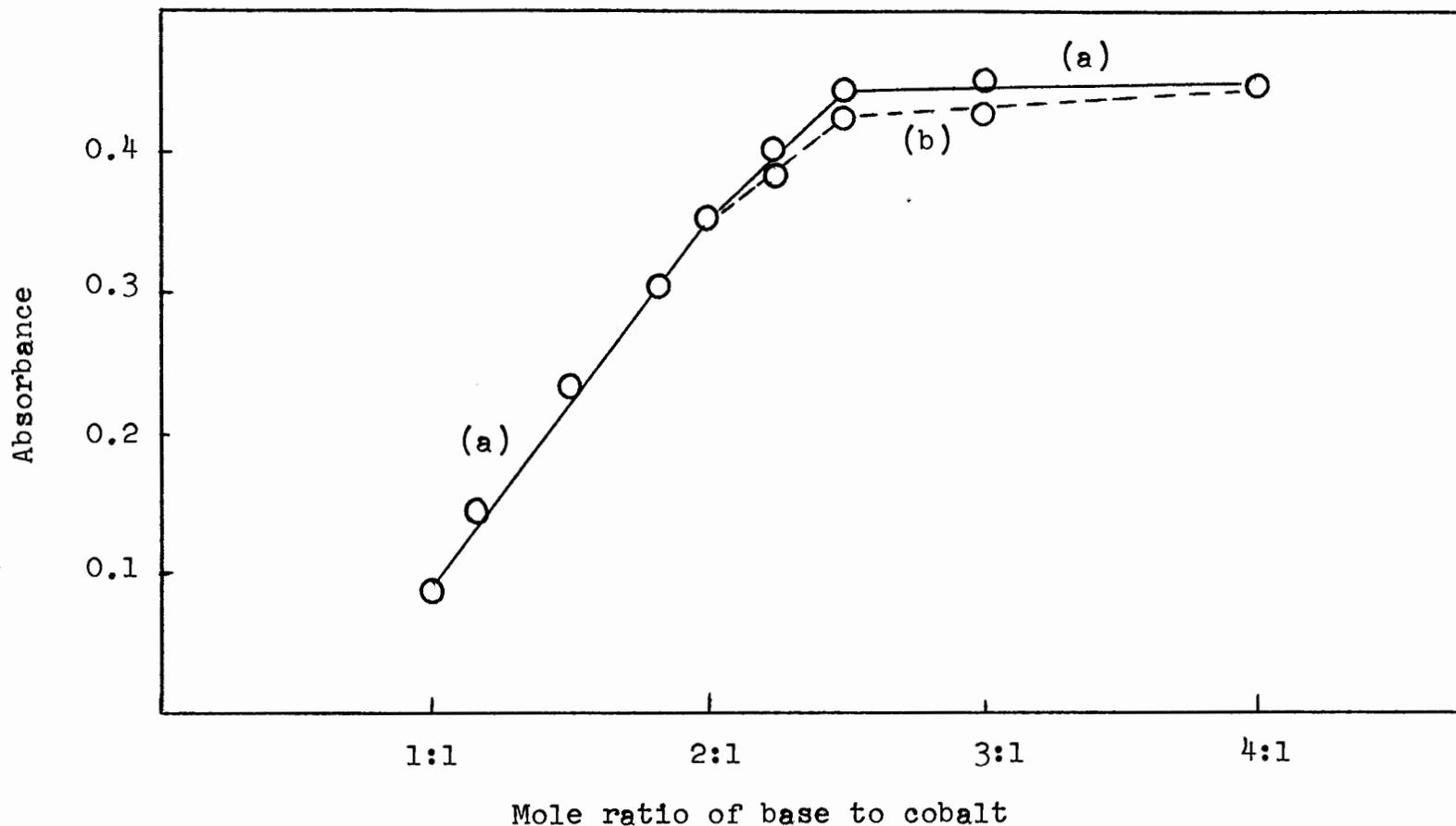


FIGURE 2

Absorbance spectra of various mole ratios of ethylenediamine to cobalt at $\lambda = 355$. In (a) the base is ethylenediamine; in (b) the base is OH^- above a 2:1 ethylenediamine to cobalt mole ratio. $[\text{Co}] = 0.0002$ moles/liter.

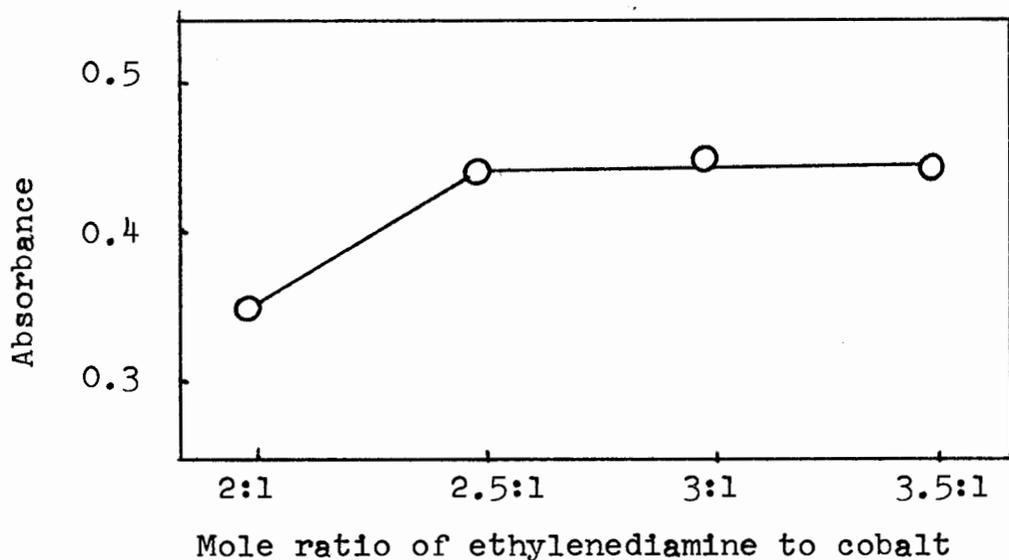
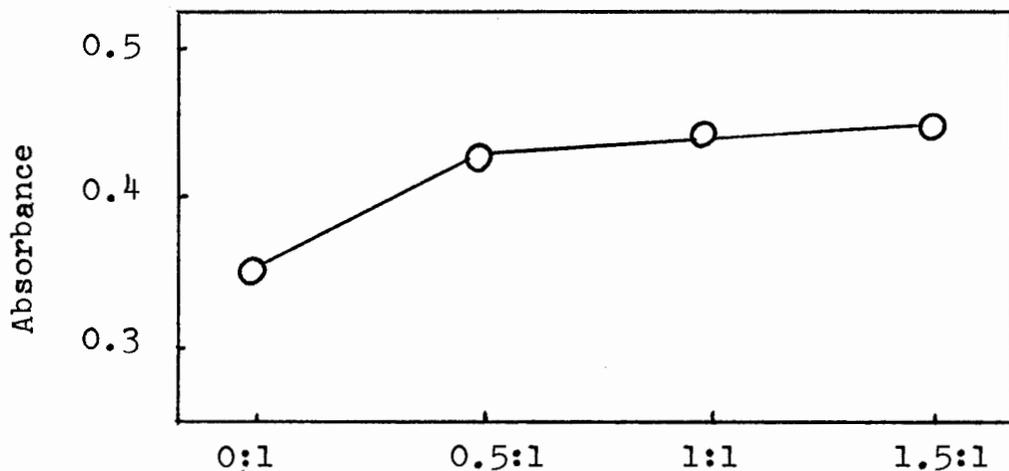


FIGURE 3

Absorbance of various ethylenediamine to cobalt mole ratios above 2:1 at $\lambda = 355$.

[Co] = 0.0002 moles/liter



Mole ratio of hydroxide to cobalt added to a 2:1 mole ratio of ethylenediamine to cobalt

FIGURE 4

Absorbance of a 2:1 mole ratio of ethylenediamine to cobalt with added hydroxide at $\lambda = 355$.

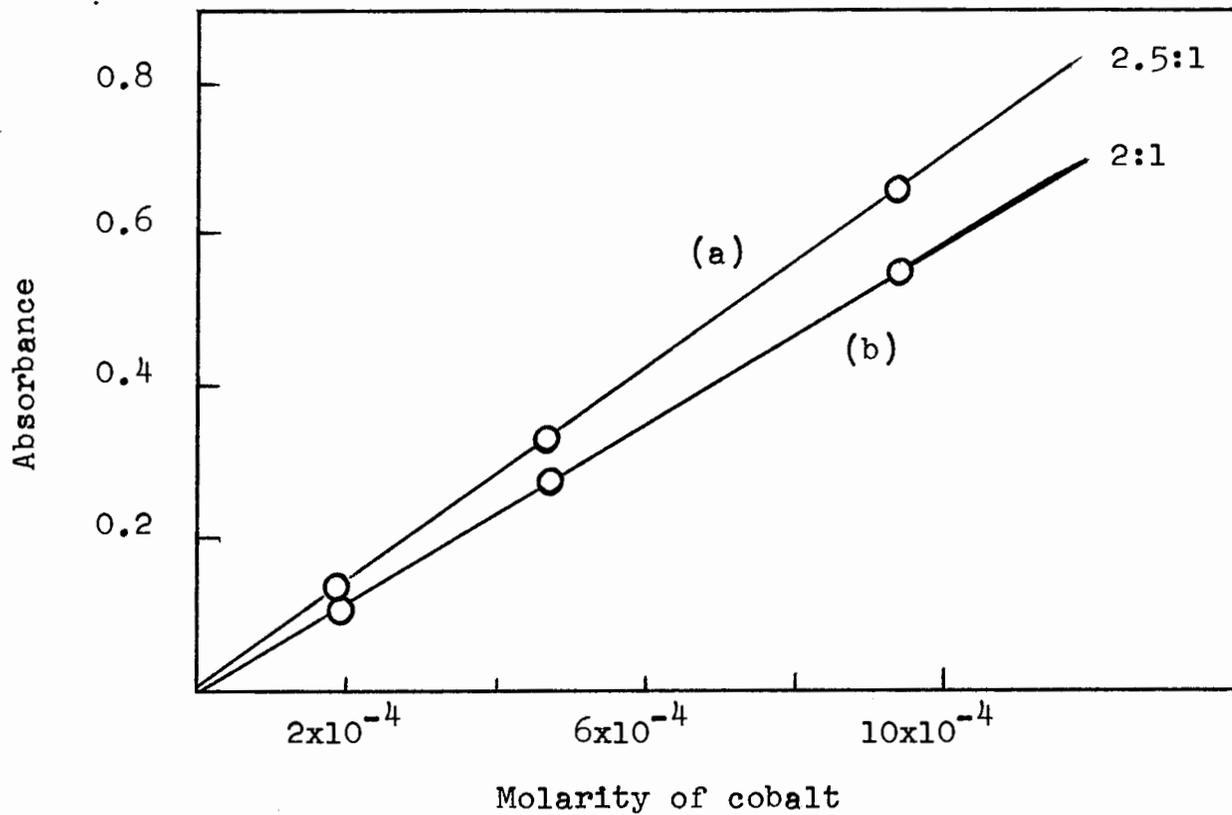


FIGURE 5

Beer's Law plot of (a) 2.5:1 mole ratio and (b) 2:1 mole ratio of ethylenediamine to cobalt. $\lambda = 355$ millimicrons.

plot of the 2:1 and 2.5:1 mole ratio complexes.

When ethylenediamine, cobalt and ammonium hydroxide were mixed together in a 2:1:1 mole ratio and then oxygenated, a brown solution was formed which showed no change in absorbance with the addition of excess hydroxide ion.

Figure 6 shows the effect on pH of titrating 0.1 molar ethylenediamine into the cobalt solution. It was noted that up to an ethylenediamine to cobalt mole ratio of 2:1 the pH remained fairly constant between 6.5 and 7.0; then the pH increased quite quickly, with an inflection at a mole ratio of 2.5:1. The titration curve beyond a mole ratio of 2.0:1 was very similar to an ordinary weak acid-base titration curve. Because the complex was slightly more acidic than water, it would be expected to undergo the weak acid-base neutralization in preference to water.

When a solution of mole ratios of ethylenediamine to cobalt to ammonia of 2.0:1:5.0 was made, oxidized and back titrated with hydrochloric acid, an amount of base equivalent to $\frac{4}{5}$ of the amount of ammonia put in was neutralized as observed in Figure 7. This indicated a complex left in solution with a mole ratio of ethylenediamine to cobalt to ammonia of 2:1:1.

The conductometric titration is noted in Figure 8. The conductance of the solution decreased as ethylenediamine was added up to a mole ratio of 2.5:1, after which the conductance increased rapidly. When sodium hydroxide was

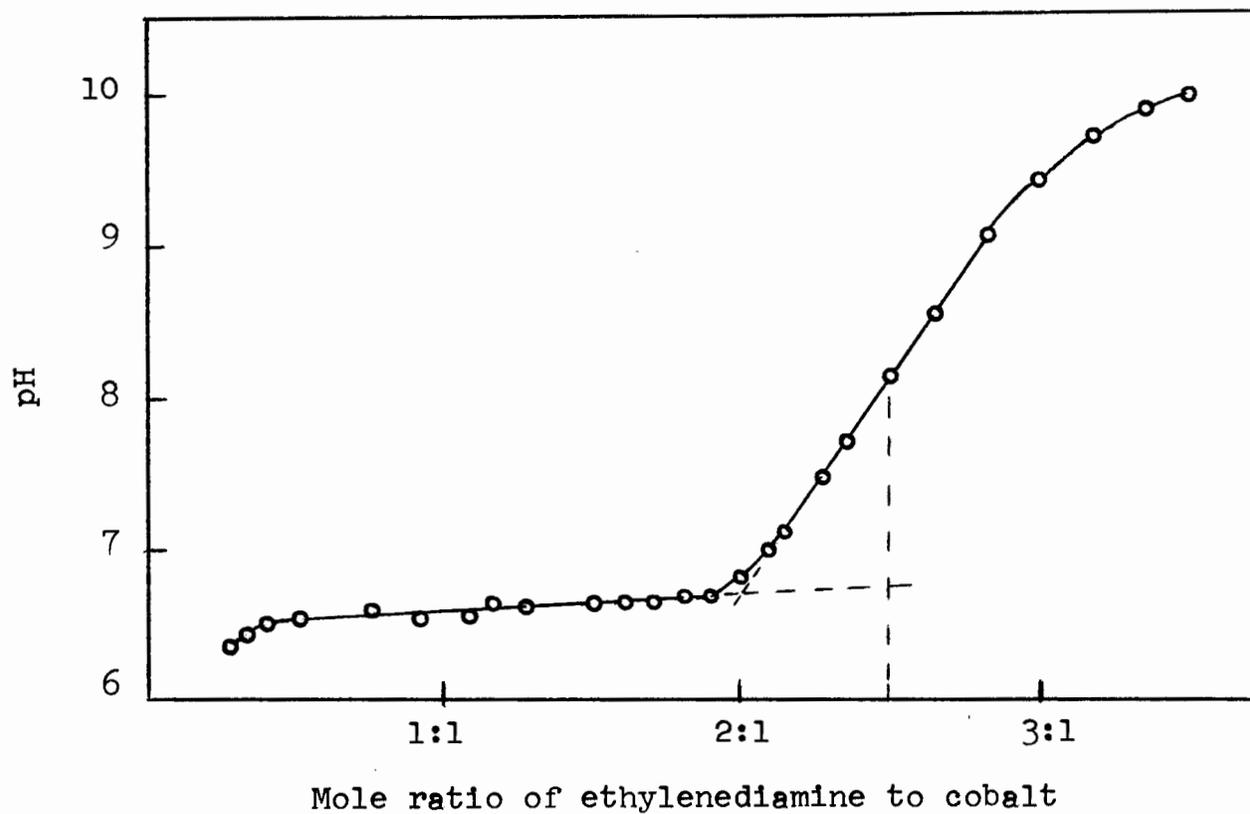


FIGURE 6

Potentiometric titration of cobalt (II) solution with ethylenediamine. $[\text{Co}] = 0.018$ moles/liter.

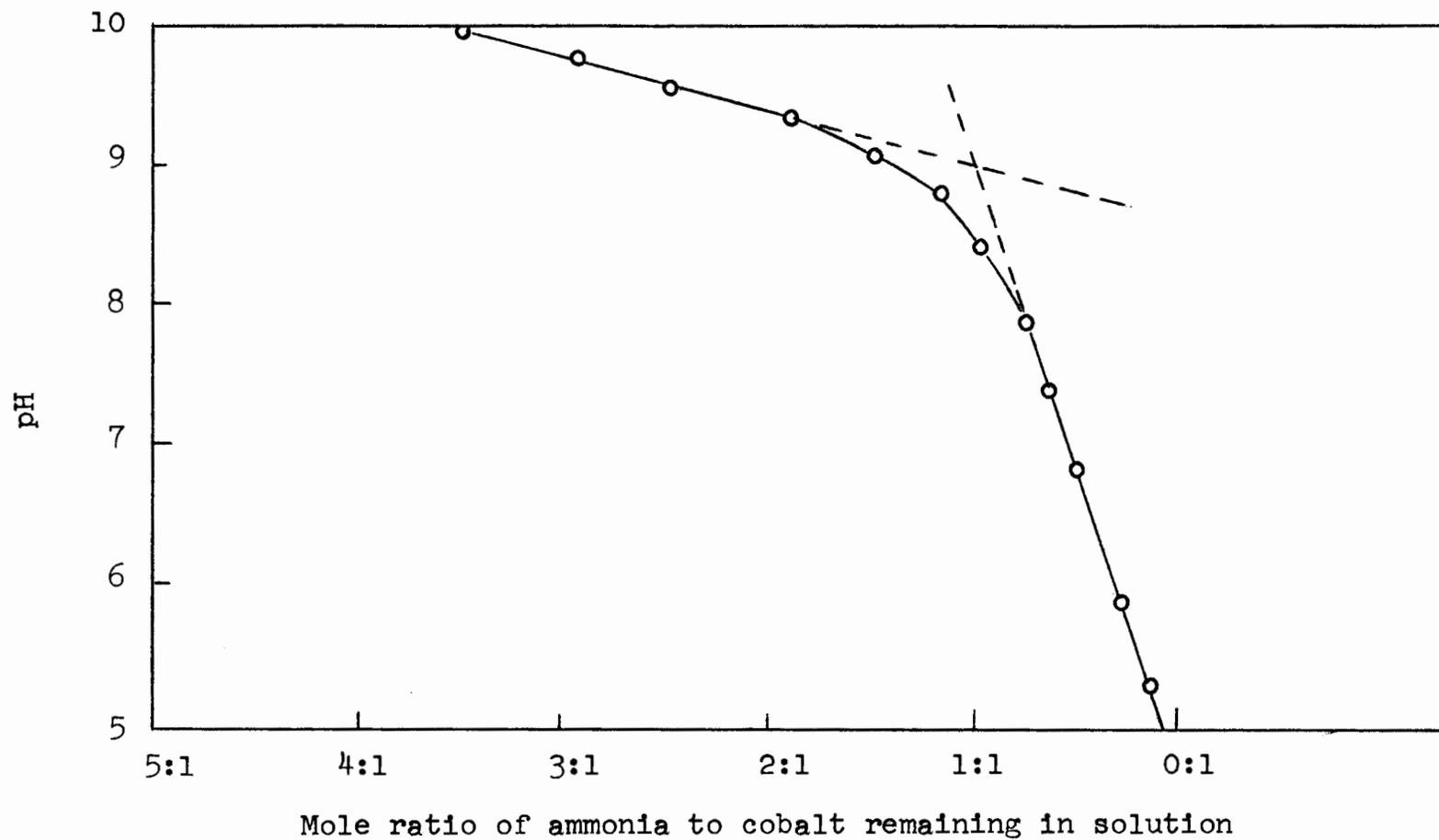


FIGURE 7

Potentiometric titration of ammonia-ethylenediamine-cobalt solution with hydrochloric acid. $[Co] = 0.018$ moles/liter.

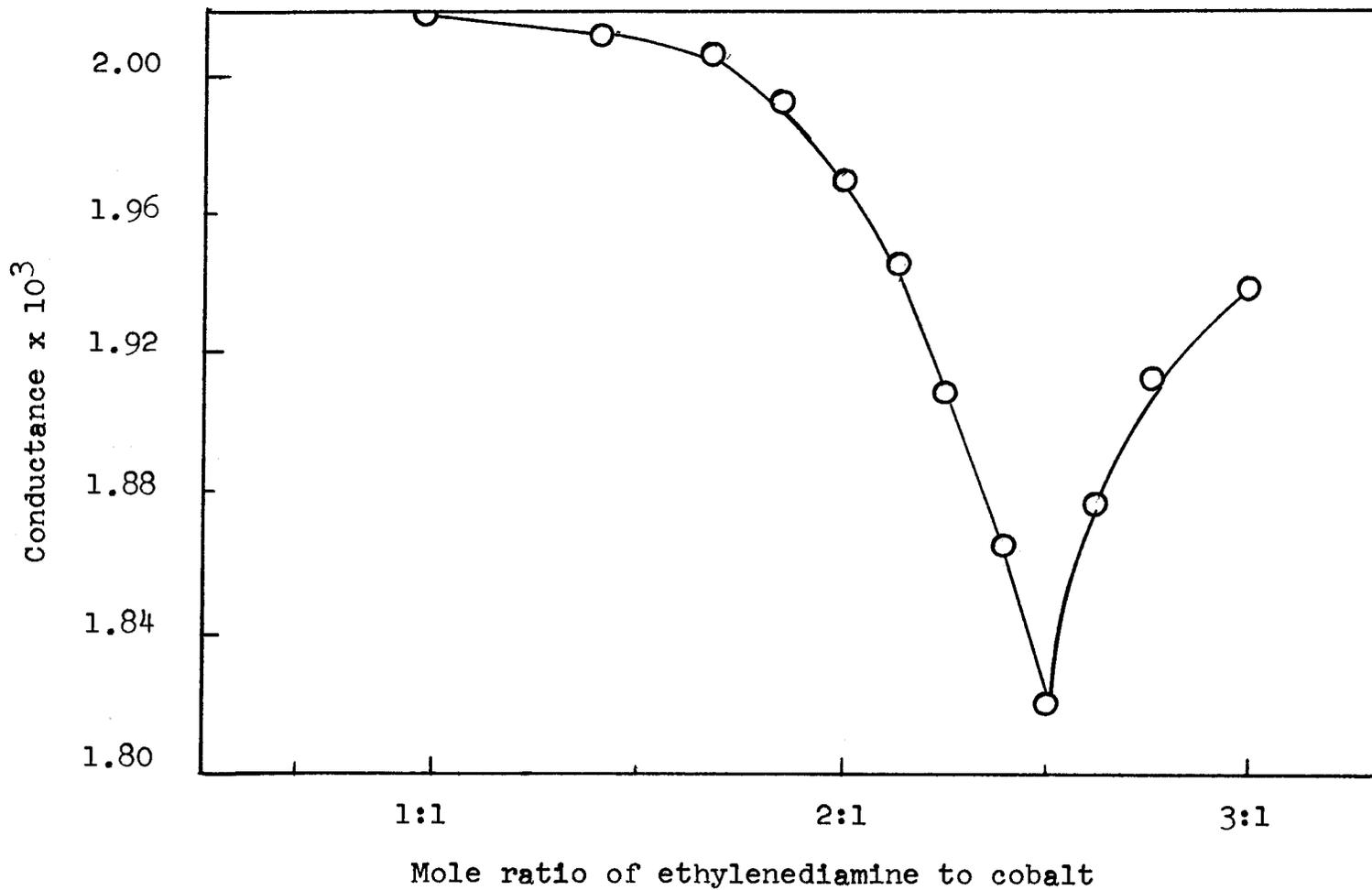


FIGURE 8

Conductometric titration of ethylenediamine with cobalt.
[Co] = 0.009 moles/liter.

titrated conductometrically into a solution of ethylenediamine to cobalt mole ratio of 2:1, a similar decrease in conductance was noted up to a hydroxide to cobalt mole ratio of 0.5:1, after which the conductance increased rapidly. This decrease in conductance seemed to indicate that as excess ethylenediamine or hydroxide was added, either there was a decrease in the number of ions in solution or for some reason the ions present became less mobile.

The relative amount of cobalt extracted from the various mole ratio solutions of ethylenediamine to cobalt is shown in Figure 9. The amount of cobalt left in the solution was calculated by subtracting the total number of moles of Co (II) extracted from the total moles of Co (II) placed in the reaction flask, and it was noted that the mole ratio of the unextracted cobalt to the amount of ethylenediamine added to the solution remained at a constant value of 1:2. Repeated extractions yielded more and more cobalt, indicating that the complex was slowly decomposing with time. Thus only the first extraction in all cases was used in the calculations.

A freezing point depression in water of 0.18 degrees Centigrade was obtained with a solution of complex with a molar concentration of cobalt of 0.031 moles per liter and a mole ratio of ethylenediamine to cobalt of 2:1. The freezing point depression indicated that each molecule of complex ionized into 5.5 particles. This suggested that either the

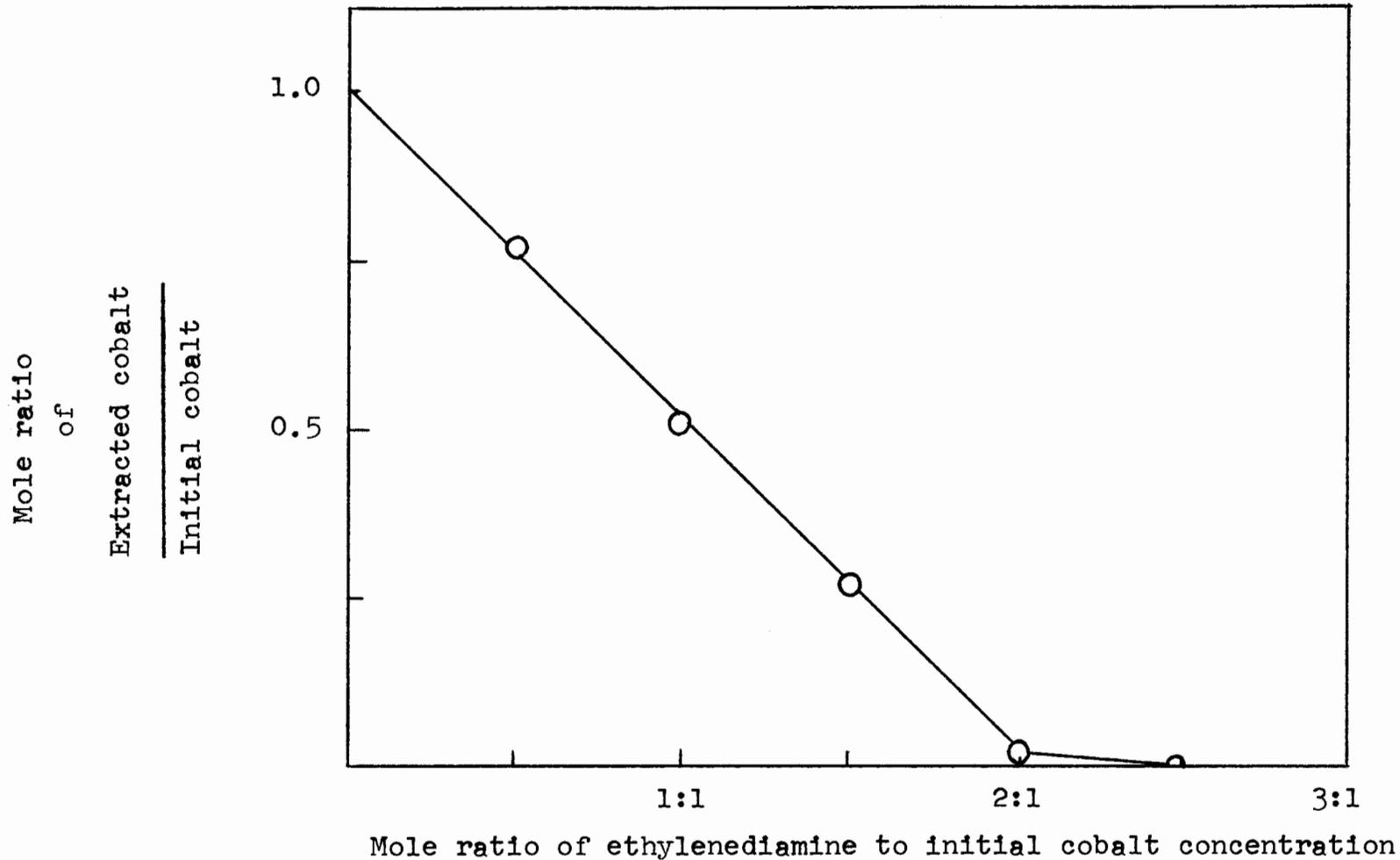


FIGURE 9

Ratios of extractable cobalt (II) from complex of various mole ratios of ethylenediamine to cobalt. $[Co(II)] = 0.009$ moles/l.

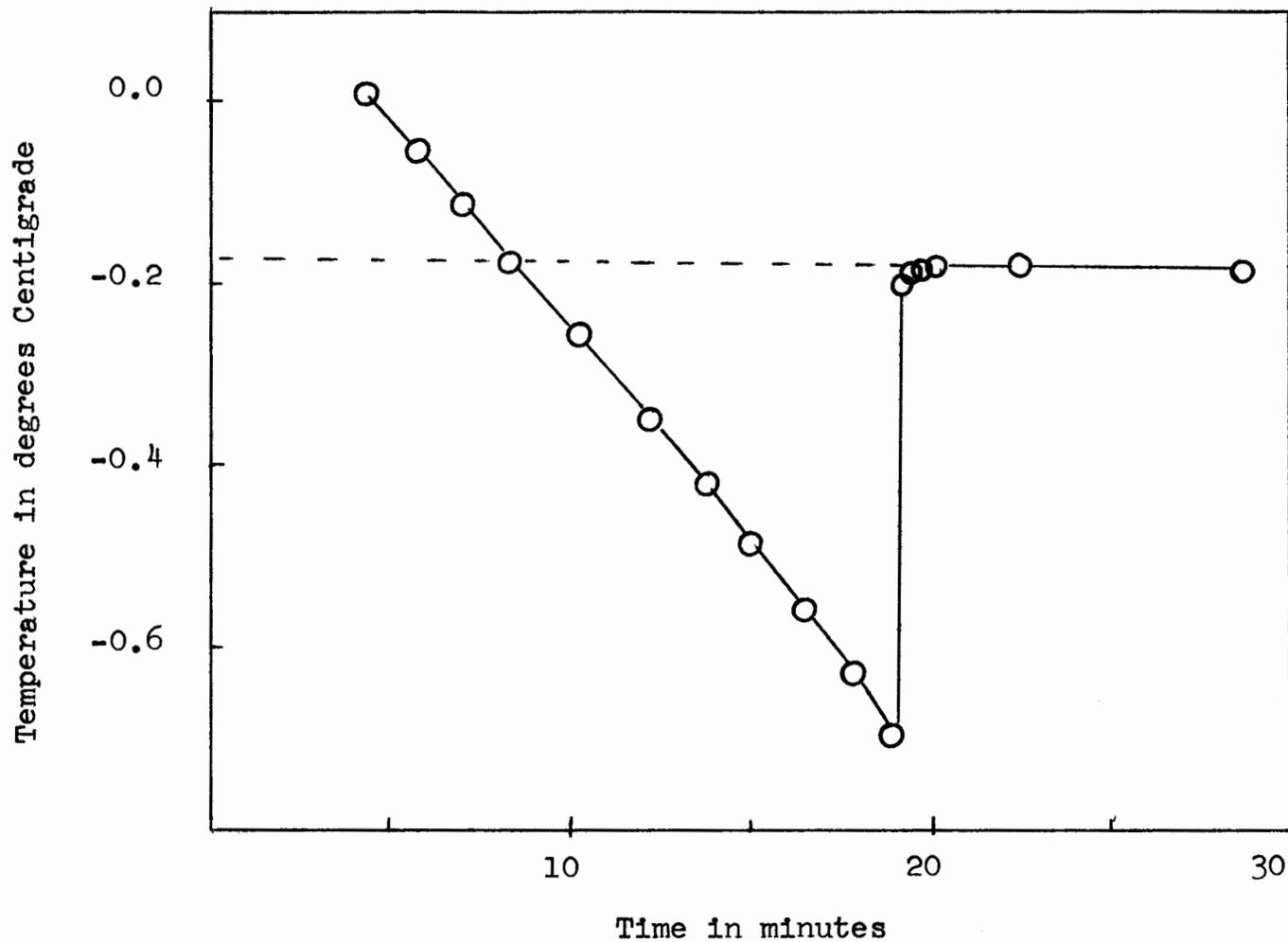


FIGURE 10

Freezing point depression of ethylenediamine cobalt complex in 2:1 mole ratio. $[\text{Co}] = 0.03$ moles/liter.

complex was not completely formed or that decomposition had already started. In terms of the stability of the complex, the latter alternative seemed plausible.

A signal was obtained when a 0.015 molar complex was scanned for electron spin resonance. However, although this seemed to indicate that the complex was paramagnetic, it should be kept in mind that the compound was allowed to stand for 45 minutes before the scan was run and also that at the time the scan was run the instrument was set to detect 10^{-5} molar manganese. Thus, although the signal may mean that the complex was paramagnetic, the presence of a signal was not conclusive proof for paramagnetism of the species of interest.

When a fresh sample was placed in the Gouy balance and the magnetic field turned on, there was a very definite thrust away from the magnetic field with the result of an observed 0.7% loss in weight for a 0.033 molar solution in cobalt.

Crystallization of the complex by itself and in a pure form was not possible due to the instability and rather short half-life of the complex. Saturated solutions formed by oxygenation of 90% ethylenediamine with solid cobalt (II) sulfate put into suspension by constant agitation turned dark brown. All the cobalt sulfate finally went into solution, but no crystals were obtained by either cooling or adding organic solvents or a combination of these.

A solution of mole ratio of ethylenediamine to cobalt to ammonia of 2:1:1 was formed and the photometric spectrum obtained was observed to be the same as the 2:1 spectrum with no ammonia present. After three days, the spectrum was still the same as the spectrum of the 2:1 mole ratio of ethylenediamine to cobalt solution. On standing three days, the 2:1 mole ratio of ethylenediamine to cobalt solution turned red and showed a second absorption peak at 505 millimicrons. The lack of the second peak for the ammonia containing complex indicated that the complex was stable. This ammonia complex crystallized readily into very fine dark brown crystals. The crystals were relatively stable to heat up to 200° Centigrade as indicated by no weight loss, but if heated excessively in an open flame they ignited and burned very quickly with an intense blue-white hot flame.

DISCUSSION

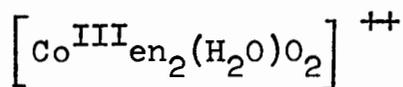
As ethylenediamine was added to an oxygenated cobalt (II) solution a number of things were observed. Figure 2 indicated that as increasing amounts of ethylenediamine were added, a single species of complex was present in increasing amount. During the ethylenediamine addition it was noted in Figure 6 that the pH remained fairly constant, indicating that as ethylenediamine was added to the cobalt (II) solution, the ethylenediamine was not free in the solution to act as a base, but chelated the cobalt immediately. The decrease in conductance at the same time indicated that as chelation was taking place, either the number of ions in solution was reduced or the mobility of the ions was reduced.

$$[\text{Co}] : [\text{en}] = \frac{[\text{Co}_{\text{initial}} - \text{Co}_{\text{extracted}}]}{[\text{Co}_{\text{initial}}]} : [\text{en}]$$

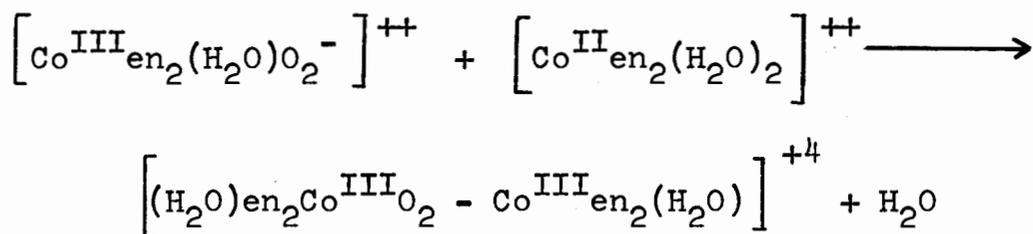
(en = ethylenediamine)

Calculations based on Figure 9 and the above equation showed that at any mole ratio of ethylenediamine to cobalt, all the ethylenediamine was chelated to available cobalt in a 2:1 ratio until all the cobalt in solution was chelated. The net result of all the data was the conclusion that some type of complex was being formed with ethylenediamine and cobalt in a mole ratio of 2:1.

Habib (44) showed that as long as uncomplexed cobalt was present, oxygen was absorbed in an oxygen to ethylenediamine mole ratio of 0.25:1. Grieb (47) observed that polarographic waves of aerated solutions of cobaltous chloride in ethylenediamine from which excess oxygen had been removed by a stream of nitrogen, showed that the cobalt (II) was oxidized to cobalt (III), and that the peroxide group formed was attached to the cobalt ion. Martell and Calvin (48) state that the reduction of oxygen goes through the peroxide. The step may involve the donation of an electron by the cobalt (II) ion to the oxygen molecule to form an unstable intermediate in which an O_2^- is attached to the cobalt (III) ion.



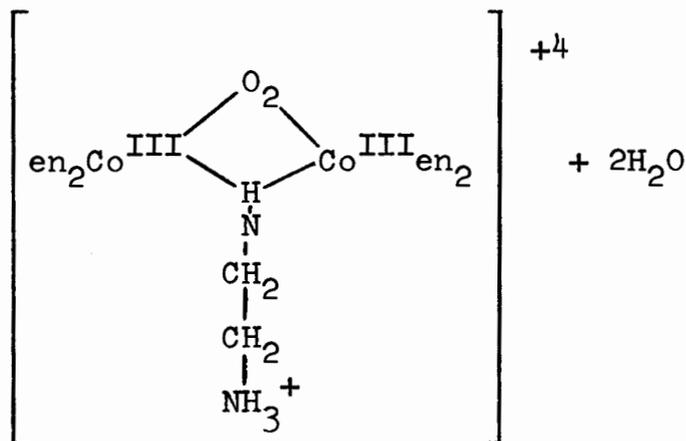
This ion may then oxidize another cobalt (II) ion, and the superoxide O_2^- would simultaneously be reduced to the peroxide $O_2^{=}$, thus forming the compound tetrakis(ethylenediamine)- μ -peroxodicobalt(III) ion proposed by Grieb.



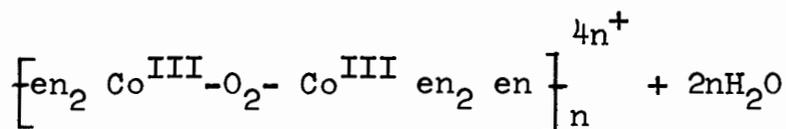
The compound proposed by Grieb was in agreement with all the data given, as well as the freezing point depression which showed five ions in solution per molecule of complex. The paramagnetic results obtained from the Gouy balance would also be explained by the above structure. However, these experimental observations are in contradiction to a statement by Schäffer in which he states that ethylenediamine and cobalt upon air oxidation in a glass system gave a mononuclear cobalt (III) species rather than a peroxo compound, but that the μ -peroxo binuclear species was formed in paraffin-lined containers only (46).

As the mole ratio of ethylenediamine to cobalt is increased from 2:1 to 2.5:1 a number of changes were noted. The pH titration took on the form of an acid-base titration and showed a sharp increase in pH with an inflection point at a mole ratio of 2.5:1 of ethylenediamine to cobalt. The slope of the graph of the spectrophotometric absorbance changed as the solution increased in absorbance. Also the conductance of the solution decreased, indicating that either the number of ions in solution had decreased or else that the mobility of the complex had shown a remarkable decrease. The additional complexing with a half mole of ethylenediamine could be explained in one of three ways.

1. Imino bridging between the two cobalt atoms forming a di-bridged species.

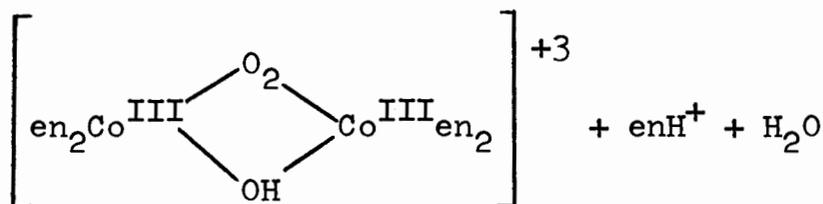


2. Ethylenediamine bridging in which the ethylenediamine bridged two μ -peroxodicobalt (III) ions.

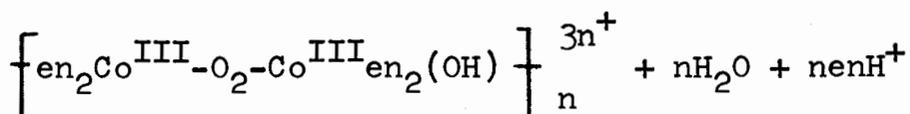


3. Olation with the amine acting as a simple base.

If the aquo groups were coordinated to the two cobalt nuclei in cis positions, internal olation was expected.



If the aquo groups were coordinated to two cobalt nuclei in a trans position, polymeric olation was expected.



When a 0.5:1 mole ratio of sodium hydroxide to cobalt was added to a 2:1 mole ratio complex of ethylenediamine to cobalt, the results observed both conductometrically and photometrically were identical to the results observed when excess ethylenediamine was added to the 2:1 complex. Because the reaction of hydroxide ion was identical to that of ethylenediamine, the imino bridging or the ethylenediamine bridging in which the ethylenediamine forms nitrogen to cobalt bonds were discredited.

Assuming that some type of olation reaction had to be taking place, the cis complex or the trans complex ion could possibly result. However, the cis olation reaction would yield an increase of one ion in the total number of ions per complex molecule. The size would not change appreciably and therefore, the mobility of the ions should not change very much. Thus the conductometric behavior could not be explained by the cis olation product. The trans olation reaction would show no increase in the total number of ions. However, the size and therefore the mobility of the complex cobalt ion changed due to the condensation of two or more complex ions into one large ion. Thus all the data would tend to support the concept of trans olation.

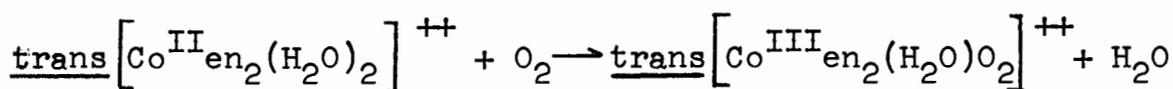
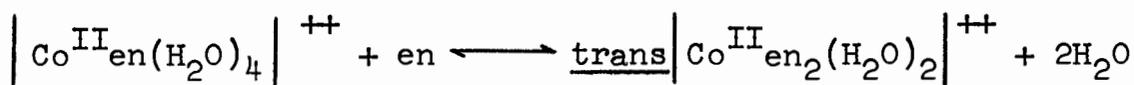
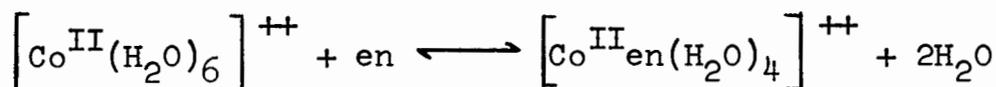
The olation reaction was dependent on the presence of a water molecule at both ends of the complex ion. Replacement of the water in the coordination sphere of the cobalt nuclei should form a complex unable to undergo a reaction

with a base. The use of ammonia as the base added to the 2:1 mole ratio complex of ethylenediamine to cobalt, resulted in the same data as the use of sodium hydroxide.

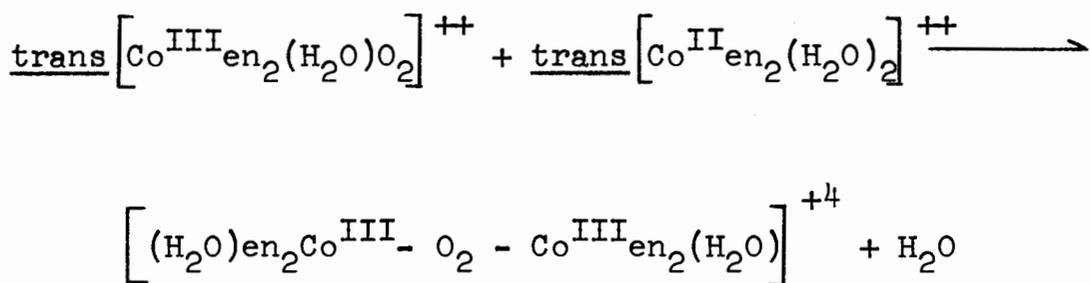
After the addition of excess base to the 2:1 mole ratio complex of ethylenediamine to cobalt, hydrochloric acid was added and the absorbance returned to the initial absorbance of the complex before the base was added. This reversibility held for use of ammonia, sodium hydroxide and ethylenediamine as the base. The apparent indication was in support of no amine incorporation into the complex, and reversibility of olation. It also indicated that the aquo groups were not very labile. When ammonia was added before oxygenation, a complex was formed in a 2:1:1 mole ratio of ethylenediamine to cobalt to ammonia. This complex was stable to decomposition and showed no change conductometrically or photometrically with the addition of excess base. When titrated with hydrochloric acid, the pH dropped rapidly indicating that there was no free base in solution. The results all indicated that the aquo positions had been substituted with ammonia and the olation reaction was no longer possible.

CONCLUSION

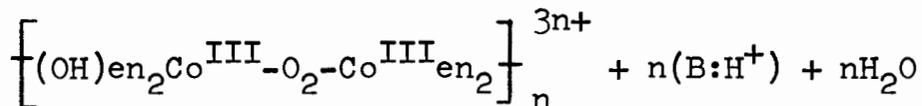
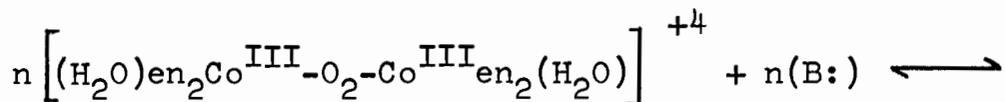
The reaction of ethylenediamine and cobalt (II) with oxygen was postulated as follows:



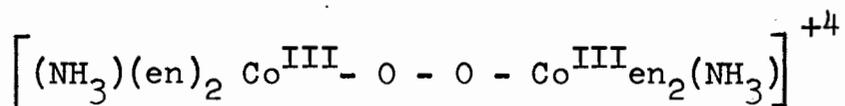
The unstable superoxide then reacted with another diaquobis (ethylenediamine) cobalt (II) ion to form the binuclear complex.



Further addition of one half mole of base per mole of cobalt results in olation to form a polymeric ion.



The substitution of ammonia for the aquo groups in the complex resulted in a complex greatly increased in decomposition stability. This complex was formulated as



and showed no tendency toward polymeric formation with the addition of excess base. Both complexes were unoxidizable with conventional oxidants.

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