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COMPLEXES OF COBALT(III) WITH 2-AMINOETHANETHIOL

By

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COMPLEXES OF COBALT(III) WITH 2-AMINOETHANETHIOL

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## INTRODUCTION

The importance of thiol compounds has come to be appreciated more widely in recent years, especially in connection with the chemistry of living organisms (1). There is much interest, therefore, in the chemical properties of the thiol group. One of its most interesting and important reactions is the ability to form rather stable complexes with certain metals, which can, accordingly, promote or inhibit other reactions; in some instances, the metal complexes act as reaction intermediates and exert a powerful catalytic effect even in trace amounts.

This study is concerned with some complexes of cobalt(III) with two and with three molecules of 2-aminoethanethiol (henceforth called AET). These complexes are distinctively colored, a fact that makes possible their investigation by means of spectrophotometry. It was expected thus conveniently to gain an understanding of their chemical properties. A complex of cobalt(III) with three molecules of AET was prepared and described in 1955 by Felder, Paoli, and Tiepolo (4), and Neville and Gorin (8) have reported on bis and tris complexes that were formed in solution, but these investigations provide only an introduction to a rather complex subject. This thesis describes

more fully the nature and properties of the complexes, with special reference to their absorption spectra and discusses the relationship between them.

## EXPERIMENTAL

### Chemicals

Two samples of AET hydrochloride were available for use; one was obtained from the California Foundation for Biochemical Research, and the other was kindly donated by the Evans Chemical Company. The samples were assayed iodimetrically by the procedure described by Lavine (7) for titration of the thiol group of cysteine. The results for both samples indicated 94-96 per cent of the theoretical content of -SH.

Hexamminecobalt(III) chloride was prepared according to Inorganic Syntheses (5). Analysis for cobalt gave 21.85 per cent; calculated, 22.03 per cent.

All other reagents were commercial samples of reagent grade, unless otherwise specified.

Nitrogen was of commercial water-pumped grade.

### Preparation of De-ionized and De-aerated Water

Distilled water was passed slowly through a column of Amberlite MB-1 ion exchange resin to remove residual anions and cations. The water then was boiled for approximately five minutes, and a stream of nitrogen gas was bubbled through the water until it had cooled to room temperature.



The water was stored in a siphon which was connected to the air through a trap of alkaline pyrogallol.

### Apparatus

#### For pH Determinations and Titrations

A Beckman model G pH meter was used to determine the pH of solutions and to determine titration curves of the complexes. The instrument was standardized with a buffer of known pH before each run.

#### For Spectrophotometric Determinations

A Beckman model DU spectrophotometer and a Beckman model DK recording spectrophotometer were used to determine the spectra of the complexes. Quartz cells, of 10 millimeter width, which had been standardized against each other, were employed in the determination of the spectra.

#### For Oxygen Absorption

The oxygen absorption apparatus consisted of a 250 ml. reaction flask, to which were fused two burettes, through which reagents could be measured into the flask without opening it to the air. A gas burette, which could be filled with mercury by raising a leveling bulb, could be connected either to the reaction flask or to the outside by means of a three-way stopcock. The gas burette was surrounded by a water jacket for controlling its temperature. The contents

of the reaction flask could be stirred with a magnetic stirrer.

#### Anaerobic Cell for Spectrophotometric Work:

A rubber cap was fitted over the neck of a Beckman quartz cell which originally had been designed for use with a ground glass stopper. Two short hypodermic needles, each of which had been bent into an L-shape, were inserted through the cap. To one of these needles the nitrogen line was attached, and the other served as a gas outlet. Solutions were injected into the cell through the rubber cap by means of a hypodermic syringe after the cell had been flushed with nitrogen for about five minutes.

#### For Electroanalysis

A Sargent-Slomin Electrolytic Analyzer and platinum electrodes were employed for cobalt analysis by electrolysis.

Tris(2-aminoethanethio)cobalt(III)

#### Preparation of Tris Complexes

(1) From Hexamminecobalt(III) Chloride--Hexamminecobalt(III) chloride, 1.16 g. (4.10 millimoles) and 1.39 g. of AET (12.2 millimoles) were dissolved in 100 ml. of de-aerated water and heated under nitrogen at 50° C. for two hours. After cooling, the precipitate was filtered, washed with water, methyl alcohol, and ether, and dried in vacuo

over concentrated sulfuric acid for two hours. Yield: 1.22 g. Cobalt analysis: found, 20.2 per cent; calculated for  $\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)_3$  20.53 per cent.

From Hexamminecobalt(III) Chloride for Direct Spectrophotometric Measurements--Hexamminecobalt(III) chloride, 0.0268 g. (0.100 millimoles), 0.1135 g. of AET hydrochloride (1.00 millimoles), and 1.21 g. (10.0 millimoles) of tris-(hydroxymethyl)aminomethane were dissolved in 100 ml. of de-aerated water and heated under nitrogen at 50° C. for a total of 24 hours. The spectrum was determined in the region 350-625 millimicrons at two hour intervals, and it was found that the reaction was essentially complete after 24 hours. The shape of the absorption curve is shown in Figure 1 (A); position of maxima: 570 and 434 millimicrons; extinction values: 620 and  $1.38 \times 10^3$ , respectively.

The tris complex also was prepared in this way from 0.0375 g. (0.033 millimoles) of AET hydrochloride and 0.0268 g. (0.01 millimoles) of hexamminecobalt(III) chloride, i.e., with a 3.3 to 1 ratio of AET to cobalt. The spectrum altered rapidly, but it was determined within fifteen minutes of the time of mixing. The shape of the absorption curve was the same [Figure 1 (A)]; position of maxima: 570 and 434 millimicrons; extinction values: 568 and  $1.24 \times 10^3$ , respectively.

(3) From Cobalt(II) Chloride in Buffered Solution--Cobalt(II) chloride hexahydrate, 0.0119 g. (0.050 millimoles), 0.0568 g. (0.50 millimoles) of AET hydrochloride,

and 1.21 g. (10.0 millimoles) of tris(hydroxymethyl)amino-  
methane were dissolved in 100 ml. of de-ionized but not  
de-aerated water. The color developed in a few minutes.  
The absorption curve had the shape shown in Figure 1 (A);  
position of maxima: 570 and 434 millimicrons; extinction  
values: 640 and  $1.46 \times 10^3$ , respectively.

The complex also was prepared in the above manner, with  
the exception that only a 4-fold excess AET hydrochloride  
was used. The spectrum was quite fleeting and was deter-  
mined within fifteen minutes of the time of mixing; position  
of maxima: 570 and 434 millimicrons; extinction values:  
580 and  $1.3 \times 10^3$ , respectively.

(4) From Cobalt(II) Chloride in Unbuffered Solution--  
Cobalt(II) chloride hexahydrate, 0.0119 g. (0.050 milli-  
moles) and 0.1135 g. (1.00 millimoles) of AET hydrochloride  
were weighed into a 100 ml. volumetric flask and dissolved  
in de-ionized water; 1.6 ml. of 1 molar sodium hydroxide was  
added and the solution then diluted to the mark. The  
complex formed rapidly. This solution was used directly to  
determine the spectrum in the region 350-625 millimicrons;  
position of maxima: 570 and 434 millimicrons; extinction  
values: 612 and  $1.36 \times 10^3$ , respectively.

The above solution then was diluted to a cobalt concen-  
tration of  $5 \times 10^{-5}$  molar, and the spectrum determined in an  
effort to locate and measure maxima in the region 220-300

millimicrons. Absorption was still too great to delineate any maximum in this region.

#### Stoichiometry for Formation of Solid Tris Complex

Cobalt(II) chloride hexahydrate, 0.238 g. (1.00 millimoles) and 0.376 g. (3.30 millimoles) of AET hydrochloride were dissolved in 100 ml. of carefully de-aerated water and placed in the reaction flask of the gas absorption apparatus. Air was drawn into the apparatus by means of the leveling bulb. Sodium hydroxide, 6.3 ml. of 1.0 molar concentration (6.3 millimoles), then was added to the reaction flask. The oxygen absorption was measured at various times until a constant reading was obtained. Oxygen absorbed: 6.14 c.c. Volume calculated from proposed equation (3),  $\sqrt{\text{temperature: } 26^{\circ} \text{ C.}; \text{ pressure: } 740.8 \text{ m.m.}}$ , 6.30 c.c.

The contents of the reaction flask then were filtered, and the mother liquor titrated potentiometrically with 1.0 molar hydrochloric acid. The titration curve began at pH 11.8 and showed an inflection at pH 10.65; the end point was taken at pH 7.0. The amount of alkali found present was 0.91 millimole; the amount calculated from equation (3) is 1.0 millimole.

#### Decomposition of Tris Complexes with Acid

(1) Cobalt(II) chloride,  $5.00 \times 10^{-5}$  moles,  $2.00 \times 10^{-4}$  moles of AET hydrochloride, and  $4.00 \times 10^{-4}$  moles of

sodium hydroxide were mixed in 100 ml. of solution, and the green color was allowed to develop. Then a small amount of concentrated hydrochloric acid was added, and the solution immediately turned brown. The spectrum was determined in the region 220-625 millimicrons. The absorption curve is shown in Figure 1 (D); no maxima were observed.

(2) Solid tris complex, 0.1435 g. (0.500 millimoles) was dissolved in 100 ml. of 0.1 molar hydrochloric acid. This solution was diluted to a cobalt concentration of  $1.00 \times 10^{-5}$  molar, and the spectrum was determined in the region 220-625 millimicrons. The absorption curve is shown in Figure 1 (C); position of maxima: 262 and 350 millimicrons; extinction values:  $6.90 \times 10^3$  and  $4.48 \times 10^3$ , respectively.

#### Solubility of Solid Tris Complex

The tris complex, 0.05 g., was added to 100 ml. of water, 1 molar sodium hydroxide, 1 molar hydrochloric acid, ethyl ether, and 95 per cent ethyl alcohol, respectively. These solutions then were shaken for several hours. Complete solution was effected only in hydrochloric acid, and the solution obtained was dark brown. Partial solution was observed (also brown) in the water and sodium hydroxide, but the color also was brown. In ether and alcohol no color was observed.

### Re-formation of Tris Complexes from Acidified Solution

A green solution, cobalt concentration  $1 \times 10^{-4}$  molar, was prepared in unbuffered solution, and the spectrum was determined in the region 350 to 600 millimicrons [Figure 1 (A)]; the extinction at 400 millimicrons was  $1.38 \times 10^3$ . The solution then was acidified with concentrated hydrochloric acid, and the spectrum was determined [Figure 1 (D)]. Enough concentrated sodium hydroxide was added to bring the solution to pH 10, and the spectrum was re-determined. The resulting absorption curve is shown in Figure 1 (E); the extinction value at 400 millimicrons was  $2.31 \times 10^3$ .

### Preparation of Diaquobis(2-aminoethanethio)cobalt(III) Complex

(1) From Hexamminecobalt(III) Chloride--Hexamminecobalt(III) chloride, 0.0268 g. (0.100 millimoles), 0.0227 g. (0.200 millimoles) of AET hydrochloride, and 1.21 g. (10.0 millimoles) of tris(hydroxymethyl)amminomethane were dissolved in 100 ml. of de-aerated water and heated under nitrogen at  $50^\circ \text{C}$ . The spectrum was determined every hour until no further change was noted; the time required was approximately ten hours. The spectrum is shown in Figure 1 (B); position of maxima: 435, 350, and 278 millimicrons; extinction values: 1.82, 5.10, and  $6.83 \times 10^3$ , respectively.

(2) From Cobalt(II) Chloride in Buffered Solution--  
Cobalt(II) chloride hexahydrate, 0.0119 g. (0.050 millimoles), 0.0114 g. (0.100 millimoles) of AET hydrochloride, and 1.21 g. (10 millimoles) of tris(hydroxymethyl)-aminomethane were dissolved in 100 ml. of de-ionized, but not de-aerated, water. The formation of the complex was rapid, and the spectrum obtained was stable for a period of several days. The shape of the absorption curve is shown in Figure 1 (B); position of maxima: 437, 350, and 279 millimicrons; extinction values:  $2.04$ ,  $4.63$ , and  $7.23 \times 10^3$ , respectively.

(3) From Cobalt(II) Chloride in Unbuffered Solution--  
Cobalt(II) chloride hexahydrate, 0.0119 g. (0.050 millimoles) and 0.0236 g. (0.200 millimoles) of AET hydrochloride were dissolved in 100 ml. of de-ionized water, and sodium hydroxide, 1.19 ml. of 0.10 molar concentration, then was added. After addition of the sodium hydroxide, the formation of the complex was quite rapid. The shape of the absorption curve is shown in Figure 1 (B); position of maxima: 438, 350, and 268 millimicrons; extinction values: 1.98, 5.49, and  $7.15 \times 10^3$ , respectively.

#### Ion Exchange with Solution of Bis Complex Prepared Directly

A solution, 0.005 molar in bis complex, prepared as described directly above, and made 0.01 molar in sodium hydroxide was passed through a short column of Dowex-50, which had been converted to the sodium form; the solution



came through colorless. Another portion of the same solution was passed through a similar column of Amberlite IRA-400 and came through with color still present.

### Stoichiometry for Formation of Bis Complex

(1) Oxygen Consumption--Cobalt(II) chloride hexahydrate, 0.119 g. (0.500 millimoles) and 0.1135 g. (1.00 millimoles) of AET hydrochloride were dissolved in 100 ml. of de-aerated water, and the solution was added to the reaction flask of the absorption apparatus. Air was drawn into the system by means of the leveling bulb. Exactly 2.00 ml. of 1.0 molar sodium hydroxide then was added. (It is important to know the exact volume of sodium hydroxide admitted, since the system is closed and a volume correction must be made.) The volume of oxygen was followed as a function of time until the reading became constant. Oxygen absorbed: 3.05 c.c.; volume calculated from proposed equation (7) [temperature 26° C.; pressure 740.8 m.m.] was 3.15 c.c.

(2) Sodium Hydroxide Consumption--Cobalt(II) chloride hexahydrate, 0.119 g. (0.500 millimoles), and 0.1135 g. (1.0 millimole) of AET hydrochloride were dissolved in 100 ml. of 0.0200 molar sodium hydroxide (2.00 millimoles). A large excess of oxygen was passed through the solution. The solution then was back-titrated with 1.072 molar hydrochloric acid. The titration curve started at pH 11.0 and showed an inflection at pH 10.7; the end point was

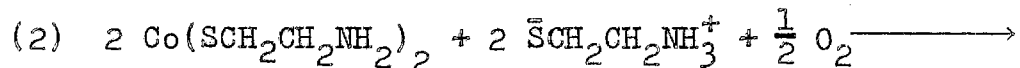
taken at pH 7.0; 0.43 millimoles of sodium hydroxide was thus shown to be present in the solution, indicating that 1.57 millimoles had been consumed in the reaction; calculated from proposed equation (7): 1.50 millimoles.

#### Cobalt Determination in Cobalt(III) Complexes

A sample of the complex was weighed accurately and placed in a Kjeldahl flask; 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulfuric acid were added, and the resulting solution heated to boiling; 50 ml. of 20:1 sulfuric acid was added, and the solution was heated to fumes of sulfuric acid. The solution then was oxidized with 0.5 g. of ammonium persulfate, made alkaline with 30 ml. of concentrated ammonium hydroxide and neutralized with dilute sulfuric acid; finally, 50-70 ml. of concentrated ammonium hydroxide was added. If the decomposition had been carried out properly, the solution was pink at this point. The solution was electrolyzed with a Sargent-Slomin Electrolytic Analyzer, the cobalt being plated onto a previously weighed electrode. Completion of plating was determined by means of a polysulfide solution.

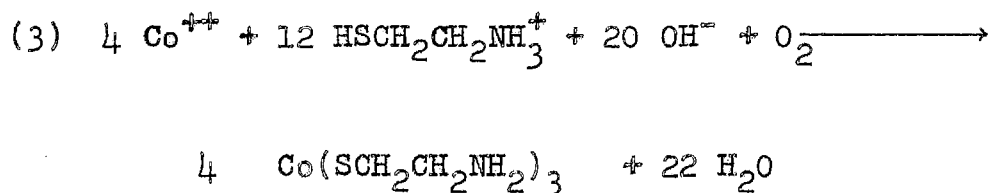
TRIS(2-AMINOETHANETHIO)COBALT(III)

As was stated in the introduction, a solid tris complex was prepared first by Felder et al. (4). Unfortunately, their paper gives no experimental details. These authors represent the formation of the complex by equations (1) and (2), but state in the discussion that sodium hydroxide must be added in order to form the bis-AET cobalt(II) complex.

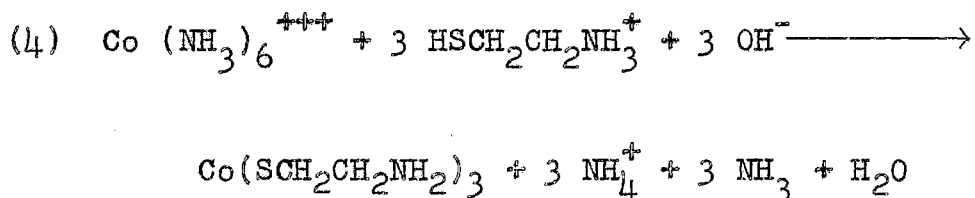


One might surmise that sufficient base would be added to neutralize the hydrochloric acid formed according to equation (1), i.e., two moles of base per gram-atom of cobalt, but the amount is not specified. In order to ascertain the stoichiometry directly, 1.00 millimoles of cobalt(II) chloride hexahydrate was mixed with 3.3 millimoles of AET hydrochloride and 6.3 millimoles of sodium hydroxide in 100 ml. of de-aerated water, in an apparatus for measuring oxygen absorption. The absorption of 0.25

millimoles of oxygen took place rapidly, and one millimole of alkali could be demonstrated in the mother liquor by back-titration with acid. The stoichiometry of the reaction may be represented, then, by equation (3):



An attempt then was made to prepare the tris complex by an alternative method, the substitution of AET into a cobalt(III) complex of lower stability. Accordingly, hexamminecobalt(III) chloride was reacted with a slight excess of AET (AET hydrochloride plus one equivalent of sodium hydroxide), and the complex was isolated in good yield after heating for two hours at 50° C. The reaction can be represented by equation (4):



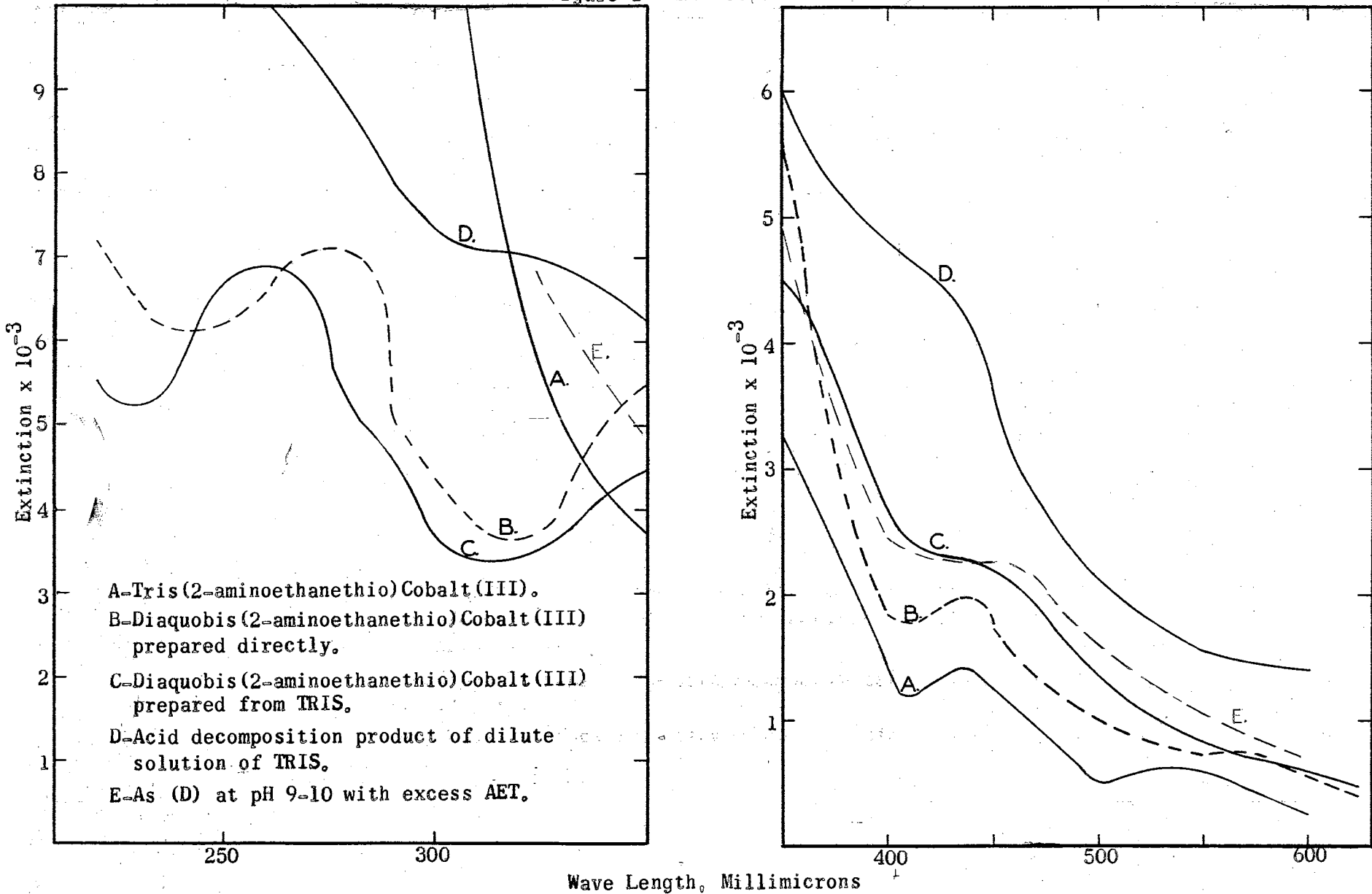
In this preparation, no oxygen need be added; indeed, it was carried out with de-aerated solutions under an atmosphere of nitrogen. This supports the formulation of the complex produced as one of cobalt(III).

Since the tris complex is colored, it was expected that its absorption spectrum would be of great assistance in its characterization and identification. Therefore, it was attempted to dissolve the complex in water or in other solvents and to determine the absorption of the solution. This, however, proved unexpectedly difficult, and the solutions obtained were always brownish in color. It seems that the complex is very sparingly soluble and that, in solution, it is susceptible to oxidation, while the oxidation products are brownish and readily soluble. Thus the spectrum could not be obtained from the solid complex. It should be pointed out, in passing, that insolubility in water is quite in keeping with the formulation of the tris complex as an "inner salt." Unfortunately, the complex is quite insoluble in organic solvents, too.

Preparation of the complex directly in solution at high dilution then was undertaken. This already had been attempted by Neville (8), but the results of this study differ quite considerably from his, possibly because he did not realize fully how easily these complexes are altered by oxidation. When the color was developed from a mixture containing only the required amount of AET, the spectra developed altered rapidly, although they could be determined approximately by working rapidly and with care.

A much more stable spectrum could be obtained, as might be expected, when a large excess of AET was used, and these

Figure 1--Extinction Curves



experiments will be described first. When  $2.5$  and  $5 \times 10^{-4}$  molar cobalt(II) chloride was mixed with a large excess of AET (AET hydrochloride to which 1.2 equivalents of sodium hydroxide had been added) in de-ionized but not de-aerated water, an emerald green color developed in a few minutes. The spectrum was stable for several hours, so it could be determined at leisure; the absorption curve is shown in Figure 1 (A). At these concentrations no precipitate formed, and the extinction values were calculated on the basis of the concentration of cobalt. The same spectrum developed from cobalt(II) chloride and AET hydrochloride when 0.1 molar tris(hydroxymethyl)aminomethane was used in place of sodium hydroxide. The tris(hydroxymethyl)aminomethane serves to buffer the solution at about pH 9.5. Although tris(hydroxymethyl)aminomethane itself complexes cobalt ion, it apparently does not interfere with the formation of the AET complex. In order to ascertain the composition of the complex formed in these circumstances, its preparation also was undertaken with a mixture of 3.3 moles of AET per gram-atom of cobalt(II) in tris(hydroxymethyl)aminomethane. The absorption curve had the same shape as that found with an excess of AET, although the extinctions at the maxima were about 10 per cent lower. The spectrum altered quickly, and these results could be obtained only within fifteen minutes from the time of mixing; subsequently, more profound changes ensued.

A spectrum identical with that obtained from cobalt(II) also could be developed from hexamminecobalt(III) chloride in tris(hydroxymethyl)aminomethane.

The spectral curve, with maxima at 570 and 440 millimicrons, differs from that reported by Neville (8), with maxima at 580 and 340 millimicrons. There is only a slight disagreement as far as the position of the first absorption peak is concerned, but a peak also was found at 440 millimicrons, while Neville did not find this. Also, a continually rising absorption in the neighborhood of 340 millimicrons was found. A possible reason for the discrepancy is indicated by the fact that the extinction value at the 570-580 maximum found by Neville is about half as large as that found in this work. This might indicate that the complex measured by Neville had been at least half-destroyed by oxidation. Oxidation, as already has been stated, gives brownish products, with an absorption similar to curve (D) in Figure 1, which exhibits a plateau from about 300 to 340 millimicrons, and formation of such material might cause the appearance of a maximum at the position reported by Neville.

The steeply rising curve which was found in this wavelength range surely forms the side of a third and very high absorption peak, which might be centered about 260 millimicrons; but to examine the top of this maximum would necessitate working with solutions more dilute than



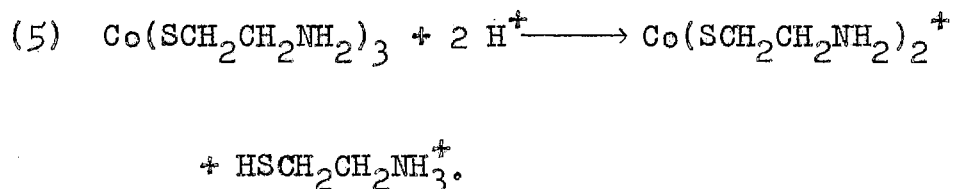
$5 \times 10^{-5}$  molar, and this was not undertaken because of their extreme lability.

It has been seen, then, that a green complex, shown by analysis to contain three molecules of AET per atom of cobalt, was precipitated from solutions approximately 0.01 molar in cobalt and that green solutions could be formed with approximately  $1 \times 10^{-4}$  molar cobalt and excess AET. Although a large excess of AET was required to obtain stable spectra, absorption curves very similar to those obtained in excess AET also could be developed, although only briefly, with only a little more than three moles of AET per atom of cobalt. This leads to the conclusion that the green color also was due to a tris complex.

For a long time, it was believed that the two complexes were the same, although it has been stated that the solid complex would not dissolve to give green solutions. However, the behavior of the solid complex and the green solution upon treatment with acid is quite different and indicates that the worker is dealing with two (or more) complexes. For convenience the writer shall henceforth refer to the solid complex as Complex I and to the complex(es) responsible for the green color in solution as Complex II.

Felder et al. (6) first observed that Complex I dissolves in acid to give brown solutions, but they did not comment upon this peculiarity. In order to investigate the

phenomenon further, a weighed amount of Complex I was placed in 0.1 molar hydrochloric acid; a brown color developed as the solid dissolved, and the absorption curve is shown in Figure 1 (C). Since the spectrum appeared to be quite stable, although the acid was present in large excess, a reaction of definite stoichiometry apparently took place, and not a gradual decomposition of the complex. It is postulated that the reaction is represented by equation (5); in other words, that



The brown color produced is due to a bis complex. This belief is based mainly on the fact that the spectrum is similar to that of a bis complex formed directly (see next chapter).

Significantly different results were obtained when the green solutions formed at low concentrations were acidified. A solution formed from  $5 \times 10^{-5}$  molar cobalt and a ten-fold excess of AET, and made acid after the green color had developed, gave the spectrum shown in Figure 1 (D). This solution then was again made basic in an attempt to restore the original spectrum. This did not occur, but the shape of the resulting absorption curve [Figure 1 (E)], which is

intermediate between curves 1 (A) and 1 (D), suggests that a partial restoration of the original complex may have occurred, while another part of the product of acidification is not changed. The change which takes place upon acidification is not a gradual one, as it could be demonstrated that, after the initial alteration had occurred, no further change would take place. It should be added that in order to effect reconversion after some time, both alkali and fresh AET hydrochloride had to be added, the original excess of AET apparently having disappeared by this time.

When Complex I was dissolved in acid, diluted to a cobalt concentration of  $5 \times 10^{-5}$  molar, and a ten-fold excess of AET hydrochloride and alkali were added, no change in the spectrum occurred in the region of 600 to 300 millimicrons, indicating that no reaction takes place like that observed with the green solution.

The writer can offer no unequivocal explanation for this puzzling behavior but would suggest, on the basis of it, that Complex II consists of a mixture of two isomeric tris complexes while Complex I contains only one of them. This isomer is changed upon acidification so that it does not form a green color upon treatment with base and excess AET, while the other isomer contained in Complex II can be converted to brown with acid, then back to green with base.

There are two stereoisomeric configurations possible for tris complexes of AET, as represented in Figure 2, and

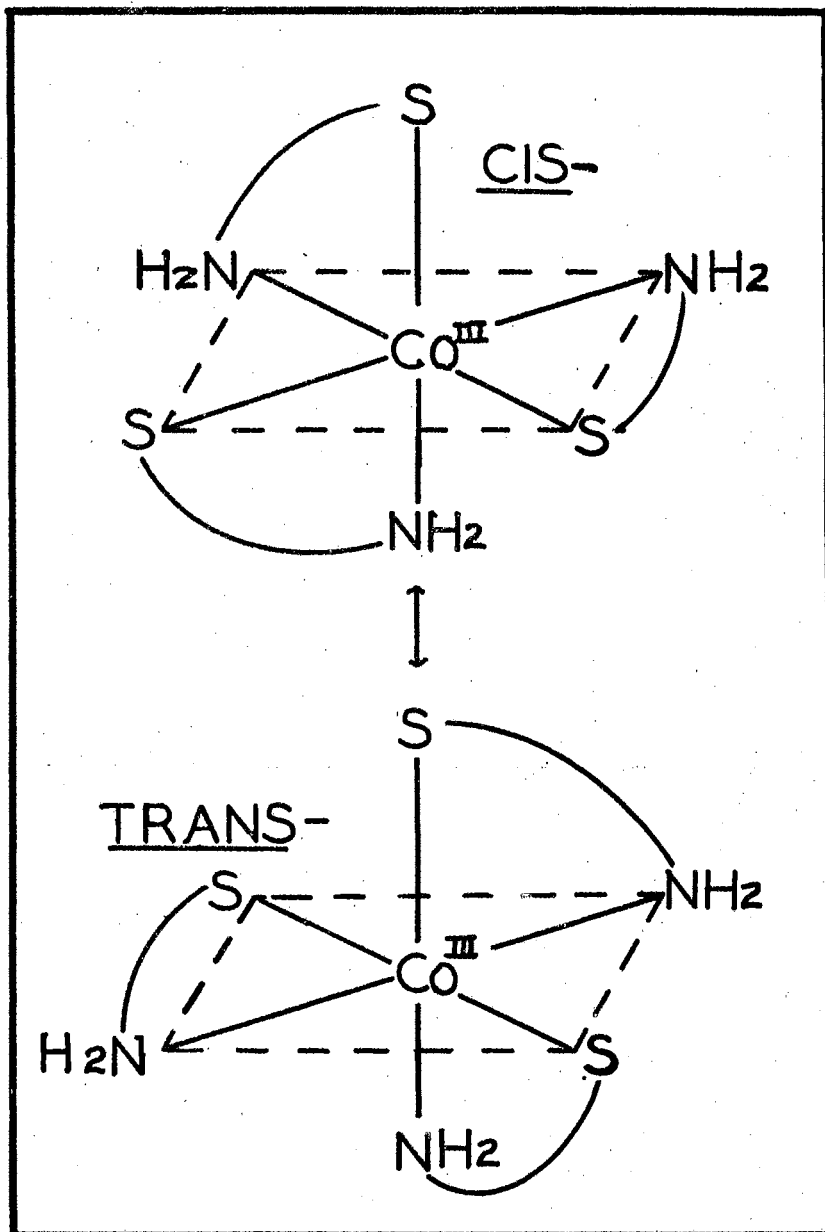


Figure 2--Cis- and Trans- forms of tris(2-aminoethanethio)Cobalt(III)

the two isomeric complexes under discussion may have these configurations. If so, the information at hand does not allow one to decide which complex has which structure. Some correlations of structure with absorption spectra have been made (9,11,12,13), but the results are not applicable to this problem. This is true, first, because the spectrum in the region of greatest interest, 280-220 millimicrons, is not available and, secondly, because the generality of the correlations is open to question.

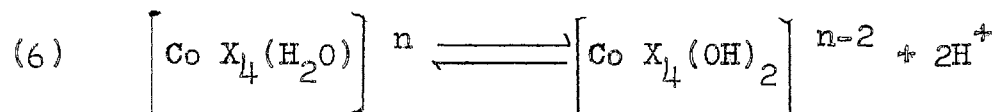
On the other hand, the difference in behavior described above indicates, perhaps, a more profound difference in structure than mere diastereoisomerism. The extreme insolubility of Complex I in both water and organic solvents suggests the possibility that this complex is polymeric, with AET molecules serving as bridges between cobalt ions. However, confirmation of this hypothesis must await study by methods other than those available in this work.

## BIS(2-AMINOETHANETHIO)COBALT(III) COMPLEXES

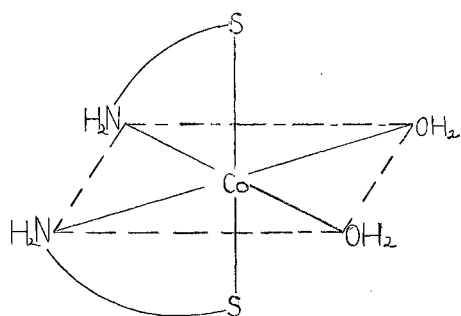
Discussion of the complexes which contain two molecules of AET per atom of cobalt involves two questions, which will be discussed at the outset.

The first question concerns the stereoisomerism of the complexes, which is somewhat more complicated than in the case of tris complexes because the two positions in the coordination sphere of cobalt(III) not occupied by AET can be cis or trans to one another. Then, the AET molecules can be attached in different ways, giving a total of five diastereoisomers (Figure 3).

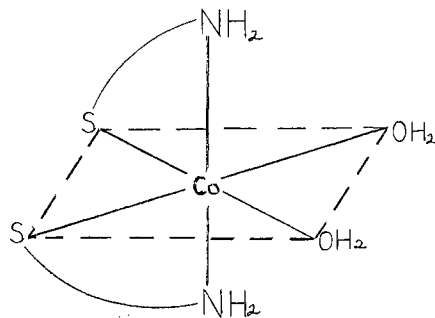
The second question concerns the possible acidity of coordinated aquo groups and arises because, in certain complexes of a similar nature, the ionization represented by equation (6) plays an important role in their chemical behavior.



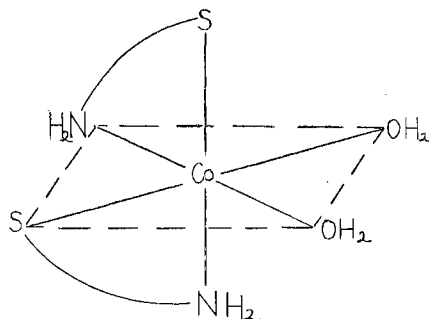
Thus, Lamb and Damon (6) report such an equilibrium in the diaquotetramminecobalt(III) ion, with pK values of 5.32 and 7.30 for the first and second dissociation constants, while Bjerrum and Rasmussen (3,10) find similar data for both the



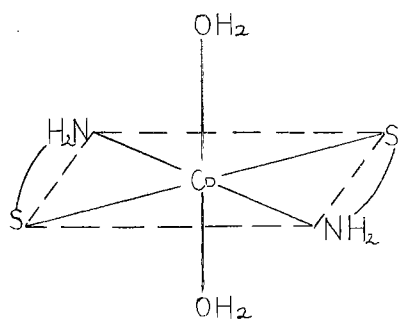
A--cis  $N_0$  diaquo.  
trans  $S_0$ .



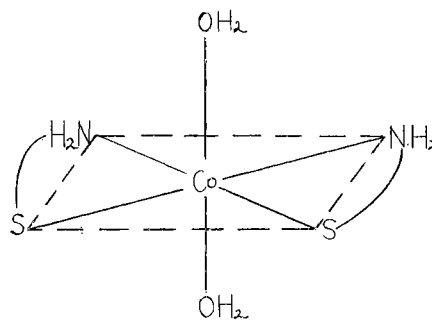
B--cis diaquo.  
trans  $N_0 S_0$ .



C--cis  $S_0 N_0$  diaquo.



D--trans  $S_0 N_0$  diaquo.

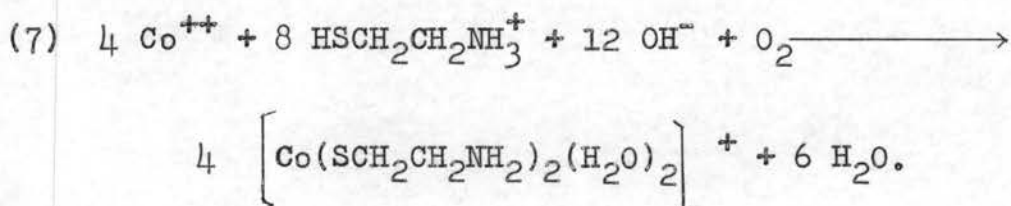


E--cis  $N_0 S_0$   
trans diaquo.

Figure 3  
Possible Isomeric Configurations of  
Diaquobis(2-aminoethanethio)cobalt(III)

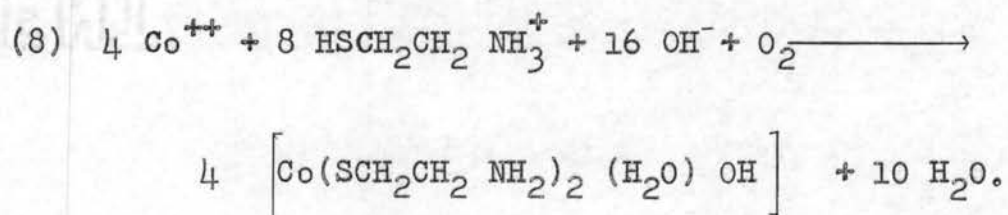
cis and trans forms of the diaquobisethylendiamine-cobalt(III) ion. Although this interesting work cannot be discussed in detail, two points that are important to the discussion will be mentioned: one, that the pK values of the aquo groups are about six and eight, and, two, that there are appreciable differences in the spectra of the hydroxo and aquo complexes with the same isomeric configuration. While it remains to be seen to what extent these results can be generalized, it is clear that comparable phenomena might be expected in the bis complexes of AET with cobalt.

With these facts in mind, the preparation of bis complex was first undertaken by mixing 0.5 millimoles of cobalt(II) chloride with 1.0 millimoles AET hydrochloride and 100 ml. 0.02 molar sodium hydroxide, and passing oxygen through the solution. At the end of the reaction, the solution had a pH of about 11, and back titration with 1.0 molar hydrochloric acid gave an end point inflection characteristic of the titration of a strong base with a strong acid, with no evidence for the existence of an acid-base equilibrium in the pH range 10-4. One-half millimole of acid was consumed, and this is in accord with the stoichiometry represented in equation (7):





If the two molecules of water included in the formulation of the complex were acidic, the reaction would have proceeded according to equation (8), and all the sodium hydroxide would have been consumed.



To the solution prepared in this way, additional sodium hydroxide was added, and then it was passed through a cation-exchange resin, Dowex 50, in the sodium form; the color was completely removed by this treatment. On the other hand, the colored solution passed unchanged through a bed of anion exchanger, Amberlite IRA-400. This confirms that the complex is a cation, as formulated in equation (7), and not an anion,  $\left[ \text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2 \right]^-$ .

The spectrum of the solution in the region 220-650 millimicrons was determined after appropriate dilution with water, with 0.01 molar sodium hydroxide, and with 0.01 molar hydrochloric acid. The resulting spectra were identical in the three cases and are represented by curve B in Figure 1. Since one can reasonably expect that a substantial change in the spectrum would accompany the conversion of a dihydroxo complex to a diaquo complex, and since the conversion surely would occur in going from 0.01 molar sodium hydroxide to

0.01 molar hydrochloric acid, these observations reinforce the conclusion that no such equilibrium occurs in the solutions under discussion.

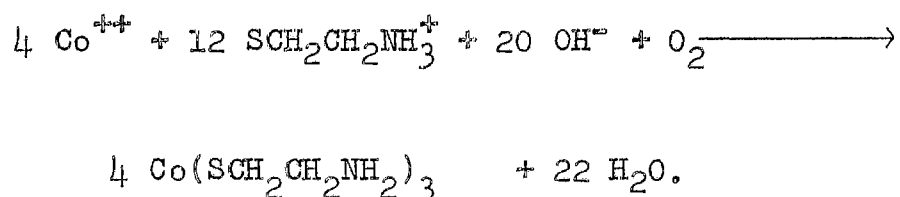
An absorption curve identical with that shown in Figure 1 (B) also was obtained directly in solution by mixing 0.05 millimole of cobalt(II) chloride with 0.1 millimole of AET hydrochloride in 100 ml. of solution, using either 0.2 millimoles of sodium hydroxide or 0.1 molar tris(hydroxymethyl)aminomethane buffer. Finally, the same spectrum also was developed by mixing 0.10 millimoles of hexamminecobalt(III) chloride with 0.20 millimoles of AET hydrochloride in 100 ml. of 0.1 molar tris(hydroxymethyl)aminomethane. The three sets of results agree, and all indicate the formation of a bis complex. It seems unlikely that the spectrum could be that of a mixture, since it is formed identically in quite different circumstances; but, on the other hand, the spectra of the possible isomers may be quite similar, so that the presence of various individual ones would not be revealed by the spectrum.

It should be recalled at this time that treatment of tris Complex I with acid gives an absorption curve similar, but by no means identical, with that of bis prepared directly. If, as has been suggested as a possibility in the previous section, tris Complex I is polymeric in form, its acid decomposition product could be a trans diaquo complex, and the bis complex prepared directly differs from

it only in the manner in which the AET molecules are attached to the cobalt(III) ion. In other words, these two bis complexes may be cis-N,S and trans-N,S isomers (9), while the aquo groups are trans in both cases.

## SUMMARY

A solid complex which contains three molecules of AET per ion of cobalt(III) has been prepared. The stoichiometry of its preparation may be represented by the following equation:

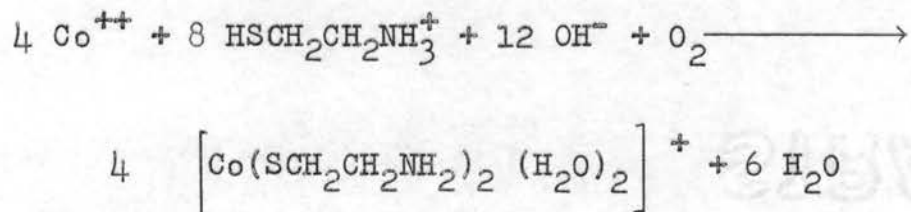


This complex also was prepared from hexamminecobalt(III) chloride. Owing to the insolubility of the complex, solutions of it could not be prepared for measurement of light absorption. A green solution could be obtained directly by mixing cobalt and AET in 1:3 ratio at high dilutions ( $1 \times 10^{-4}$  molar cobalt). The spectrum developed in this way was different from that previously reported by Neville (8). This solution gave, upon acidification, a brown color, the spectrum of which was different from that obtained when the solid tris complex was treated with acid. Furthermore, the product of acidifying the green solution gave, upon being made basic in the presence of excess AET, a spectrum that might be due to partial reconversion to the original

complex, while the product of acidifying the solid tris complex does not do so. This suggests that the green solutions may consist of a mixture of two isomeric tris complexes, one of which is irreversibly changed by acidification, while the other can be changed to brown and then regenerated; the solid tris complex contains only the former isomer.

The two isomers might have diastereoisomeric structures as shown in Figure 2, page 23, but it is difficult to explain why one of these structures would not be regenerated. The behavior of its acid decomposition product and its insolubility in organic solvents suggest that the solid tris complex may have a peculiar structure, e.g., that it may be a polymer in which cobalt(III) units are joined by AET molecules. In this case, a product of acidification would be a trans diaquo complex.

A bisAET-cobalt complex also has been prepared, the stoichiometry being represented by the following equation:



The water molecules shown present in the complex are not sufficiently acidic to give rise to aquo-hydroxo ionization in 0.1 molar sodium hydroxide. Although diaquobis(2-aminoethanethio)cobalt(III) complexes can exist in several

isomeric forms, the bis complex prepared directly is not believed to be a mixture of isomers. The spectrum of this complex and the one obtained by treating the solid tris complex with acid are very similar. If the solid tris complex is polymeric in nature, the bis complex prepared by acidifying it and the bis complex prepared directly could be isomeric trans-diaquo forms in which the sulfide and amino ends of the two AET molecules are attached in cis or in trans positions, as shown in Figure 3, D. and E.

## BIBLIOGRAPHY

1. Barron, E. S. G., Adv. Enzymology, 2, 201 (1951).
2. Basolo, F., Ballhausen, C. J., and Bjerrum, J. Acta Chem. Scand., 9, 810 (1955).
3. Bjerrum J. and Rasmussen, S. E., Acta Chem. Scand., 6, 1265 (1952).
4. Felder E., Paoli, E., and Tiepolo, U., Il Farmaco, Ed. Sci., 10, 863 (1955).
5. Inorganic Syntheses, 2, 217 (1946).
6. Lamb, A. B. and Damon, E. B., J. Am. Chem. Soc., 59, 383 (1937).
7. Lavine, T. F., J. Biol. Chem., 109, 141 (1935).
8. Neville, R. G. and Gorin, G., J. Am. Chem. Soc., 31, 176 (1954).
9. Trimble, R. F., J. Chem. Ed., 31, 176 (1954).
10. Rasmussen, S. E. and Bjerrum J., Acta Chem. Scand., 8, 1056 (1954).
11. Shimura, Y., J. Am. Chem. Soc., 73, 5079 (1951).
12. Tsuchida, R. and Kasimoto, S., Chem. Soc. Japan, 11, 785 (1936).
13. Yamada, S. and Tsuchida, R., Chem. Soc. Japan, 25, 127 (1952).

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