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Preparation and Properties of Trisethanolamine Cobalt(III) Complexes

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Two types of trisethanolamine cobalt(III) complexes were prepared. One (complex II) was an inner complex $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_3]$; analyses indicated that the other (complex I) was a 1:1 mixture of two kinds of complex salts, $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})]X_2$ and $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_2]X$. Since the composition of complex I did not change with variation of the anion X, it is improbable that this is a double salt composed of two complex salts; therefore another possibility is suggested.

In previous investigations¹ on the absorption spectra of transition metal complexes having various amines as ligands, it was found that the tendency of an amine toward complex formation is strengthened or weakened by the introduction of a positive or negative inductive substituent into the amine molecule. In our opinion the strong tendency of ethylenediamine to form complexes in contrast to that of ethylamine is due to a mutual positive inductive effect of the two amino groups in the ethylenediamine molecule. If this interpretation is correct, ethanolamine, which contains an hydroxyl group exerting a positive inductive effect, should form a stable cobalt(III) complex like ethylenediamine. We, therefore, prepared ethanolamine complexes of cobalt(III) and obtained two new complexes.

Results and Discussion

When some cobalt(III) ammine complexes were treated with ethanolamine, we obtained purple-red crystals (complex I) which dissolved easily in water to give a purple-red solution. The addition of sodium hydroxide to a concentrated solution of this complex gave another complex (complex II) which separated as a violet crystalline powder. The analyses of these two complexes are given in Table I.

TABLE I
ANALYTICAL RESULTS^a

| Type I complex | | Co | C | H | N | Br |
|-----------------|---------------------|-------|-------|------|-------|-------|
| Nitrate | Found | 17.55 | 21.43 | 5.93 | 18.76 | |
| | Calcd. ^b | 17.66 | 21.60 | 5.89 | 18.89 | |
| Bromide | Found | 14.90 | 18.09 | 5.95 | 10.65 | 30.26 |
| | Calcd. ^c | 14.86 | 18.15 | 5.97 | 10.60 | 30.23 |
| Perchlorate | Found | 15.02 | 18.38 | 5.10 | 10.68 | |
| | Calcd. ^d | 15.12 | 18.46 | 5.05 | 10.78 | |
| Type II complex | Found | 24.61 | 30.05 | 7.51 | 17.52 | |
| | Calcd. ^e | 24.64 | 30.11 | 7.58 | 17.57 | |

^a Percentage compositions. ^b Calcd. for $\text{CO}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_3(\text{NO}_3)_3$. ^c Calcd. for $\text{CO}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_3\text{Br}_3 \cdot 4\text{H}_2\text{O}$. ^d Calcd. for $\text{CO}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_3(\text{ClO}_4)_3$. ^e Calcd. for $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_3$.

These results indicate that I and II are both trisethanolamine cobalt(III) complexes. Since ethanolamine as a bidentate ligand can assume a dissociated form $\text{NH}_2\text{CH}_2\text{CH}_2\text{O}^-$ (eta') as well as an undissociated form $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ (eta), four formulas are possible for the trisethanolamine cobalt(III) complex radical

$[\text{Co eta}_3]^{+3}$, $[\text{Co eta}_2 \text{ eta}']^{+2}$, $[\text{Co eta eta}'_2]^{+1}$ and $[\text{Co eta}'_3]^{0}$

(1) H. Yoneda, *Bull. Chem. Soc. Japan*, **30**, 130 (1957); **30**, 924 (1957); **31**, 708 (1958).

It is obvious that II corresponds to $[\text{Co eta}'_3]^{0}$. This formula is supported by the extremely low conductivity of the complex in solution. As the ratio of cobalt to anion in complex I is 2:3 in all three salts, I cannot consist of a single salt such as $[\text{Co eta}_3]X_3$, $[\text{Co eta}_2 \text{ eta}']X_2$ or $[\text{Co eta eta}'_2]X$, and we must assume that it is a 1:1 mixture of $[\text{Co eta}_2 \text{ eta}']X_2$ and $[\text{Co eta eta}'_2]X$. The conductivity data in Table II support this conclusion.

TABLE II

| MOLAR CONDUCTIVITIES OF COBALT(III) COMPLEXES AT 25° | Dilution (l./mole) | | | |
|--|--------------------|-------|-------|-------|
| | 128 | 256 | 512 | 1024 |
| 1. Complex I bromide | 148.0 | 160.8 | 167.9 | 176.0 |
| 2. 2:1 Complex salts | | | | |
| $[\text{Co}(\text{NH}_3)_6\text{Cl}]\text{Br}_2^a$ | 232.5 | 247.7 | 259.3 | 270.0 |
| $[\text{Co}(\text{NH}_3)_6\text{Br}]\text{Br}_2^b$ | | 230.5 | 244.7 | 257.6 |
| $[\text{Co}(\text{NH}_3)_6\text{NO}_2]\text{Br}_2^b$ | | 205.8 | 224.6 | 236.8 |
| $[\text{Co}(\text{NH}_3)_6\text{Cl}]\text{Cl}_2^c$ | 203.7 | 213.7 | 221.7 | 230.5 |
| $[\text{Co}(\text{NH}_3)_6\text{OH}](\text{NO}_3)_2^d$ | 229.5 | 241.5 | 253.4 | 266.2 |
| Mean | 222 | 228 | 240 | 252 |
| 3. 1:1 Complex salts | | | | |
| $[\text{Co en SO}_4]\text{Br}^e$ | 106.9 | 114.0 | 119.7 | 125.2 |
| $[\text{Co en SO}_3]\text{Br}^f$ | 108.1 | 115.1 | 122.8 | 127.6 |
| $[\text{Co en S}_2\text{O}_8]\text{Br}^f$ | 96.4 | 104.1 | 113.0 | 118.5 |
| $[\text{Co en CO}_3]\text{Br}^f$ | 101.4 | 103.5 | 105.4 | 106.1 |
| $[\text{Co en C}_2\text{O}_4]\text{Br}^f$ | 100.1 | 103.9 | 107.6 | 107.7 |
| Mean | 103 | 108 | 114 | 117 |

^a A. Werner and A. Miolatti, *Z. physik. Chem.*, **21**, 237 (1896). ^b A. Werner and A. Miolatti, *ibid.*, **12**, 43 (1893). ^c A. Werner and C. Herty, *ibid.*, **38**, 337 (1901). ^d H. J. S. King, *J. Chem. Soc.*, 2107 (1925). ^e J. C. Duff, *ibid.*, 52 (1922). ^f J. C. Duff, *ibid.*, 452 (1922).

The molar conductivity value of complex I at every dilution falls between the values of MX_2 and $\text{M}'\text{X}$, where X is a univalent anion. Accordingly we may regard I as a rare example of a double salt made up of two kinds of complex salts.

When the cobalt(III) ion is surrounded by an octahedron of three nitrogen and three oxygen atoms the configurations shown in Fig. 1 are possible. In fact the trisglycinato-cobalt(III) complex exists in two forms (α and β) to which these configurations have been assigned on the basis of their absorption spectra.²

As is now generally recognized, the splitting of the first absorption band of the cobalt(III) complex³ becomes marked as the symmetry of the ligand field decreases. Because the first band of the α form is split, and that of the β form is not,

(2) Y. Shimura and R. Tsuchida, *ibid.*, **29**, 311 (1956).

(3) E.g., M. Linhard and M. Weigel, *Z. anorg. u. allgem. Chem.*, **271**, 101 (1952).

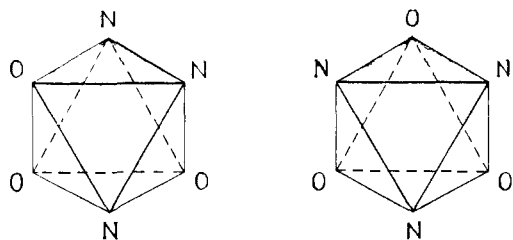


Fig. 1.—Left, *cis-trans* configuration and right, *cis-cis* configuration.

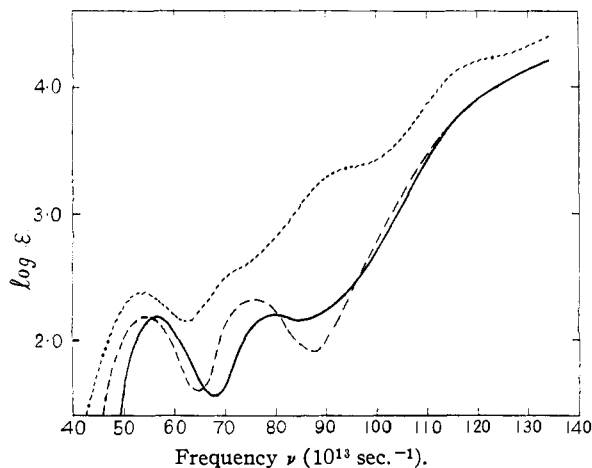
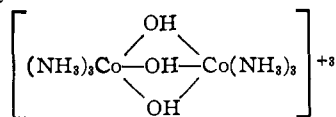


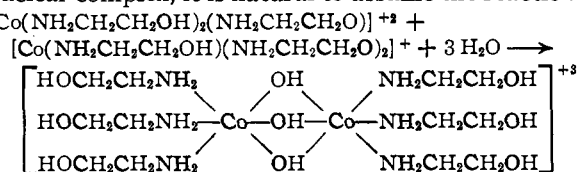
Fig. 2.—The absorption spectra of: —, the nitrate of complex I; ---, complex II; - · - · - ·, the binuclear triol complex.

Shimura and Tsuchida assigned the *cis-trans* configuration to the α form and the *cis-cis* configuration to the β form. In the present case, the first bands of complex I and II are both nearly symmetrical parabolic curves with absorption maxima at $55.5 \times 10^{13} \text{ sec.}^{-1}$ and $54.5 \times 10^{13} \text{ sec.}^{-1}$, respectively (Fig. 2). As there is no indication of splitting, we can assume that I and II have the *cis-cis* configuration.

The assignment of the *cis-cis* configuration is supported by the following finding. Upon standing, the dilute aqueous solution of I changes from a purple-red to a transparent dark brown solution in a few days. The absorption spectrum of this brown solution, which is included in Fig. 2, resembles that of the binuclear olate complex, particularly



complex.⁴ The band of high intensity at $\nu = 95 \times 10^{13} \text{ sec.}^{-1}$ is characteristic of the olate cobalt(III) complex. For the formation of this binuclear complex, it is natural to assume the reaction



(4) Y. Inamura and Y. Kondo, *J. Chem. Soc. Japan (Pure Chem. Sec.)*, **74**, 627 (1953).

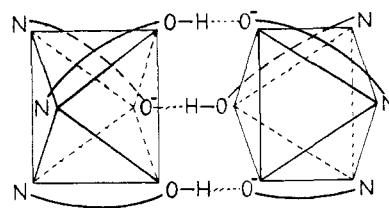


Fig. 3.—Face-to-face bonding.

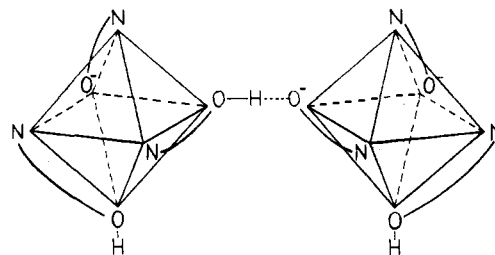


Fig. 4.—Corner-to-corner bonding.

The formation of this triol complex is permitted only when the original complexes have a *cis-cis* configuration.

The composition and behavior in solution of complex I indicate that it is a double salt composed of two kinds of complex salts. However, it is very doubtful that this new compound is actually a double salt. For in the case of ordinary double salts, substitution of the anion, e.g., the replacement of nitrate by bromide or perchlorate ion, often results in decomposition. In the present case the anion had no effect on the composition of the complex, *i.e.*, it was a 1:1 mixture of $[\text{Co eta}_2 \text{ eta}']\text{X}_2$ and $[\text{Co eta eta}']\text{X}$ in all cases. Therefore, although the new compound may be regarded as a double salt from the viewpoint of composition, it is possible that two different cations, $[\text{Co eta}_2 \text{ eta}']^{+2}$ and $[\text{Co eta eta}']^+$, do not exist in the crystal but that they exist in an indistinguishable form due to hydrogen bonding; two possible structures are illustrated in Figs. 3 and 4. This problem should be investigated by X-ray analysis.

Experimental

Complex I.—The trisethanolamine cobalt(III) complex is easily prepared by heating a cobalt(III) pentammine or tetrammine complex⁵ with ethanolamine. A slight excess of ethanolamine is effective in preventing thermal decomposition of the desired complex; a large excess results in an increase of the viscosity of the reaction mixture which makes crystallization difficult. Strong heating for evaporation should be avoided. The bromide and perchlorate also were prepared by the following method.

A mixture containing 10 g. (0.03 mole) of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$, 6 g. (slightly more than 0.09 mole) of distilled ethanolamine (b.p. 171°) and 50 ml. of water was heated with frequent stirring. When the temperature exceeded 90° , the reaction took place and ammonia was evolved. The liquid became purplish red. After heating 30 minutes (the water lost by evaporation was compensated for), the mixture was kept at room temperature for an hour. The small amount of $[\text{Co}(\text{NH}_3)_5](\text{NO}_3)_3$ produced by the disproportionation of the pentammine complex was filtered and the filtrate was evaporated by gentle heating to half of its original volume and kept at room temperature for two or three days. Purple-red crystals separated (yield 8 g.) which were recrystallized from 20 ml. of warm water (about 50°).

The crystalline nitrate, bromide and perchlorate com-

(5) The reaction between the luteo salt and ethanolamine proceeds smoothly only under the catalytic action of activated charcoal.

plexes are all prisms or plates belonging to the monoclinic system. The nitrate and bromide are very soluble in water, the perchlorate considerably less so. Although in dilute solution the complex hydrolyzes readily to a binuclear complex, it is very stable in concentrated solution, at least at room temperature.

Complex II.—To an ice-cooled solution of complex I nitrate (4 g.) in 15 ml. of water was added dropwise 5 ml. of an ice-cooled 6 *N* sodium hydroxide solution with stirring. The violet crystalline powder which separated was washed with a small amount of cold water and then with alcohol and

dried in air; yield 2 g. As complex II is not as soluble in water or as stable in solution as complex I, recrystallization from water was not attempted. The yield depends upon the concentration of the solution of the original complex. The crystals obtained from dilute solution were small cubes.

Measurement of Absorption Spectra.—A Shimadzu Quartz Spectrograph and a Beckman DU Spectrophotometer were used for the absorption measurements. As both complexes are rather unstable, the measurements were made as quickly as possible on freshly prepared solutions which were replaced frequently.

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The Amine Complexes of Aluminum Hydride. I.

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A new synthesis has been developed for the tertiary alkyl amine complexes of aluminum hydride utilizing lithium aluminum hydride and an amine hydrochloride. Substituted amino aluminum hydrides also have been prepared. Molecular weight determinations on the products have shown them to be associated and their probable structure is discussed.

Aluminum hydride has been found to form a 1:1 and a 2:1 complex with trimethylamine.¹ Several other 1:1 complexes with tertiary alkyl amines were reported² later in a brief communication. These complexes were prepared by direct combination of aluminum hydride with the appropriate anhydrous amine.

The formal similarity between diborane and aluminum hydride suggested an alternate route to these compounds which was analogous to the preparation of trimethylamine borane from lithium borohydride and trimethylammonium chloride,³ the reaction between lithium aluminum hydride and trialkyl ammonium chlorides.

Experimental

All the alkylamine alanes prepared were extremely sensitive to oxygen and moisture. Therefore all handling and storage of the products, melting points and preparation of solutions were performed in a nitrogen filled dry box.

Materials.—The lithium aluminum hydride used was the commercial grade obtained from Metal Hydrides, Inc. The alkylammonium chlorides were prepared from the anhydrous amine and hydrogen chloride gas in diethyl ether solution and were handled under a blanket of nitrogen and dried under high vacuum before use.

Trimethylamine Alane. Method A.—A sample of finely ground lithium aluminum hydride weighing 2.2 g. was placed together with 4.5 g. of trimethylammonium chloride in a 200 ml. flask. The flask was attached to the vacuum line and 100 ml. of dried ether was condensed into it with liquid nitrogen. The flask was allowed to warm slowly to room temperature with stirring. After gas evolution had ceased the flask was attached to a vacuum sublimation apparatus. The solvent was removed under vacuum until a paste remained in the flask. Then a -50° bath (Dry Ice and acetone) was placed around the trap of the sublimator. A warm water bath ($35-40^{\circ}$) was placed around the flask and the product collected in the trap. Sublimation was complete in approximately 2 hr. The sublimation apparatus was removed to the dry box where it was opened. The yield was 3.7 g. or 89%.

Method B.—A sample of finely ground lithium aluminum hydride weighing 4.0 g. was stirred in 150 ml. of dry ether in the dry box for twenty minutes. Then 8.0 g. of trimethylammonium chloride was added slowly to the ethereal solu-

tion. About half way through the addition more ether had to be added to the mixture to replace that lost by evaporation. After gas evolution had ceased the mixture was filtered and the clear filtrate was poured into a 200 ml. flask. The flask was removed from the dry box and attached to the vacuum sublimation apparatus. It was treated as described in Method A. The yield was 7.3 g. or 88%.

The other trialkylamine alanes and the *N*-dialkylaminoalanes were prepared similarly. All sublimed readily at temperatures up to 40° except the tri-*n*-propylamine alane which sublimed very slowly. It also could be recrystallized from hexane at -80° .

Analysis.—The products were analyzed for active hydrogen in the following manner. A sample of the compound was weighed directly in a small flask. The flask was attached to the vacuum line and evacuated briefly. Then about 20 ml. of dry ether was condensed into the flask, followed by 10 ml. of methanol. The mixture was allowed to warm. After the reaction was complete the mixture was cooled to -196° and the gas that was evolved was transferred to a system of calibrated storage bulbs *via* a Toepler pump.

Aluminum analysis was accomplished by preparing a standard ethereal solution of the compound in the dry box. The ethereal solution was carefully hydrolyzed with methanol and a mixture consisting of 40 ml. of isopropyl alcohol and 5 ml. of concd. nitric acid was added to it. The solution was evaporated on a water-bath to near dryness before taking up with dilute hydrochloric acid. The aluminum content of the aqueous solution was determined by the 8-hydroxyquinoline method.

A weighed sample of the polymer prepared by heating dimethylallylamine alane was hydrolyzed with methanol and the amount of active hydrogen present determined. The aluminum content of the resulting methanol solution also was determined. The molar ratio of active hydrogen to aluminum was found to be 2.10. For a sample of 0.261 g., 4.76×10^{-3} mole of hydrogen gas was produced and 2.27×10^{-3} mole of aluminum was found. The percentage of aluminum content, 23.5, agrees closely with that calculated for the monomer (see Table I).

Molecular Weights.—The molecular weight apparatus consisted of a cell within a vacuum jacket. Two thermocouple wells and a magnetically driven stirrer were fitted into the top of the cell so that a closed system resulted when the apparatus was assembled. Temperature measurements were made with eight multiple copper-constantan thermocouples. A Leeds and Northrup potentiometer (Mod. 8662) and galvanometer (Mod. 2430-C) were used to measure e.m.f.

The benzene used as solvent was dried over lithium aluminum hydride at the reflux temperature for several hours prior to distillation. The molal freezing point depression constant was determined in mv. by utilizing standard solutions of toluene in benzene. An average value of 1.499 ± 0.005 mv. g./mole was obtained for five runs.

(1) E. Wiberg, H. Grat and R. Uson, *Z. anorg. u. allgem. Chem.*, **272**, 221 (1953).

(2) E. Wiberg and H. Noth, *Z. Naturforsch.*, **106**, 237, 1955.

(3) G. W. Schaeffer and E. T. Anderson, *THIS JOURNAL*, **71**, 2143 (1949).