determined by using a gas measuring tube in such a way that the materials were confined over mercury. First, a sample of gas was placed in the tube and measured. Second, a measured sample of trifluoroacetic acid was added from a hypodermic syringe. The apparatus was then shaken mechanically for several hours until repeated measurements of the volume of gas in the tube indicated that the solution had become saturated. By using the measured changes in the volume of gas and by applying a correction for the partial pressure of trifluoroacetic acid vapor, it was possible to calculate the solubility coefficients given in Table XI. The coefficient given is that of Ostwald. It is the volume of gas (ml.) absorbed in unit volume of solvent (1 ml.), the pressure of the gas being that existing over the solution. The pressure given in the table is the difference between atmospheric pressure and the partial pressure of trifluoroacetic acid. To permit a comparison, the table also gives the corresponding solubility coefficients for aqueous solutions of the same gases as found in the literature[8,9] for a temperature of 25°, and partial pressures of 74 to 76 cm.

TABLE XI

SOLUBILITIES OF GASES IN TRIFLUOROACETIC ACID

Gas	Temp., °C.	Partial pressure of gas, cm.	Ml. of gas dissolved in one ml. of solvent In CF_3COOH	In H_2O_2[8,9]
CO_2	27	65.2	3.5	0.826
CO	26	64.6	0.0	0.0208
Cl_2	25.5	65.6	9.3	1.985
HBr	26	65.7	6.6	580
HCl	26	65.2	4.1	423
H_2S	26	65.7	8.6	2.46
N_2	26	63.6	0.1	0.0156
N_2O	24.5	66.5	4.3	0.65
O_2	27	64.2	0.2	0.0309
PH_3	26	65.3	15.9	?
SO_2	26	66.7	23.4	35.7

Discussion

Although trifluoroacetic acid is not a good ionizing solvent, rapid reactions resembling ionic reactions in water do occur. Many of these changes proceed to completion. The ease with which they occur suggests that the reactants exist as ion pairs. Many precipitation reactions which do not occur in water proceed in trifluoroacetic acid. Generally speaking, precipitation reactions of hydrogen sulfide which take place in acidic aqueous solutions also occur in anhydrous trifluoroacetic acid. An exception to this is the failure of lead sulfide to precipitate in trifluoroacetic acid. A large number of precipitates were obtained in trifluoroacetic acid which are not produced in water. This is especially true for the precipitation of the perchlorates.

The observed high solubilities of gases confirm other studies[2,4] which have indicated the excellence of trifluoroacetic acid as a solvent. Most of the gases tested are considerably more soluble in the acid than in water. The exceptions to this are the hydrogen halides and sulfur dioxide which are highly soluble in water, because they react with the solvent.

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SEATTLE 5, WASHINGTON

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[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XII. Cobalt(II) Complexes of Tetraethylenepentamine

BY HANS B. JONASSEN AND FRED W. FREY[1]

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The complexing tendency of tetraethylenepentamine (abbrev. tetren) with the cobalt(II) ion has been determined. The data indicates that all five amino groups of tetren coördinate. The sixth coördinating position can be occupied by H_2O, CH_3OH or the OH^- ion. The complexity constants of $[\mathrm{CotetrenH_2O}]^{2+}$ have been determined at 25, 35 and 45°. The complex ion $[\mathrm{CoTetrenOH}]^{1+}$ has been shown to oxygenate reversibly with only a slight amount of oxidation.

Introduction

The metal complexes of polyamines containing up to four amino groups have been investigated extensively.[2,3]

The purification of tetraethylenepentamine (abbrev. tetren) the next higher polyamine has only recently been accomplished.[4]

The present study was undertaken to investigate the type of complexes formed between the cobalt(II) ion and tetren.

Experimental

A. **Materials.**—The tetren was obtained from the Carbide and Carbon Corporation and purified as described previously.[4] All other chemicals were C.P. materials.

B. **Instruments.**—The *p*H measurements were made with a Model G *p*H meter standardized with Beckman buffer solutions of *p*H 4, 7 and 10. The solutions were measured in constant temperature baths at 25 ± 0.2°, 35 ± 0.2°, and 45 ± 0.2°. The spectrophotometric measurements were made on a Beckman Model B spectrophotometer with matched Corex cells. The conductometric titrations were performed as described earlier.[5]

C. **Determination of Log *K* Values of** $[\mathrm{CotetrenH_2O}](ClO_4)_2$.—The complexity constants of the cobalt tetren complex were determined by the method of Bjerrum[6] at 25,

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[1] Abstracted in part from the Ph.D. dissertation of Fred W. Frey, Tulane University, 1954.

[2] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).

[3] H. B. Jonassen, G. G. Hurst, R. B. LeBlanc and W. Meibohm, THIS JOURNAL, **56**, 16 (1952).

[4] H. B. Jonassen, F. W. Frey and A. Schaafsma, *ibid.*, **61**, 504 (1957).

[5] H. B. Jonassen, R. E. Reeves and L. Segal, *ibid.*, **77**, 2667 (1955).

[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

35 and 45°; 100 ml. of a solution 0.001 M in tetren 0.5 M in HNO_3 and 0.0005 M in $Co(ClO_4)_2$ were titrated with 0.01 M NaOH. The values of log K are 15.07 at 25°, 14.97 at 35° and 14.87 at 45°.

D. Conductometric Titrations. 1. Titration of Tetren with $CoCl_2$.—In the titration of 2 ml. of 0.2134 M tetren in acetone with 0.051 M $CoCl_2$ in acetone breaks occur at mole ratios of about 0.98 cobalt to 1 tetren and 1.98 cobalt to 1 tetren (Fig. 1). A precipitate forms which initially is brown but becomes green as excess of $CoCl_2$ is added.

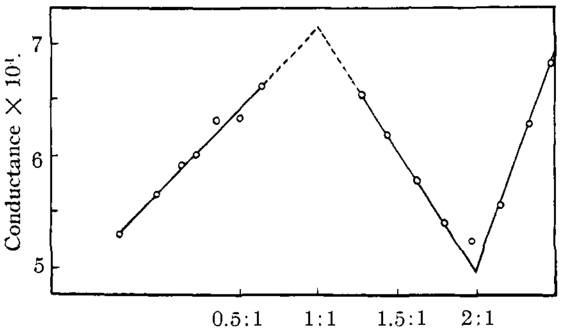

Fig. 1.—Ratio Co/amine.

2. Titration of $CoCl_2$ with Tetren.—Ten ml. of 0.051 M $CoCl_2$ in acetone was titrated with 0.2134 M tetren in acetone. A break occurs at a ratio of 2 moles Co to 1 of amine. The precipitate is initially green but turns brown as more tetren is added.

3. Titration of Tetren with $Co(ClO_4)_2$.—A methanol solution of tetren was titrated with $Co(ClO_4)_2$ in methanol, since the complex is insoluble in methanol. Two ml. of 0.599 M tetren was titrated with 0.559 M $Co(ClO_4)_2$ at 1 and 30°. A break in the curve occurs at a mole ratio of 1.08 moles tetren to 1 mole cobalt.

E. Preparation of the Solid Complexes. 1. $[CotetrenCH_3OH]Cl_2$.—Since the conductometric titration curves indicated the brown species formed in excess tetren, this complex was precipitated from a solution containing an excess of tetren. Three hundred ml. of 0.041 M $CoCl_2$ in acetone was added to 100 ml. of 0.2134 M tetren in acetone. Acetone was added to complete precipitation. The precipitate was filtered by suction, recrystallized from methanol and acetone.

Anal. Calcd. for $[CotetrenCH_3OH]Cl_2$: Cl, 20.2; N, 19.9. Found: Cl, 19.76; N, 19.29.

2. $[CotetrenCH_3OH]CoCl_4$.—Seventy-five ml. of 0.234 M tetren in acetone was added to 400 ml. of 0.051 M $CoCl_2$ in acetone. The precipitate was filtered and recrystallized from methanol and acetone.

Anal. Calcd. for $[CotetrenCH_3OH]CoCl_4$: N, 14.5; Cl, 29.5. Found: N, 14.04; Cl, 29.90.

In order to establish the existence of the $CoCl_4^{2-}$ ion the precipitate was allowed to come to equilibrium with acetone at 25° and the spectra observed. A maximum is observed at about 695 mμ which has been described by Katzin[7] to the $CoCl_4^{2-}$ ion.

3. $[CotetrenCH_3OH](ClO_4)_2$.—Twenty-two ml. of 0.56 M $Co(ClO_4)_2$ was added to 20 ml. of 0.6015 M tetren in methanol and precipitation completed by addition of 25 ml. of ether. The brown precipitate was filtered and washed with methanol and dried in an oven at 90°.

Anal. Calcd. for $[CotetrenCH_3OH](ClO_4)_2$: Co, 12.2; N, 14.7. Found: Co, 12.2; N, 14.35.

4. $[CotetrenOH]_2PtCl_6$.—Although the perchlorate complex is only slightly soluble in CH_3OH, it dissolves very rapidly in methanolic NaOH or KOH. From this it was concluded that the methanol molecule was replaced by hydroxide ions. Chloroplatinic acid in methanol was added and a brown precipitate was formed.

Anal. Calcd. for $[CotetrenOH]_2[PtCl_6]$: Pt, 20.6; Co, 12.4. Found: Pt, 20.6; Co, 12.1.

F. Oxygenation and Deoxygenation of $[CotetrenOH]ClO_4$. **1. Oxygenation.**—Attempts to oxygenate $[CotetrenH_2O]^{2+}$ in water solution were unsuccessful in neutral or basic solution, oxidation to cobalt(III) occurs.

However, when 10 ml. of methanolic NaOH solution containing 0.0913 g. of the complex was placed in an oxygen atmosphere at 32° a rapid pickup of oxygen occurred during the first 10 minutes, as determined in a vapor pressure apparatus. After 15 minutes, further volume changes were very slight indicating that only extremely slow oxidation occurs.

Figure 2 shows the curve obtained when volume is plotted against time in minutes. A blank of 10 ml. of methanolic NaOH in the system produced a negligible volume decrease of 0.1 ml.

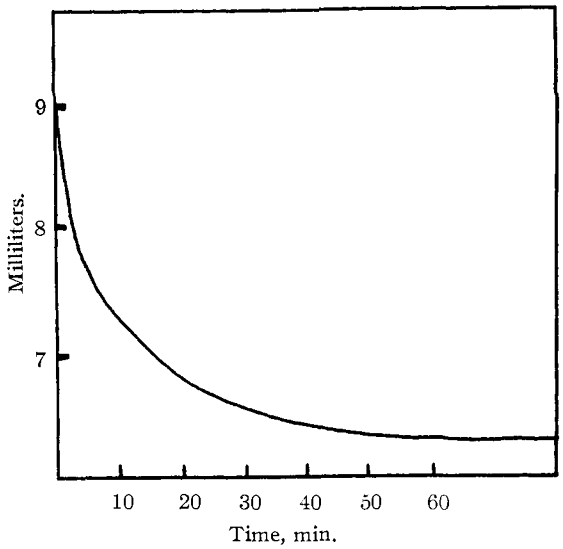

Fig. 2.—Rate of oxygenation.

2. Deoxygenation of the Complex.—Eighteen ml. of a methanolic NaOH solution containing 0.15 g. of the oxygenated complex were placed in a vapor pressure apparatus until equilibrium vapor pressure was obtained. Similarly the vapor pressure of a blank 18 ml. of methanolic NaOH solution was measured. The corrected volume of oxygen released by the oxygenated complex was 4.09 ml.

Discussion of Results

As expected, the log K values for the 1:1 complexes are greater for $[Cotetren]^{2+}$ (log K formation = 15.1) than for $[Cotrien]^{2+}$ (log K formation = 11.1). Analysis of the precipitates indicate that methanol and hydroxide ions seemingly can occupy the sixth position in this complex.

As the oxygenation and deoxygenation data show only in a methanolic NaOH solution can the complex become oxygenated; in water solution *oxidation* occurs immediately. If it is assumed that oxygenation occurs through an oxygen–oxygen bridge between two cobalt complexes the theoretical volume of oxygen recovered from the sample should have been 4.43 ml. whereas experimentally only 4.09 ml. was recovered, a decrease of about 8%. This seems to indicate some oxidation occurred for these complexes in line with the observation of the slight decrease in volume during the oxygenation studies.

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NEW ORLEANS, LA.

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