In 1910 Zemezuzny and Rambach,[7] using thermal analysis, reported that both potassium chloride and rubidium chloride form a solid solution with cesium chloride and that each of these salts lowers the transition temperature of cesium chloride but that this lowering could no longer be detected when the amount of the potassium chloride or rubidium chloride exceeded a few per cent. Preliminary results of the X-ray analysis indicate that these salts do indeed produce lowering of the transition temperature of cesium chloride. The extent of this lowering and its correlation with composition will be reported shortly in another publication.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XVII. Reaction of Complexes of Cobalt(II) and Quadridentate Amines with Hydroxide Ions

BY HANS B. JONASSEN AND GAYLE T. STRICKLAND[1]

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When hydroxide ions are added to solutions containing the triethylenetetramine-cobalt(II) ion (abbrev. [Cotrien]$^{2+}$), the existence of the complexes [CotrienOH]$^+$ and the oxolated polymer (–O–Cotrien–O–) are indicated. Under similar conditions the tris-(2-aminoethyl)-amine-cobalt(II) (abbrev. [Cotren]$^{2+}$) ion forms [CotrenOH]$^+$ and the dimer [Co$_2$tren$_2$(OH)$_{3/2}$]$^+$. Studies have shown that of these tetramine complexes only the [Co$_2$tren$_2$(OH)$_{3/2}$]$^+$ can decompose H_2O_2. The stereochemical reasons for this are discussed.

Introduction

The complex compounds formed between polyamines and cobalt(II) have been investigated in various laboratories.[2-4] Jonassen and Frey[5] reported that the complex formed by the cobalt(II) ion and tetraethylenepentamine (abbrev. tetren) was able to be oxygenated in basic methanol solution.

The purpose of this study was to determine the types of complexes formed between cobalt(II) ion and the tetramines, triethylenetetramine and tris-(2-aminoethyl)-amine (abbrev. trien and tren, respectively) in the presence of hydroxide ions and to attempt to elucidate the stereochemical structure of the possible hydroxy complexes.

Experimental

A. **Reagents.** (1) **Separation and Purification of Trien and Tren.**—The amine mixture containing approximately 62% trien and 38% tren, which was obtained from Carbide and Carbon Chemical Corporation, was separated and purified as follows.

Two hundred grams of the mixture was dissolved in ethanol and cooled to approximately 5° in an ice-bath. Concentrated hydrochloric acid was added dropwise from a buret at such a rate that the temperature was kept below 10°. A white crystalline precipitate formed after a time and this was removed in several fractions.

The addition of hydrochloric acid was eventually continued until a thick creamy white precipitate formed. Again fractions were taken until precipitation ceased. The dark reddish mother liquor was discarded.

The middle fractions of the white crystalline precipitate were combined and the first and last fractions were discarded. This was also done with the creamy white precipitate. Each salt was recrystallized several times by dissolving it in a minimum of hot water and precipitating it with an excess of cold ethanol. The salts were washed with acetone, then ether and then dried in a vacuum desiccator.

The salts were analyzed mercurimetrically[6] for chloride. The crystalline salt which precipitated first was found to be 99.5% tren·3HCl. The slightly cream-colored salt with a satiny luster was found to be 99.8% pure trien·4HCl.

(2) **Other Reagents.**—Carbonate-free solutions of sodium hydroxide were prepared and standardized against potassium acid phthalate. The solution of cobalt(II) ion was standardized electrolytically. All other reagents used were of C.P. quality. All aqueous solutions were prepared with oxygen-free water.

Oxygen-free nitrogen was prepared by leading the gas through an acid solution of chromous ion in a continuous cycle so that the oxidized chromic ion immediately was reduced by zinc amalgam.

B. **Apparatus.**—The conductometric titrations were performed with a standard potentiometer in a Wheatstone Bridge arrangement using vertical platinized electrodes.

Potentiometric measurements were obtained with a Beckman Model G *p*H meter. Spectrophotometric measurements were made with a Model B spectrophotometer. Standard one cm. matched Pyrex cells were used. Much difficulty was encountered because of oxidation of the solution during transfer to the absorption cell. The oxidation product was intense reddish-brown and absorbed strongly at 360 mμ. Even slight oxidation obscured all measurements up to about 550 mμ. A number of techniques were tried to prevent oxidation; the one which gave the most reproducible results is given in detail below.

A Pyrex cell, hypodermic syringe, two hypodermic needles and a 50-ml. flask with a nitrogen inlet tube near the bottom and a nitrogen exit tube near the top were thoroughly cleaned and dried at 120°. Pure nitrogen was bubbled through the component solutions for a period of 30 minutes to remove dissolved oxygen. The nitrogen was introduced into each solution through a pipet of the proper size to transfer a portion of the solution into the sample flask. This also served to flush the air out of the pipet. The Pyrex cell was fitted with a rubber cap made from the upper portion of a medicine dropper bulb. A trace of glycerol was used to form a seal between the cell and cap. Also, a strip of Scotch Tape was placed around the cap and cell in such a manner that the cap was securely held in place. Two hypodermic needles were inserted into the cap, one of which served as a nitrogen inlet and the other as a nitrogen outlet. In this manner the atmospheric oxygen was flushed out of the cell. The outlet needle was then coupled to the hypodermic syringe. The nitrogen was allowed to force the plunger back and thus fill the syringe. The syringe was then disconnected from the needle and the nitrogen was forced out with the plunger. This was repeated several times in order to flush all atmospheric oxygen out of the syringe.

The 50-ml. flask was flushed out with nitrogen. Then the proper amount of each component was transferred into this flask, using the pipets which were serving as nitrogen

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[1] Abstracted in part from the M.S. Thesis of Gayle T. Strickland, June, 1956.

[2] J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

[3] G. Schwarzenbach and J. E. Prue, *Helv. Chim. Acta*, **33**, 963 (1950).

[4] H. B. Jonassen and F. W. Frey, THIS JOURNAL, **75**, 1524 (1953).

[5] H. B. Jonassen and F. W. Frey, *ibid.*, in press.

[6] I. N. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 576.

inlets for each container of component solution. The hypodermic syringe and needle were withdrawn from the rubber capped cell with the syringe filled with nitrogen. A few drops of water were placed around the plunger at the rear of the syringe to form a moisture seal. This prevented the leakage of air between the ground glass surfaces into the chamber when the syringe was being filled with sample. The moisture seal was small enough so that it was not pulled down into the chamber at the same time that the solution was being drawn up into the syringe.

The sample was then injected into the cell through the rubber cap. During the time that the nitrogen outlet needle was used to transfer the sample, the cell was maintained under a positive pressure of nitrogen through the inlet needle. After the cell was filled with a sample, both needles were withdrawn.

It was observed that best results were obtained if the sample was allowed to flow slowly from the needle as the tip was passed into the rubber cap on the cell. This excluded the portion of the sample in the tip of the needle that was exposed to the air.

Magnetic susceptibility measurements were made with a modified Curie Cheneveau balance. The sample vial was a 9.5 cm. piece of 12 mm. glass tubing, sealed at one end. At the other end a small cork served to seal the tube and a piece of copper wire through the cork was used to support the vial on the quartz torsion wire.

In all measurements, techniques similar to those described for the spectrophotometric investigation had to be used to prevent oxidation or oxygenation of the solutions.

C. **Decomposition of H_2O_2.**—To a 0.08 molar solution of $[Cotrien]^{2+}$ containing slightly more than 3/2 equivalents of NaOH, five ml. of 30% H_2O_2 was added. The solution changed from violet to brown without evolution of gas. This was repeated for the $[Cotren]^{2+}$; after addition of 5 ml. of 30% hydrogen peroxide, the solution turned from green to red and vigorous evolution of oxygen occurred.

Discussion of Results

1. **Conductometric Titrations.**—Figure 1 shows the conductometric data obtained when mixtures of 0.2 mmole each of $CoCl_2$ and trien·4HCl and of $CoCl_2$ and tren·3HCl, respectively, were titrated conductometrically with 1 *N* NaOH. In the trien system breaks are evident at 1, 4, 5 and 6 equivalents of NaOH. After the sixth equivalent, the slope of the line is equal to that obtained with NaOH of the same concentration.

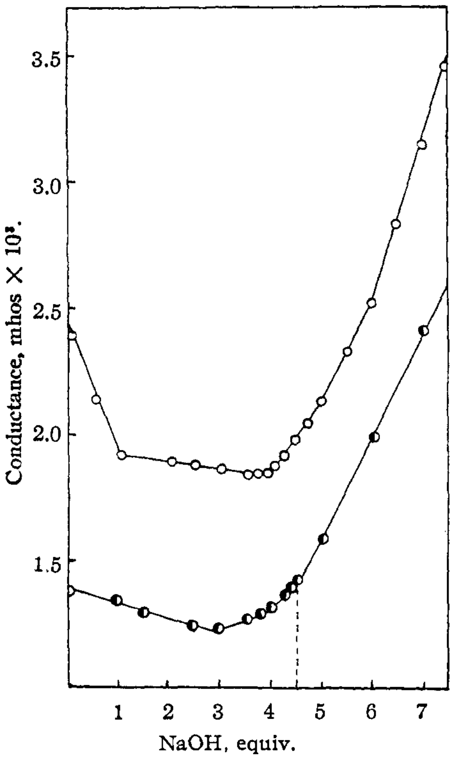


Fig. 1.—Conductometric titration of $CoCl_2$ + trien·4HCl and $CoCl_2$·tren·3HCl with NaOH: ○, $CoCl_2$ + trien·4HCl; ◐, $CoCl_2$ + tren·3HCl.

The break at 1 equivalent seems to indicate that the first reaction is the neutralization of the first hydrogen of the tetra-hydrochloride tetren. From 1 equivalent to the break at 4 equivalents, complexation of the cobalt(II) ion occurs, which is complete at 4 equivalents, giving a 1:1 complex.

Since only hydroxide ions are added, the breaks at 5 and 6 equivalents then seem to indicate two possible hydroxy complexes, $[Cotrien(H_2O)OH]^+$ and $[Cotrien(OH)_2]$. Jonassen and Frey[5] found indication of a similar hydroxy complex $[Cotetren\text{-}OH]^+$ when the $[Cotetren]^{2+}$ complex ion was treated with hydroxide ion.

In the tren system breaks can be observed at 3, 4 and 4.5 equivalents of NaOH. The break at 3 equivalents of NaOH indicates that all the hydrogen ions of tren·4HCl have been neutralized and the free amine complexes with the cobalt(II) ions. After 3 equivalents again hydroxy complexes seem to be formed—the first $[Cotren(OH)H_2O]^+$ at 4 equivalents. The next break occurs at 4.5 equivalents, which can best be explained by assuming the formation of the binuclear species, $[Cotren(OH)_{3/2}]_2^+$.

2. **Potentiometric Titrations.**—The titrations of the cobalt(II) ion with the quadridentate trien·4HCl and tren·3HCl reported by Schwarzenbach and Prue were repeated and carried to a larger excess of NaOH. The changes in *p*H obtained from these data are plotted against equivalents of NaOH in Fig. 2.

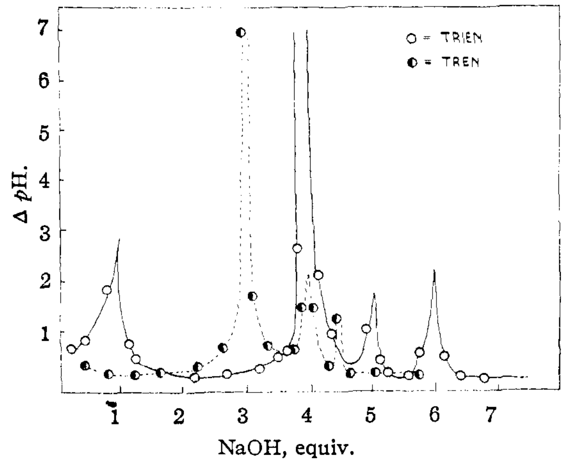
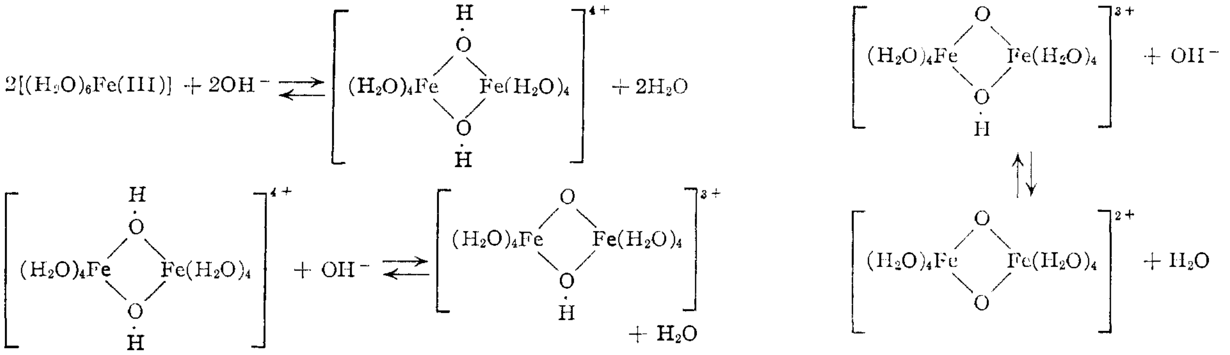


Fig. 2.—Potentiometric titration of $CoCl_2$ + trien·4HCl and $CoCl_2$ + tren·3HCl with NaOH.

For the trien complexes, maxima are observed at 1, 4, 5 and 6 equivalents. The maxima at 1 and 4 are due to neutralization of the hydrogen ions of the trien·4HCl. The breaks at 5 and 6 equivalents can best be interpreted by the formation of the hydroxy complexes $[CotrienH_2O(OH)]^+$ and $[Cotrien(OH)_2]$ (or the oxolated polymer).

For the Cotren complexes the *p*H titration data indicate maxima at 3, 4 and 4.5 equivalents. An



interpretation similar to that discussed for the conductometric data explains the breaks as being due to (a) neutralization of tren·3HCl at 3 equivalents, (b) formation of the complex $[\mathrm{Cotren(OH)H_2O}]^+$ at 4 and the dimer $[\mathrm{Cotren(OH)}_{3/2}]_2$ at 4.5 equivalents.

3. Spectrophotometric Data.—Twenty ml. of a solution containing 0.4 mmole each of $CoCl_2$ and trien or tren, respectively, were titrated spectrophotometrically with NaOH at a wave length of 540 mμ for trien and 630 mμ for tren.

Figure 3 shows the plot of absorbance difference *versus* ratio of $CoCl_2$ to cobalt(II) amine complex. The curve for trien shows breaks at a ratio of 1, 1.5 and 2.

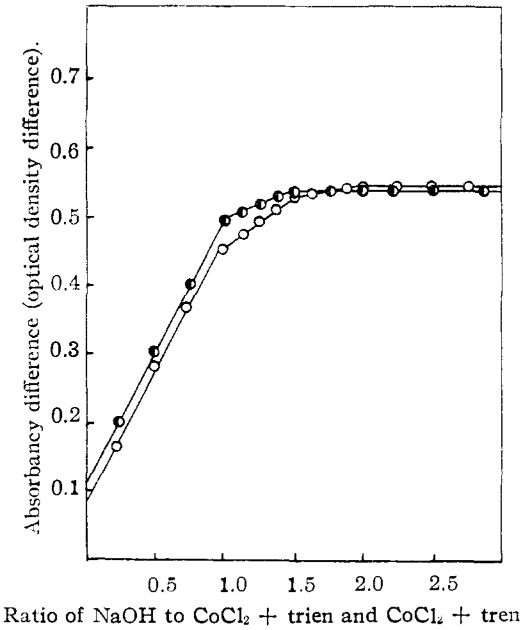


Fig. 3.—Spectrophotometric titration of $CoCl_2$ + trien and $CoCl_2$ + tren with NaOH: ○, $CoCl_2$ + trien at 540 mμ; ◐, $CoCl_2$ + tren at 630 mμ. Performed using Beckman Model B spectrophotometer at 25°. Twenty ml. of solution containing 0.4 mmole $CoCl_2$ and trien or tren titrated with NaOH. Absorbancy used as synonymous with optical density.

The breaks at 1 and 2 are in line with the previous postulation, but the break at 1.5 seems to indicate that also in the case of the cobalt(II) trien hydroxy complexes, polymers are formed which seem to be oxolation polymers.

Jander and Jahn[7] have postulated such oxolation polymers for the ferric ion in the presence of excess hydroxide ions, as indicated in the three equilibria above. Analogous hydroxychromium complexes have been discussed recently by Wilmarth and coworkers.[8]

The data obtained for the tren complexes indicate breaks at 1 and 3/2 OH^- excess. This would lead to the conclusions previously described, namely, the existence of the complexes $[\mathrm{CotrenH_2O(OH)}]^+$ and $[\mathrm{Cotren(OH)}_{3/2}]_2$.

4. Magnetochemical Data.—Mulay and Selwood[9] interpreted decreases in paramagnetic susceptibility for hydrated ferric ions as evidence of hydroxy bridge formation through which spin exchange could occur. Dunitz and Orgel[10] explained similar magnetic susceptibility decreases in the binuclear ruthenium complex, $K_4[Cl_5Ru–O–RuCl_5]$, from the molecular orbital point of view, describing the bonding situation as "resonance between a number of structures, the extremes of $(Cl_5Ru^{IV}–O–Ru^{IV}Cl_5)$ and $(Cl_5Ru^{II}{=}O{=}Ru^{II}Cl_5)$." Such decrease also has been observed by Jonassen and Schaafsma[11] who postulate bridging through hydroxy groups for ferrous polyamine complexes.

It became of interest, therefore, to see whether such decrease in susceptibility also occurred in the cobalt(II) quadridentate amine complexes. As the curves in Fig. 4 indicate, breaks are observed at 3 and 4.5 equivalents of hydroxide ion for the tren complexes and at 4 and 6 for the trien complexes.

Magnetic susceptibility titration data were obtained with a Curie–Cheneveau type balance on solutions of 0.4 mmole of $CoCl_2$ and of the quadridentate amine hydrochloride in 5 ml. of solution. Figure 4 shows the plot of torsion deflection against equivalent NaOH concentration.

The susceptibility values at three equivalents of hydroxide ion for the tren complex and at four equivalents for trien complex are the normal one unpaired electron for cobalt(II) amine complexes. After these breaks a further decrease in susceptibility occurs for the tren and trien complexes, which seems to indicate polymerization, to $[\mathrm{Cotren(OH)}_{3/2}]_2{}^+$ and $[\mathrm{Co_2trien_2O_2}]$, respectively.

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(7) G. Jander and K. F. Jahn, *Koll. Beih.*, **43**, 315 (1936).

(8) W. K. Wilmarth, H. Graff and S. T. Gustin, THIS JOURNAL, **78**, 2683 (1956).

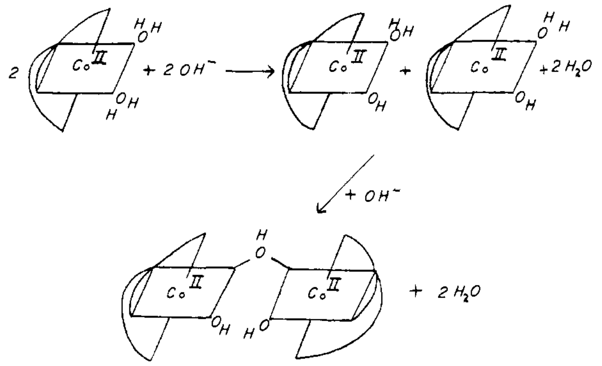
(9) L. N. Mulay and P. W. Selwood, *ibid.*, **77**, 2653 (1955).

(10) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953).

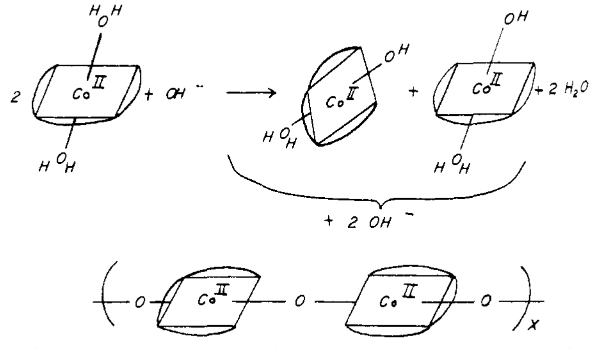
(11) A. Schaafsma, Dissertation, Tulane University, 1955.

5. Stereochemistry of the Complexes.—The above data permit certain conclusions about the stereochemistry of these complexes.

It is well known that tren imposes certain stereochemical restrictions on the configuration of its complexes. Because of its tertiary amino group, tren can only coördinate in an octahedron in such a way that the coördinating groups are *cis* to each other. In the presence of hydroxide ions the following reaction presumably takes place when there are 3/2 hydroxide ions per cobalt complex.



For the trien complex, on the other hand, the trien can coördinate in such a way that the two solvated positions are either *cis* or *trans*. However, of these, the *trans* complex is the one more stable in solution. For the trien hydroxy complexes the following reaction then seems likely.



Such structural considerations also explain why $[\text{Cotren(OH)}_{3/2}]_2$ should decompose H_2O_2 catalytically, whereas $(\text{–O–Cotrien–O–})_x$ should not. The mechanism for H_2O_2 decomposition should be similar to that proposed by Wang[12] for the $[\text{Fe(III)trien(OH)}_2]^+$ complex, but in the cobalt amine binuclear complex the decomposition of the peroxide ions should occur through hydroxide groups *cis* to each other.

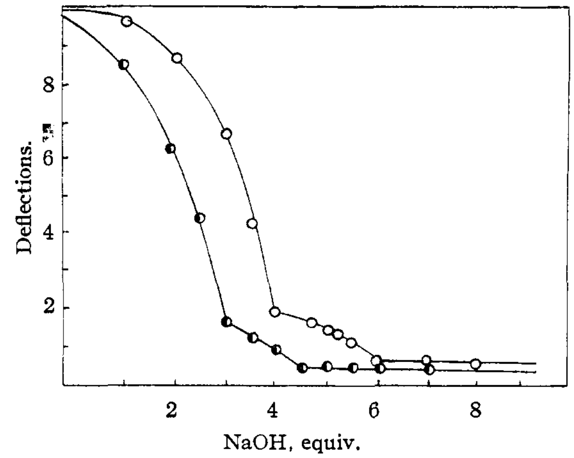


Fig. 4.—Magnetic titration of $CoCl_2$ + trien·4HCl and $CoCl_2$ + tren·3HCl with NaOH: ○, $CoCl_2$ + trien·4HCl; ◐, $CoCl_2$ + tren·3HCl.

The trien hydroxy complex on the other hand should only become oxidized since it contains no *cis* hydroxide groups in the complex. The experimental results show indeed that $[\text{Cotren(OH)}_{3/2}]_2$ decomposes H_2O_2 catalytically whereas the [Cotrienhydroxy] complex becomes oxidized.

Experiments are under way to determine the kinetics of this decomposition of hydrogen peroxide and to find out whether such a binuclear species is present with other metals and ligands.

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NEW ORLEANS 18, LOUISIANA

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(12) J. H. Wang, THIS JOURNAL, **77**, 4716 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A Polarographic Study of Thiourea Complexes of Cadmium and Lead in Aqueous Media

BY T. J. LANE, C.S.C., J. A. RYAN[1a] AND E. F. BRITTEN[1b]

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Polarographic studies of coördination complexes of thiourea with cadmium(II) ion and lead(II) ion in aqueous solution have been carried out using 0.1 *M* potassium nitrate as supporting electrolyte and Triton X-100 as maximum suppressor. Application to the data of the Hume and DeFord method of mathematical analysis showed the existence of mono-, bis-, tris- and tetrakis-coördinated species for cadmium(II) and lead(II) complexes. Their formation constants also were calculated. These results do not agree with those obtained by other workers.

Federova[2] reported the results of polarographic studies of thiourea complexes of cadmium(II) and lead(II) in aqueous solution by varying the concentration of excess ligand from 0.2 to 0.8 *M* and obtaining results indicating the presence of tris-thioureacadmium(II) ion and tris-thiourealead(II) ion. His calculations of formation constants for the respective species were made according to the

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(1) (a) Carroll College, Helena, Montana. (b) Xavier Jr. College, Sydney, N.S., Canada.

(2) O. S. Federova, *Sbornik Statei Obshchei Khim. Akad. Nauk S.S.S.R.*, **1**, 206 (1953).