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Inorganic Complex Compounds Containing Polydentate Groups. IX. Complexes of Cobalt(II) Perchlorate with Tetraethylenepentamine[1]

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RECEIVED AUGUST 18, 1952

The complex compounds formed between tetraethylenepentamines and cobalt(II) ion have been studied by spectrophotometric methods. The presence of one-to-one and two-to-one amine–cobalt complexes were indicated. The one-to-one complex was isolated and analyzed. Magnetic susceptibility measurements on the one-to-one complex, [Co tetren(H_2O)](ClO_4)$_2$, indicated an ionic octahedral complex with an effective moment corresponding to three unpaired electrons.

Introduction

The complexes formed between cobalt(II) ion and polyethyleneamines have undergone considerable investigation. Bjerrum[2] determined the complexity constant of the cobalt–ethylenediamine complex. Le Blanc[3] and Schwarzenbach[4] independently determined the constants for the complexes formed between cobalt(II) ion with diethylenetriamine and triethylenetetramine. Perrault[5] studied by spectrophotometric methods the complex formed between cobalt(II) ion and triethylenetetramine and succeeded in isolating a complex which had the formula [Co trien (H_2O)$_2$]Cl_2.

This investigation was undertaken to determine the complex or complexes formed between cobalt(II) ion and tetraethylenepentamine and to determine their structures.

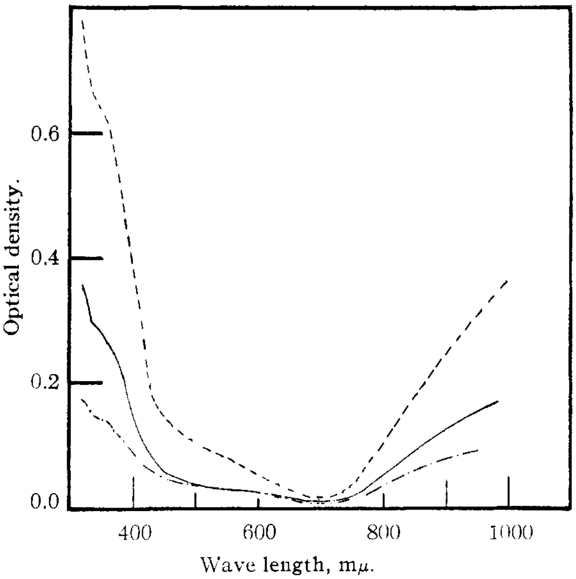

Fig. 1.—Absorption spectra of solutions containing 0.0002 *M* cobalt(II) perchlorate and varying concentrations of tetraethylenepentamine for green solutions in which ratio of amine to cobalt was 1:2, 1:1 and 3:1; optical density = log (1/transmittance); T = 30°: 3:1 amine cobalt ratio, - - -; 1:1 amine cobalt ratio, ——; 1:2 amine cobalt ratio, -·-·-. The spectra of water solutions of these complexes were determined using 1-cm. matched Corex cells.

Experimental

A. **Reagents.**—Cobalt(II) perchlorate pentahydrate was prepared by treating solid cobalt(II) carbonate with an excess of 70% perchloric acid, driving off the excess acid at 110° and evaporating to crystallization.[6] The cobalt(II) carbonate was prepared by heating a solution of Baker C.P. sodium carbonate, saturated with carbon dioxide, with Baker cobaltous chloride hexahydrate for 18 hours in a sealed tube at 150°.

The tetraethylenepentamine (abbreviated tetren) was purified by means of an anion exchange column using Ion-X Resin as the adsorbent.[7]

B. **Instruments.**—All absorption measurements were made with a model B Beckman spectrophotometer, using 1-cm. matched corex cells. The measurements are given in optical density units where OD = log (1/transmittance). The magnetic susceptibility measurements were made with a modified Curie–Cheneveau balance.[8]

C. **Absorption Studies.**—Absorptions were determined between the wave lengths of 320 and 950 mμ on solutions prepared from standard solutions 0.001 *M* with respect to cobalt(II) perchlorate and tetren. The solutions were prepared in distilled water which had been previously boiled and through which oxygen-free hydrogen and nitrogen were bubbled for several hours.

A marked change in the color of the solution was observed. Immediately after mixing the color was brownish-green. However, on standing the solutions changed to a light red color.

Absorption spectra were measured for both the red and the green solutions. All of the green solutions were 0.0002 *M* with respect to cobalt(II) perchlorate but the amine concentration varied from 0.00004 to 0.0006 *M*. For the red solutions the concentration of cobalt(II) perchlorate varied from 0.0001 to 0.0002 *M*, while the amine concentration varied from 0.0001 to 0.0006 *M*. Higher concentrations could not be employed because of the formation of a precipitate of cobalt(II) hydroxide. Figure 1 shows the absorption of three of the green solutions. The upper curve is the absorption spectrum of the solution 0.0006 *M* with respect to amine; the middle curve is the spectrum of the solution 0.0002 *M* with respect to amine; the bottom curve is the spectrum of the solution 0.0001 *M* with respect to amine. Figure 2 shows the absorption of two of the red solutions. The top curve is the absorption spectrum of the solution 0.0003 *M* with respect to amine and 0.0002 *M* with respect to cobalt perchlorate; the bottom curve is the spectrum of the solution 0.0003 *M* with respect to amine and 0.0001 *M* with respect to perchlorate. The absorption of the cobalt(II) ion and tetren solutions was below an optical density of 0.01 at all wave lengths measured and is not shown.

Using the continuous variation method as modified by Vosburgh and Cooper[9] the cobalt(II)–amine complex solutions of 0.001 *M* cobalt(II) perchlorate and 0.001 *M* tetren were prepared with varying proportions of the components

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[1] Abstracted in part from the Master's Thesis of Fred W. Frey, Tulane University, June, 1952.

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," I Kommission Hos Einar Munksgaard, Copenhagen, 1945.

[3] R. Le Blanc, H. Jonassen, G. Hurst and A. Meibohm, *J. Phys. Chem.*, **56**, 16 (1951).

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[5] E. Perrault, Thesis, Tulane University, New Orleans, Louisiana, 1948.

[6] H. Goldblum and F. Terlikowski, *Bull. soc. chim. France* (II), **102**, 146 (1912).

[7] E. Gause, H. B. Jonassen and T. B. Crumpler, THIS JOURNAL, **73**, 5457 (1951).

[8] F. W. Gray and J. Farquharson, *J. Sci. Instruments*, **9**, 1 (1932).

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such that the total solute concentration was the same in each solution.

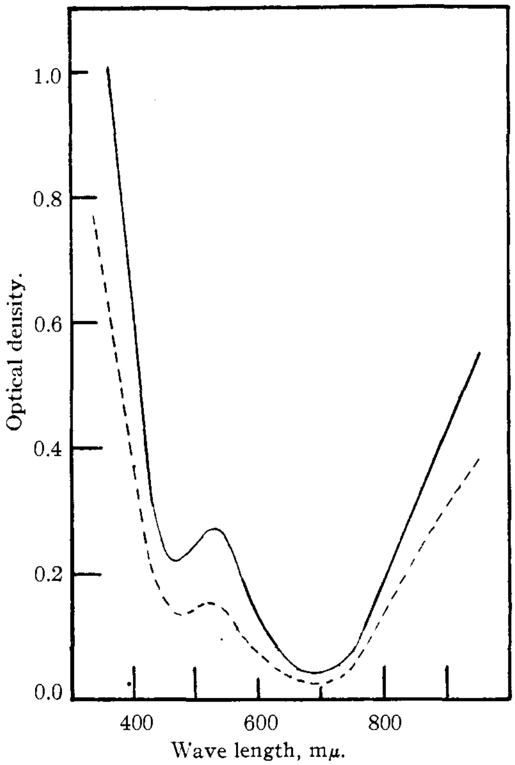

Fig. 2.—Absorption spectra of solutions containing 0.0002 *M* cobalt(II) perchlorate and varying concentrations of tetraethylenepentamine for red solutions in which ratio of amine to cobalt is 3:1 and 3:2; optical density = log (1/transmittance); $T = 30°$: 3:2 amine to cobalt ratio, ——; 3:1 amine to cobalt ratio, – – –. The spectra of water solutions of these complexes were determined using 1-cm. matched Corex cells.

Discussion of Results

A. Continuous Variation Studies. 1. Green Solutions.—The optical density of the green solutions was measured immediately after the solutions were prepared at several wave lengths, all of which indicated a two-to-one amine–cobalt complex. The data obtained for wave lengths of 320 and 350 mμ are plotted in Fig. 3, where the difference between the calculated optical density and the observed optical density was plotted against the mole fraction of tetren.

The resultant curves indicate that the green complex contained two moles of tetren to one of cobalt(II) perchlorate, since the peak in the curve occurs at a mole fraction of 0.67.

2. Red Solutions.—The green solutions turned red after 72 hours, and the optical densities were measured. The difference between the calculated optical density and the observed optical density was plotted against the mole fraction of tetren in Fig. 4.

The resultant curves indicate that the red complex contained one mole of tetren to one of cobalt(II) perchlorate, since the peak in the curve occurs at a mole fraction of 0.50.

B. Magnetic Susceptibility Studies.—Since the continuous variation studies on the red solutions indicated the presence of a one-to-one complex, the solid complex was prepared by evaporating 250 ml. of a 0.1 *M* aqueous solution of cobalt(II) perchlorate and tetren, present in a one-to-one mole ratio, to crystallization in an oven at 90°. A bluish-green precipitate formed immediately after mixing, but dissolved as evaporation proceeded. The crystals were washed with two 20-ml. portions of alcohol and ether and dried in an oven at 65°.

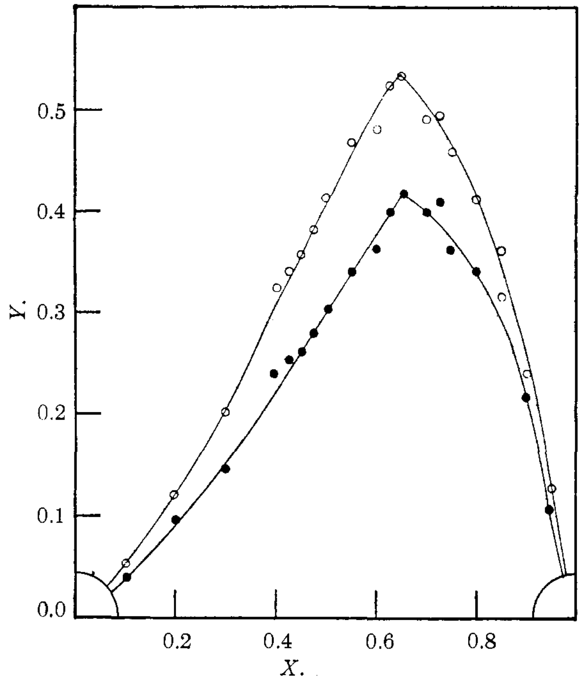

Fig. 3.—Optical density difference (*Y*) curves for green solutions containing $1-X$ mole fraction cobalt(II) perchlorate and *X* mole fraction tetraethylenepentamine at 320 and 350 mμ: ○, 320 mμ; ●, 350 mμ; optical density = log (1/transmittance); $T = 30°$. The spectra of water solutions of these complexes were determined using 1-cm. matched Corex cells.

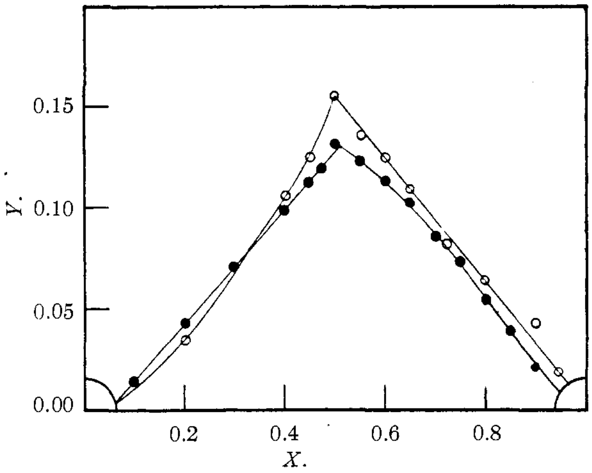

Fig. 4.—Optical density difference (*Y*) curves for red solutions containing $1-X$ mole fraction cobalt(II) perchorate and *X* mole fraction tetraethylenepentamine at 400 and 530 mμ: ●, 530 mμ; ○, 400 mμ; optical density = log (1/transmittance); $T = 30°$. The spectra of water solutions of these complexes were determined using 1-cm. matched Corex cells.

The crystals obtained by the preceding method were analyzed electrolytically for cobalt and for nitrogen by the micro-Dumas method.

Anal. Calcd. for Co(tetren)(ClO$_4$)$_2$·H$_2$O: Co, 12.7; N, 16.3. Found: Co, 12.6; N, 16.2.

The magnetic susceptibility of this complex was measured, using ferrous ammonium sulfate as the calibrating agent. The effective Bohr magneton number, u_{eff}, was found to be 4.52 Bohr magnetons. The theoretical Bohr magneton number of the ionic octahedral cobalt(II) ion should be 3.88 Bohr magnetons,[10] assuming complete quenching of the orbital moment. However, the orbital moment is not always completely quenched, which causes a moment higher than expected.[11]

The magnetic data indicate that an octahedral cobalt(II) complex is present. In order to explain the analytical results, the polyamine must be a pentadentate group and the water must occupy the sixth position, since the perchlorate ion has practically no coördinating tendency. This necessitates the assignment of the structure [Co(tetren)(H$_2$O)](ClO$_4$)$_2$ to the complex.

Acknowledgments.—The authors wish to thank the Office of Ordnance Research for the support of this and continuing investigations.

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[10] P. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 89.

[11] P. Selwood, *ibid.*, p. 100.

[Contribution from the Departments of Chemistry and Organic Chemistry of the University of Sydney]

Sexadentate Chelate Compounds. V

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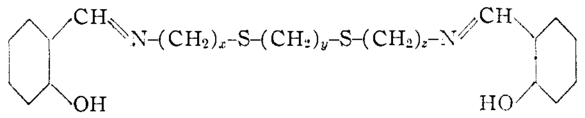
Received September 30, 1952

1,8-Bis-(salicylideneamino)-3-oxa-6-thiaoctane (I), 1,8-bis-(salicylideneamino)-3,6-dioxaoctane (II) and 1,2-bis-(γ-salicylideneamino-α-oxapropyl)-benzene (III) have been prepared and the first two shown to function as sexadentate chelate compounds. The complex ions given by I with cobalt (III) are asymmetric and the dextro and levo forms of the complex cobalt(III) iodide have been obtained pure. The complex ions given by II with cobalt(III) are unstable but a crystalline perchlorate has been prepared and analyzed.

The capacity of molecules of anils of the type



(SH$_2$) to lose two protons and then to attach themselves to metal ions, such as cobalt(III) ions, in such a way as to give complex salts of the type (CoS)A, where A is a monovalent anion, is dependent on the ability of each of the oxygen, nitrogen and sulfur atoms to function as a donor atom and to unite with the central metal atom by coördination covalences. In the complex ions so formed, the chelate moiety winds itself round the metal atom in such a way that the donor atoms become octahedrally disposed about it and, at the same time, have their own normal spatial valence demands satisfied.[2] It would appear, then, to be a logical extension of the investigation of such substances to endeavor to prepare typical anils in which one or both of the sulfur atoms have been replaced by other donor atoms which have or can have similar spatial distribution of their valences.

The valences of a 3-covalent sulfur atom are directed pyramidally, the sulfur atom and the three atoms to which it is attached occupying the apices of a flat tetrahedron. At first glance the most suitable replacing atom for sulfur would seem to be nitrogen which, in the 4-covalent state, as in the ammines, has the same spatial arrangement of the nitrogen atom and any three of its four attached atoms as the 3-covalent sulfur atom. Moreover, 1,8-diamino-3,6-diazaoctane (triethylenetetramine) is a readily available chemical. However, it seems more than probable that its condensation with aldehydes such as salicylaldehyde leads to formation of substances containing imidazolidine rings. Diehl and his co-workers[3] have reported on coordination compounds derived from such condensation products. An anil derived from a base such as 1,8-diamino-3,6-dimethyl-3,6-diazaoctane, on the other hand, might well be expected to function as a sexadentate, the two central tertiary nitrogen atoms, despite the lowered coördination capacity of tertiary aliphatic amino nitrogen, functioning in much the same way as the two sulfur atoms in the type anil. It is worth recalling here that as far back as 1925, Mann and Pope[4] had demonstrated the capacity of a tertiary aliphatic nitrogen atom to function as a coördinating atom under conditions of favorable molecule structure.

We have now prepared 1,8-bis-(salicylideneamino)-3-oxa-6-thiaoctane (I) by causing β,β'-dichlorodiethyl ether to react with potassium phthalimide to yield 1-chloro-5-phthalimido-3-oxapentane, condensing this with the sodium salt of β-phthalimidoethyl mercaptan to 1,8-bisphthalimido-3-oxa-6-thiaoctane, removing the phthalyl groups by the method of Ing and Manske[5] and condensing the resulting diamine with salicylaldehyde. Treatment of the resulting oily yellow anil I with cobalt(II) acetate, followed by oxidation, and addition of potassium iodide leads to formation of 1,8-bis-(salicyli-

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[1] Commonwealth Research Assistant, University of Sydney.

[2] *Cf.* Parts I and III, This Journal, **72**, 1545 (1950); **74**, 4188 (1952).

[3] H. Diehl, L. M. Liggett, C. C. Hach, G. C. Harrison, L. Henselmeier, R. W. Schwandt and J. Mathews, *Iowa State Coll. J. Sci.*, **22**, 110 (1947).

[4] F. G. Mann and W. J. Pope, *Proc. Roy. Soc. (London)*, **A109**, 444 (1925); *J. Chem. Soc.*, 482 (1926).

[5] H. R. Ing and R. F. H. Manske, *ibid.*, 2348 (1926).