

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

Anal. Calcd. for $\text{Co}(\text{tetren})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: 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, μ_{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

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

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 coordinating tendency. This necessitates the assignment of the structure $[\text{Co}(\text{tetren})(\text{H}_2\text{O})](\text{ClO}_4)_2$ to the complex.

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(11) P. Selwood, *ibid.*, p. 100.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

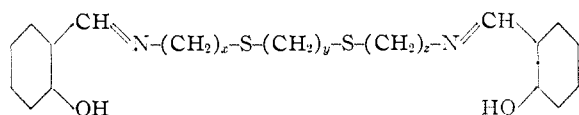
Sexadentate Chelate Compounds. V

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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 $(\text{CoS})\text{A}$, 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 coordination 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 amines, 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-workers³ 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 coordination 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 Pope⁴ had demonstrated the capacity of a tertiary aliphatic nitrogen atom to function as a coordinating 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 Manske⁵ 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-

(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).

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(2) Cf. Parts I and III, *THIS JOURNAL*, **72**, 1545 (1950); **74**, 4188 (1952)

deneamino)-3-oxa-6-thiaoctane cobalt (III) iodide which can be isolated as a dark brown crystalline salt containing two molecules of water of crystallization. This salt was readily resolved with the help of tartar emetic, and the pure enantiomorphous iodides were obtained as anhydrous salts.

There seems little doubt, therefore, that I functions as a sexadentate chelate compound and that in the complex ion it forms with cobalt(III) all three oxygen atoms as well as the sulfur and the two nitrogen atoms behave as donor atoms and occupy one apex each of the circumscribing coordination octahedron. The coordinating capacity of ethereal oxygen atoms for metal atoms is not usually considered high, notable examples of ethereal coordination compounds being, of course, the Grignard reagents. However, ethers and polyethers do not figure largely in coordination chemistry. When a molecule of I loses two protons and then winds itself about a central triply positively charged cobalt atom the ethereal oxygen atom is brought strainlessly into the correct position for coordination.

After this success with I it was thought possible that the bis-salicylidene derivative of 1,8-diamino-3,6-dioxaoctane in which both sulfur atoms of the type anil have been replaced by oxygen atoms might function as a sexadentate chelate compound, not because of any inherent powerful coordinating capacity of the ethereal oxygen atoms but because of their convenient location to the cobalt (III) atom in the derived complex ion. Experiment showed that II can so function but the complex salts it forms with cobalt (III) salts are unstable. The perchlorate was isolated pure but it was not possible to effect an optical resolution and obtain optically active salts.

Finally, alkylation of catechol with β -bromoethylphthalimide, followed by hydrolysis led ultimately to the formation in very bad yield of 1,2-bis-(γ -amino- α -oxapropyl)-benzene. The bis-salicylidene derivative of this base (III) appeared by the color changes to coordinate with cobalt(III) ions but it was impossible to isolate any pure complex salt. Attachment of the ethereal oxygen atoms to a benzene ring must lower their already low coordinating capacity, so that such a result is not unexpected.

The absorption curves for an optically active form of I, for II and for the bis-salicylidene derivative of EEE base are shown in Fig. 1.

Experimental

1-N-Phthalimido-5-chloro-3-oxapentane.—The method of Cretcher, Koch and Pittenger⁶ was found unsatisfactory and was modified as follows: β,β' -dichlorodiethyl ether (4 moles) was mixed with potassium phthalimide (1 mole), a few drops of diethylamine added and the mixture heated at 125° for 3 hours. Excess dichlorodiethyl ether was removed by steam distillation and the residue, which solidified on cooling was dried and recrystallized from petroleum ether; colorless needles (yield 70%) m.p. 70°.

1,8-Bis-(phthalimido)-3-oxa-6-thiaoctane.—A solution of N-(β -mercaptoethyl)-phthalimide (41.4 g.) in hot absolute ethanol (180 ml.) was added to a solution of sodium ethoxide obtained by dissolving sodium (4.6 g.) in absolute ethanol (90 ml.). A hot solution of 1-N-phthalimido-5-chloro-3-

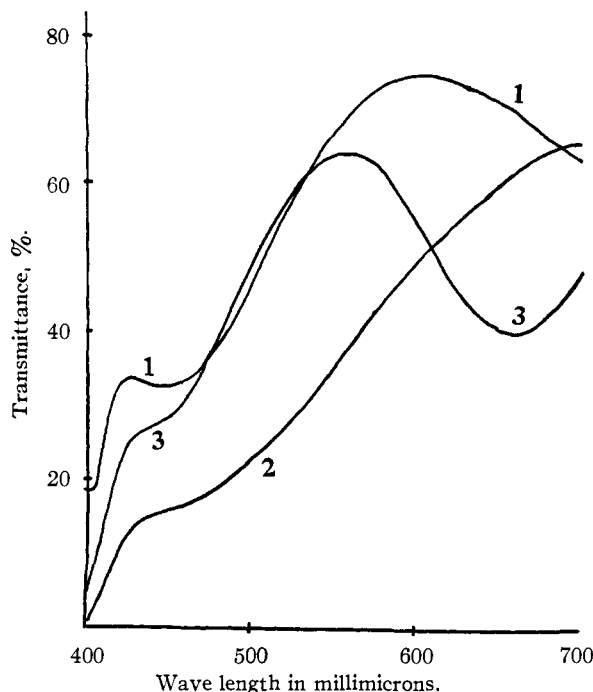


Fig. 1.—1, *d*-1,8-Bis-(salicylideneamino)-3-oxa-6-thiaoctane cobalt(III) iodide, 0.02% solution in water at 20°; 2, *dl*-1,8-bis-(salicylideneamino)-3,6-dioxaoctane cobalt(III) perchlorate trihydrate, 0.02% solution in *N*/100 aqueous nitric acid containing 4% of acetone at 20°; 3, *dl*-1,8-bis-(salicylideneamino)-3,6-dithiaoctane cobalt(III) chloride monohydrate, 0.02% solution in water at 20°.

oxapentane (50.7 g.) in absolute ethanol (140 ml.) was then added and the mixture refluxed for 5 hours. Most of the ethanol was then distilled off and water added. The oil which separated was induced to crystallize and recrystallized from ethanol; colorless needles (yield 75%), m.p. 117°.

Anal. Calcd. for $C_{22}H_{20}N_2O_5S$: C, 62.3; H, 4.7; N, 6.6. Found: C, 62.5; H, 5.0; N, 6.4.

1,8-Diamino-3-oxa-6-thiaoctane.—The bis-phthalimido compound just described (63.6 g.) was suspended in ethanol (650 ml.) boiling under reflux and hydrazine hydrate (52.5 ml. of 50%) added, the refluxing being continued for two hours. Hydrochloric acid (90 ml. of 10 *N*) was added and the boiling continued for 30 minutes after which as much ethanol as possible was distilled off and a little water added. The precipitated phthalhydrazide was removed and the base recovered with the help of ether from the filtrate after making it strongly alkaline. It was eventually obtained as a colorless oil (yield 81%), b.p. 120–121° (1.5 mm.). It was characterized by conversion to its bis-5-bromosalicylidene derivative; yellow micro-crystalline powder (from ethanol), m.p. 133°.

Anal. Calcd. for $C_{20}H_{22}N_2O_3SBr_2$: C, 45.3; H, 4.2; N, 5.3. Found: C, 45.2; H, 4.3; N, 5.4.

The dipicrate: minute orange prisms (from ethanol) m.p. 157°.

Anal. Calcd. for $C_{18}H_{22}N_2O_{16}S$: C, 34.7; H, 3.6; N, 18.0. Found: C, 34.5; H, 3.7; N, 17.8.

***dl*-1,8-Bis-(salicylideneamino)-3-oxa-6-thiaoctane Cobalt (III) Iodide Dihydrate.**—1,8-Bis-(salicylideneamino)-3-oxa-6-thiaoctane (I) could be obtained only as a yellow oil by mixing hot ethanolic solutions of salicylaldehyde (2 moles) and the above described diamine (1 mole). The separated oil was shaken out several times with petroleum ether and then used. To a solution of it (0.93 g.) in hot methanol (25 ml.) was added a solution of cobalt(II) acetate tetrahydrate (0.63 g.) in hot methanol (25 ml.). Air was then drawn through the brown solution for a few minutes, hydrogen peroxide (2 ml. of 3%) added and after warming again the aspiration of air continued for 30 minutes. Sufficient water was then added to effect complete precipitation of a

(6) L. H. Cretcher, J. A. Koch and W. H. Pittenger, *THIS JOURNAL*, **47**, 1175 (1925).

small amount of a brown solid which was filtered off and discarded. After cooling and scratching, the clear brown filtrate deposited brown crystals which after recrystallization from hot water formed very dark brown needles, m.p. 178°, soluble in methanol, acetone and hot chloroform but insoluble in benzene or ether.

Anal. Calcd. for $(\text{CoC}_{20}\text{H}_{22}\text{N}_2\text{O}_3\text{S})\text{I}\cdot 2\text{H}_2\text{O}$: C, 40.6; H, 4.4; I, 21.4; Co, 10.0. Found: C, 40.5; H, 4.4; I, 21.2; Co, 9.9.

***d*-1,8-Bis-(salicylideneamino)-3-oxa-6-thiaoctane Cobalt(III) Iodide.**—The above described racemic iodide (0.83 g.) was converted to the chloride by solution in hot water (75 ml.) and shaking with freshly precipitated silver chloride for 20 minutes. The filtered solution of the chloride was then evaporated under reduced pressure to a volume of about 7 ml. to which was added a hot concentrated solution of potassium *d*-antimonyl tartrate (0.24 g. 0.5 mole). On scratching, almost pure *d*-complex *d*-antimonyl tartrate separated. It was collected and recrystallized from hot water and obtained in dark brown needles which charred on heating. A 0.02% aqueous solution at 20° gave α_D 0.70° (1-dm. tube), whence $[\alpha]^{20}_D +3,500^\circ$.

An aqueous solution of this salt was gently warmed with sodium acetate and the precipitated antimony oxide filtered off. Solid potassium iodide was added to the filtrate and the precipitated active iodide, which was shown to be optically pure, recrystallized from hot water. It formed dark brown needles, m.p. 199°.

Anal. Calcd. for $(\text{CoC}_{20}\text{H}_{22}\text{N}_2\text{O}_3\text{S})\text{I}$: C, 43.2; H, 4.0; I, 22.8; Co, 10.6. Found: C, 43.2; H, 3.9; I, 22.9; Co, 10.7.

A 0.02% aqueous solution at 20° gave $\alpha_D +1.04^\circ$ and $\alpha_{4481} +1.41^\circ$ (1-dm. tube), whence $[\alpha]^{20}_D +5,200^\circ$, $[\alpha]^{20}_{4481} +7,050^\circ$, $[\text{M}]^{20}_D +28,900^\circ$ and $[\text{M}]^{20}_{4481} +39,200^\circ$.

***l*-1,8-Bis-(salicylideneamino)-3-oxa-6-thiaoctane Cobalt(III) Iodide.**—The levorotatory filtrate left after precipitation of the *d*-complex *d*-antimonyl tartrate described above was treated with solid potassium iodide, and two fractions of complex iodide precipitated. The first of these had a small levo rotation and the second a strong levo rotation. By repeated fractional crystallization of this latter fraction from hot water with the help of potassium iodide it was eventually possible to obtain the pure *l*-iodide in dark brown needles, m.p. 199°.

Anal. Found: C, 43.3; H, 3.9; I, 22.6; Co, 10.6.

A 0.01% aqueous solution at 20° gave $\alpha_D -0.52^\circ$ (1-dm. tube), whence $[\alpha]^{20}_D -5,200^\circ$ and $[\text{M}]^{20}_D -28,900^\circ$.

1,8-Bis-phthalimido-3,6-dioxaoctane.—1,8-Dibromo-3,6-dioxaoctane⁷ (27.6 g.) and potassium phthalimide (41 g., 1.1 moles) were heated together at 140° after addition of a few drops of diethylamine for 3 hours. After cooling the solid mass was broken up and extracted with water to remove unchanged potassium phthalimide and then recrystallized several times from glacial acetic acid, the product being obtained in minute colorless needles, m.p. 178–179°. The yield was only 34% but it could not be improved despite many variations of conditions.

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_6$: C, 64.7; H, 4.9. Found: C, 64.4; H, 5.2.

1,8-Diamino-3,6-dioxaoctane.—The bis-phthalimido compound just described (22.4 g.) was suspended in ethanol (225 ml.) boiling under reflux, hydrazine hydrate (19 ml. of 50%) added and refluxing continued for 2 hours. Most of the phthalimido compound had reacted within 15 minutes and the intermediate compound separated. Hydro-

chloric acid (25 ml. of 10 *N*) was added and refluxing continued for 0.5 hour. Most of the alcohol was distilled off, a little water added, the precipitated phthalhydrazide filtered off and the base recovered from the cooled filtrate with solid alkali and ether. It distilled as a pale yellow oil (yield 52%), b.p. 88° (0.5 mm.) or 95° (1 mm.).

Its bis-5-bromosalicylidene derivative formed minute yellow needles from ethanol, m.p. 97°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4\text{Br}_2$: N, 5.4. Found: N, 5.6.

The dipicrate formed yellow leaflets (from ethanol), m.p. 194.5°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_6\text{O}_{16}$: N, 18.5. Found: N, 18.2.

1,8-Bis-(salicylideneamino)-3,6-dioxaoctane (II) was obtained by interaction of hot methanolic solutions of salicylaldehyde (2 moles) and the above-described base (1 mole), cooling, precipitating as a yellow oil with petroleum ether and washing the oil repeatedly with petroleum ether. After freeing completely from solvents the oil crystallized and could be recrystallized from a mixture of ether and petroleum ether and thus obtained in minute yellow needles, m.p. 44–45°, which were very soluble in methanol.

Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$: C, 67.4; H, 6.8. Found: C, 67.6; H, 7.1.

***dl*-1,8-Bis-(salicylideneamino)-3,6-dioxaoctane Cobalt(III) Perchlorate Trihydrate.**—II (0.7 g.) was added to a hot solution of cobalt(II) acetate tetrahydrate (0.5 g.) in methanol (18 ml.). The solid rapidly dissolved to give a red-brown solution which, after 2 minutes was cooled to 4°. Hydrogen peroxide (0.5 ml. of 3%) was then added. The solution became dark greenish-brown over 2–3 minutes and after 5 minutes nitric acid (1 ml. of 3 *N*) was added, followed by an equal volume of ice-water. The solution was then filtered and the complex perchlorate precipitated by the addition of 20% sodium perchlorate solution (2–3 ml.). The precipitated solid was recrystallized by solution in warm methanol containing a few drops of perchloric acid and then adding ether and was thus obtained in brown nodular prisms which explode on heating. It was found to dissolve readily in acetone or alcohol to greenish-brown solutions which faded in color to yellow during the course of a day. The greenish brown aqueous solution decomposes rapidly on warming, a green solid separating. This aqueous solution can also rapidly decompose soluble iodides liberating iodine.

Anal. Calcd. for $(\text{CoC}_{20}\text{H}_{22}\text{N}_2\text{O}_4)\text{ClO}_4\cdot 3\text{H}_2\text{O}$: C, 42.4; H, 5.0; N, 4.9; Co, 10.4. Found: C, 42.2; H, 5.0; N, 4.9; Co, 10.3.

1,2-Bis-(γ -salicylideneamino- α -oxapropyl)-benzene (III).—Catechol (1 mole) was added to a solution of potassium ethoxide (2 moles) in absolute ethanol under nitrogen and then β -bromoethylphthalimide (2 moles) was added and the mixture refluxed for 12 hours. After removal of the ethanol, water was added and the oily product taken up in ether and washed free of catechol with alkali. The residual yellow oil was treated in alcoholic solution with hydrazine hydrate and then hydrochloric acid in the usual way and eventually a small amount of a yellow oily base was separated. This was treated with salicylaldehyde to give a solid Schiff base; yellow needles from ethanol, m.p. 213–214°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4$: C, 71.3; H, 6.0. Found: C, 71.6; H, 5.7.

Interaction of a methanolic solution of this compound with cobalt(II) acetate tetrahydrate in the usual way gave a brown solution but decomposition occurred very readily, a dirty yellow precipitate separating.

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(7) Prepared in 62% yield by the method of K. Ziegler and H. Holl, *Ann.*, **528**, 152 (1937).