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Cobalt(IV) Ammine Complexes with 5-Nitrosalicylato or Similar Ligands. II.[*1] Preparation and Properties of Derivatives

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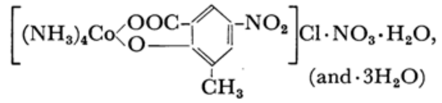
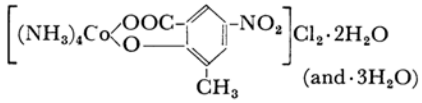
Cobalt(IV) compounds of the formulae:


(A)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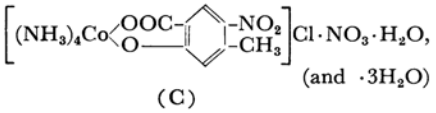
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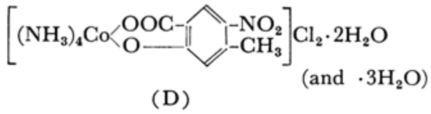
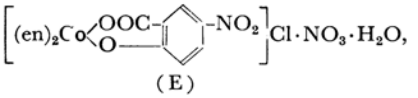
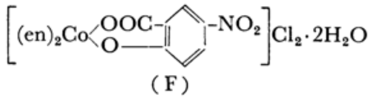

(D)


(E)


(F)

have been obtained by procedures analogous to that reported for cobalt(IV) ammine complexes with 5-nitrosalicylato ligands.

In the previous work,[1] cobalt(IV) ammine complexes with 5-nitrosalicylato ligands were isolated from the reaction product of salicylatotetraamminecobalt(III) chloride monohydrate and 14 N nitric acid.

In the present report the preparation and some

[*1] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, 1967.

[1] Y. Yamamoto, the Late K. Ito, H. Yoneda and M. Mori, This Bulletin, **40**, 2580 (1967).

fundamental properties of analogous compounds containing ethylenediamine and those containing 3-methyl or 4-methylsalicylato ligands will be described.

Experimental

Preparation. *Salicylatotetraamminecobalt(III) Chloride Monohydrate, Salicylatobis(ethylenediamine)cobalt(III) Chloride Dihydrate, 3-Methylsalicylatotetraamminecobalt(III) Chloride Monohydrate and 4-Methylsalicylatotetraamminecobalt(III) Chloride Monohydrate.* These were prepared by Morgan and Smith's method[2] and recrystallized from water. In the preparation of the latter two compounds, equimolar amounts of the 3-methyl and 4-methylsalicylic acid were used as ligands instead of salicylic acid.

Found in 3-methylsalicylato cobalt(III) ammine complex: C, 29.22; H, 6.23; N, 16.55; Cl, 10.80%. Found in 4-methylsalicylatocobalt(III) ammine complex: C, 28.99; H, 5.81; N, 16.49; Cl, 10.97; NH_3 20.22%. Calcd for $[CoC_8H_{18}N_4O_3]Cl\cdot H_2O$: C, 29.06; H, 6.10; N, 16.94; Cl, 10.72; NH_3, 20.60%.

5-Nitro-3-methylsalicylatotetraamminecobalt(IV) Chloride Nitrate (Abbreviated as A), 5-Nitro-4-methylsalicylatotetraamminecobalt(IV) Chloride Nitrate (Abbreviated as C) and 5-Nitrosalicylatobis(ethylenediamine)cobalt(IV) Chloride Nitrate (Abbreviated as E). The following procedure is an improvement of that reported in paper I for the preparation of 5-nitrosalicylatotetraamminecobalt(IV) salts, and is applicable to the preparation of the original compound as well.

Five milliliters of 14 N nitric acid was added to 5 g of 3-methylsalicylatotetraamminecobalt(III) chloride monohydrate, 4-methylsalicylatotetraamminecobalt(III) chloride monohydrate or salicylatobis(ethylenediamine)cobalt(III) chloride dihydrate. Heat was evolved and the color of the solution changed from russet to green. To the cooled solution was added 10 m*l* of 14 N nitric acid. The solution was filtered with a glass filter (G4), and the green filtrate was added to acetone. The green substance separated out was filtered with a glass filter (G3), washed with acetone, and dried in a vacuum desiccator. Two grams of this green substance was dissolved in 4 m*l* of 14 N nitric acid, and the green solution was added into acetone. The precipitated green substance was filtered, washed with acetone and dried. It was reprecipitated twice more by dissolution in 14 N nitric acid and addition of acetone. Yield, 2 g in each case. When dried in a silicagel desiccator, trihydrates were obtained, whereas drying in a desiccator over phosphorus pentoxide yielded monohydrates.

Found in Monohydrate (A): C, 21.99; H, 4.35; N, 19.22; Cl, 7.96; Co, 13.78; NH_3, 15.79%. Found in Monohydrate (C): C, 22.23; H, 4.31; N, 19.10; Cl, 7.98; Co, 13.10; NH_3, 15.60%. Calcd for $[CoC_8H_{17}N_5O_5]\cdot Cl\cdot NO_3\cdot H_2O$: C, 21.955; H, 4.375; N, 19.20; Cl, 8.10; Co, 13.47; NH_3, 15.55%.

Found in Trihydrate (A): C, 20.29; H, 4.41; N, 17.73%. Found in Trihydrate (C): C, 20.10; H, 4.10; N, 17.64%. Calcd for $[CoC_8H_{17}N_5O_5]\cdot Cl\cdot NO_3\cdot 3H_2O$: C, 20.28; H, 4.89; N, 17.74%.

Found in Monohydrate (E): C, 28.17; H, 4.42; N, 18.06; Cl, 7.35%. Calcd for $[CoC_{11}H_{19}N_5O_5]Cl\cdot NO_3\cdot H_2O$: C, 27.77; H, 4.45; N, 17.67; Cl, 7.45%.

5-Nitro-3-methylsalicylatotetraamminecobalt(IV) Dichloride (Abbreviated as B), 5-Nitro-4-methylsalicylatotetraamminecobalt(IV) Dichloride (Abbreviated as D) and 5-Nitrosalicylatobis(ethylenediamine)cobalt(IV) Dichloride (Abbreviated as F). Two grams of substance A, C or E was dissolved in 2 m*l* of 12 N hydrochloric acid, and the solution was filtered with a glass filter (G4). Acetone was added to the green solution, and the substance separated out was filtered with a glass filter (G3), washed with acetone and dried in a vacuum desiccator. It was reprecipitated from hydrochloric acid solution by addition of acetone. Yield 1.6 g.

When the product was dried in a desiccator over phosphorus pentoxide, dihydrates were formed. In the case of (B) and (D) drying in a silicagel desiccator produced trihydrates.

Found in Dihydrate (B): C, 22.71; H, 4.85; N, 16.37; Cl, 15.58; Co, 14.59%. Found in Dihydrate (D): C, 22.65; H, 4.42; N, 16.21; Cl, 15.67%. Calcd for $[CoC_8H_{17}N_5O_5]Cl_2\cdot 2H_2O$: C, 22.39; H, 4.93; N, 16.32; Cl, 16.52; Co, 13.75%.

Found in Trihydrate (B): C, 21.14; H, 5.06; N, 15.94%. Found in Trihydrate (D): C, 20.66; H, 5.29; N, 15.53%. Calcd for $[CoC_8H_{17}N_5O_5]Cl_2\cdot 3H_2O$: C, 21.49; H, 5.18; N, 15.66%.

Found in Dihydrate (F): C, 28.20; H, 4.97; N, 15.01; Cl, 15.20%. Calcd for $[CoC_{11}H_{19}N_5O_5]Cl_2\cdot 2H_2O$: C, 28.28; H, 4.96; N, 14.99; Cl, 15.18%.

Determination of Organic Ligands. In order to identify the organic ligand, 3 g of A or C was heated in 3 N potassium hydroxide at 60°C for 3 hr. The mixture was filtered and acidified with hydrochloric acid. The ligand acid thus isolated was extracted with ethylether, with subsequent evaporation, to yield the free acid; the acid from A was identified as 3-methyl-5-nitrosalicylic acid and that from C as 4-methyl-5-nitrosalicylic acid by melting point measurements.

Chromatography. In order to examine the purity of the substances, the samples dissolved in mixture solvents of water and acetone (1 : 3 by volume, pH=3 with hydrochloric acid) were chromatographed on acid alumina (Merck, Germany) or silica gel (Wako Pure Chemical Ind., Japan). Each sample was found to contain substantially a single species.

Physicochemical Measurements. The magnetic susceptibilities of the complexes were measured by the Gouy method with a magnetic balance (Shimadzu Seisaku Sho) in the temperature range between 80°K and room temperature.

The visible and ultraviolet absorption spectra were recorded with a recording spectrophotometer, Hitachi EPS-2.

The NMR spectra were recorded at $25+2°C$ with a Varian A-60-type instrument, and were quoted for a trifluoroacetic acid or deuterium oxide solution using tetramethylsilane as an external standard.

The electric conductivities of the aqueous solutions of the salts were determined by the use of a conductometer, CM-1DB, Toa Denpa Kogyo.

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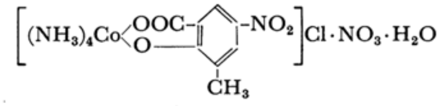
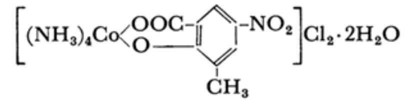
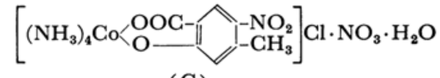
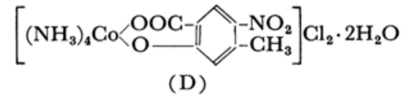
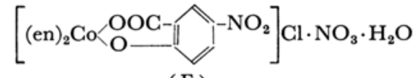
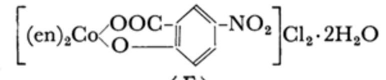
[2] G. T. Morgan and J. D. M. Smith, *J. Chem. Soc.*, **1922**, 1956; *ibid.*, **1924**, 1924.

TABLE 1. PROPERTIES OF THE COBALT(IV) AMMINE COMPLEXES

	Magnetic moment μ_{eff}, (B.M.)	Equivalents of iodine liberated per formula weight	Electric conductivity of aqueous solution ℧/cm	Absorption bands in slightly acidic (H_2SO_4) solution mμ	ε
 (A)	1.7	1.90	236.2	440 690	2000 6400
 (B)	1.7	1.84		440 690	2100 6800
 (C)	1.7	1.86	220	440 656	4000 6600
 (D)	1.7	1.90		440 656	4300 7000
 (E)	1.6	1.76		450 682	3200 10000
 (F)	1.6	1.78		450 682	2800 9800

Result and Discussion

The Constitution of the Compounds. The constitution of each compound was inferred as in the previous study,[1] on the basis of elemental analyses, isolation of the ligand acid (*cf.* Experimental), iodometry, magnetic susceptibility, and the electric conductivity and the absorption spectrum of the aqueous solution. Some of these data are given in Table 1 and Fig. 1.

Recently, Garbett and Gillard[3] studied the reaction of salicylatobis(ethylenediamine)cobalt(III) complex with nitric acid. From the reaction mixture, they obtained a dark green weakly paramagnetic material which, however, they considered impure; they tentatively formulated it as [Co en$_2$(5-NO-salH)(NO$_3$)$_2$·4H$_2$O, *i. e.* as a complex containing nitrososalicylate ligand. In its absorption spectrum they found strong absorption maxima at 375 mμ (ε=8700) and 682 mμ (ε=2640). Although the method of preparation of this green material is more or less analogous to the procedure of preparing green complex (E) of the present paper, the spectrum of E (Fig. 1, Table 1) was quite different from their spectra; it showed an absorption peak of much higher intensity (ε=10000) at 682 mμ and also a peak at 450 mμ (ε=3200), but only a very weak peak or a shoulder at 365—375 mμ which was barely perceptible under the strong absorption background (ε=3200) present in this range. It seems possible that the complex of Garbett and Gillard is different from that obtained in the present research. If, instead, their sample were to contain the same green complex as that obtained in the present research, their sample would contain less than 30% of the true green complex as judged from the absorptivity of the peak at 682 mμ. In this latter possibility the very high intensity of the peak at 375 mμ observed by these investigators might be explained as caused by contamination by [Co en$_2$-(5-NO$_2$-salH)](NO$_3$)$_2$·H$_2$O which ha san absorption peak of very high intensity at this wavelength (374 mμ, ε=21400).

Chromatography of the green complex obtained by the present authors has shown that the material is substantially pure and single. The success in obtaining comparatively pure materials may be due to the fact that all the compounds contained at least one outer chloride ion; complete removal of the chloride ion *e. g.* by use of silver nitrate has been

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[3] K. Garbett and R. D. Gillard, *Chem. Commun.*, **1967**, 694; *J. Chem. Soc., (A)*, **1968**, 979.

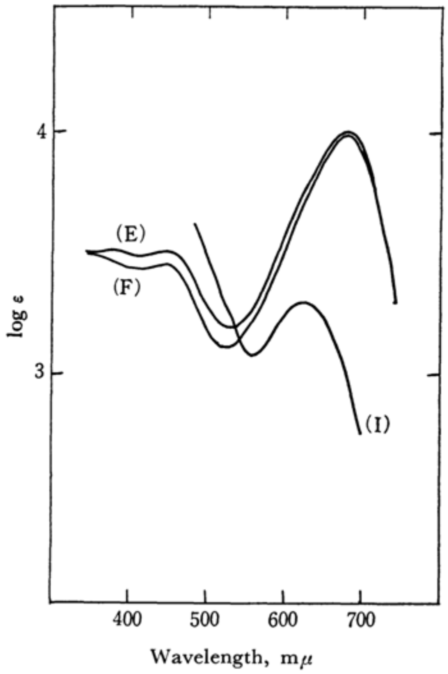
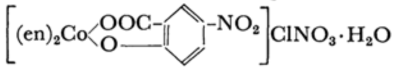


Fig. 1. Absorption spectra of complexes.

(E)



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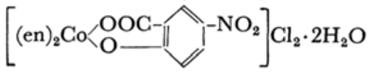
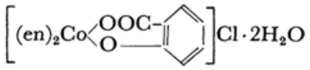


(I)



found to make the complex very unstable.

In the present paper we shall continue to formulate the compounds as nitro compounds because the only experimental fact so far obtained about this problem was isolation of nitrosalicylic acid or nitrocresotic acid. Of course we can not deny the possibility that the ligand was initially nitroso compound which was oxidized during the treatment with alkalis; the final decision should await further experimental proofs.

There seems to be no ambiguity as to the fact that the formal oxidation state of cobalt is four, this, of course including the possibility that the complex ion as a whole is a free radical carrying one electron vacancy. This can be verified by the effective Bohr magneton number, the charge of +2 and the high oxidizing ability of the complex. Our sample tested neutral in freshly prepared aqueous solution, so that the formulation as the protonated ion is not acceptable.

The magnetic susceptibilities of the compounds obeyed the Curie-Weiss law down to liquid nitrogen temperatures. The effective magnetic moment μ_{eff} in Bohr magnetons (Table 1) was obtained using the formula, $\mu_{\mathrm{eff}}=2.84\sqrt{\chi_{\mathrm{mol}}^{\mathrm{cor}}(T-\theta)}$ where $\chi_{\mathrm{mol}}^{\mathrm{cor}}$ was obtained by correcting the observed molar magnetic susceptibility χ_{mol} for the diamagnetic contribution of the molecule. A more detailed study on the magnetic susceptibilities will be reported elsewhere.

Solubilities. The cobalt(IV) ammine complexes obtained in the present study are soluble in water, dimethylsulfoxide, methanol, nitric acid, hydrochloric acid, trifluoroacetic acid and several acidic solvents, but insoluble in acetone, chloroform, benzene, acetonitrile and other organic solvents of similar nature.

On the other hand, the salts of tetraphenylboric acid, picric acid, 3,5-dinitrosalicylic acid or chloranilic acid are soluble in acetone, chloroform, benzene and similar organic solvents, but are almost insoluble in water.

Stability. The solution of 5-nitrosalicylato-(bisethylenediamine)cobalt(IV) complexes did not undergo any color change after 12 hr, but the solution of 5-nitrosalicylatotetraamminecobalt(IV) complex and its methyl derivatives changed from green to yellowish brown after several hours. The greater stability of the ethylenediamine complexes as compared with the corresponding ammine complexes as shown in this example could be explained in terms of the entropy effect.[4] Another such example is offered by a series of μ-peroxodicobaltammine and μ-peroxodicobalt ethylenediamine complexes, the latter being much more stable toward decomposition.

NMR Spectra. The NMR spectra of 5-nitrosalicylatobis(ethylenediamine)cobalt(IV) chloride

TABLE 2. THE PROTON MAGNETIC RESONANCE OF CH_2 OR NH_2 IN SALICYLATOAMMINE COBALT(IV) COMPLEX (E)

	Methylene protons		Ammine protons	
	cps		cps	
			*trans**	*cis*
CF_3COOH	106.5	148.0	236.5	284.0
Number of proton	2H	6H	4H	4H
D_2O	121.4	157.4	d. a.	d. a.
Number of proton	2H	6H		

d. a.: Disapppeared signal

*: NMR studies on cobalt(III) ammine complex[5] indicate the proton magnetic resonance for ammonia trans to anion appears on strong field side. We assume that the relation holds in the present case also.

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[4] A. E. Martell and M. Calvin, "The Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J. (1952), p. 149.

[5] W. L. Jolly, A. D. Harris and T. S. Briggs, *Inorg. Chem.*, **4**, 1064 (1965).

nitrate were measured in trifluoroacetic acid or deuterium oxide. The spectra had signals at 106.5, 148.0, 236.6 and 284.0 cps for trifluoroacetic acid solution and at 121.4 and 157.4 cps in the case of deuterium oxide solution (Table 2).

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