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Cobalt(IV) Amminecomplexes with 5-Nitrosalicylato Ligands. I*1

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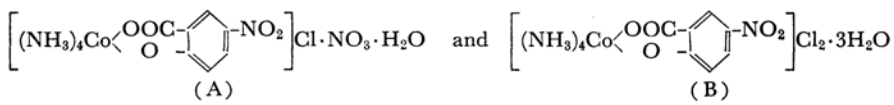
Co(IV) compounds of the formulae:



(A) (B)

have been isolated from the reaction product of salicylatotetraamminecobalt(III) chloride and 60% nitric acid. Valency four was ascertained by magnetic measurements (μ_{eff}=1.98 B. M. (A), 1.71 B. M. (B)) and iodometry.

Morgan[1] observed that when russet salicylatotetraamminecobalt(III) chloride is treated with 60% nitric acid, a very deep green solution is formed.

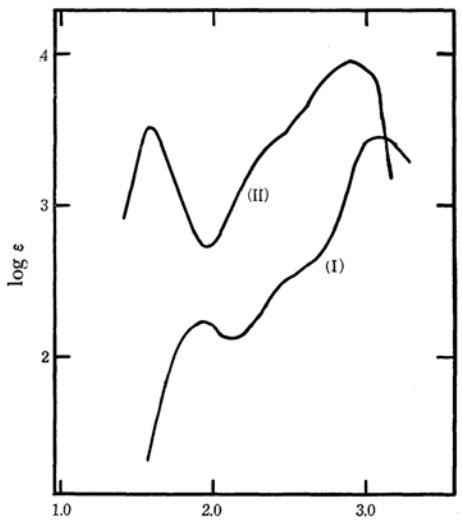


Fig. 1. Absorption spectra.
(I) Salicylatotetraamminecobalt(III) chloride in H_2O
(II) Salicylatotetraamminecobalt(III) chloride in 60% HNO_3

(ε=3200 at 1.53×10^4 cm^{-1}, Fig. 1). The present authors were deeply interested in this phenomenon; in an attempt to elucidate it, they succeeded in isolating new compounds, which, by means of analytical, magnetic, and spectroscopic methods, have been shown to be cobalt compounds with odd electrons and containing 5-nitrosalicylato ligands.

Although some cobalt compounds having the oxidation states other than two and three have been reported,[2-8] they are still quite meagre in number; the present paper will describe a new series of unusual cobalt compounds in which the valence state of cobalt is at least formally four.

Experimental

Preparation. *Salicylatotetraamminecobalt(III) Chloride Monohydrate.* This was prepared by Morgan's method[1] and was recrystallized twice from distilled water.

5-Nitrosalicylatotetraamminecobalt(IV) Chloride Nitrate Monohydrate (Abbreviated as A). To 5 g of the salicylatotetraamminecobalt(III) chloride monohydrate, 15 m*l* of 60% nitric acid were added. Heat was evolved, and the solution turned green. The solution was filtered with a glass filter, and the green filtrate was added to

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1) G. T. Morgan and J. D. M. Smith, *J. Chem. Soc.*, **1922**, 1956.
2) N. Maki and M. Yamagami, *J. Am. Chem. Soc.*, **86**, 514 (1964).
3) K. Glen and R. Rehm, *Z. anorg. u. allgem. Chem.*, **237**, 79 (1938).
4) L. Malatesta, *Gazz. chim. Ital.*, **218**, 907 (1944).
5) A. Werner and A. Mylius, *Z. anorg. Chim.*, **16**, 245 (1898).
6) R. Hoppe, *Rec. trav. chim.*, **75**, 569 (1956).
7) C. Brendel and W. Klemm *Z. anorg. u. allgem. Chem.*, **320**, 159 (1963).
8) R. Scholder, *Bull. Soc. Chim. France*, **1965**, 1112.

acetone. The green substance separated out was filtered with a glass filter, washed with acetone, and dried in a desiccator over phosphorus pentaoxide. It was reprecipitated four times from a 60% nitric acid solution by the addition of acetone.

Found: C, 19.73; H, 4.06; N, 19.93; Co, 13.91; NH_3, 15.79; NO_3, 14.51; Cl, 7.53%. Calcd for $(CoC_7H_{15}N_5O_5)Cl\cdot NO_3\cdot H_2O$: C, 19.83; H, 4.07; N, 19.83, Co. 13.97; NH_3, 16.08; NO_3, 14.66; Cl, 8.38%.

5-Nitrosalicylatotetraamminecobalt(IV) Chloride Trihydrate (Abbreviated as B). Two grams of Substance A were dissolved in 2 m*l* of 35% hydrochloric acid. Acetone was added to the green solution, and the green substance which separated out was filtered, washed with acetone, and dried in a desiccator. It was reprecipitated twice from a 35% hydrochloric acid solution by the addition of acetone. Finally it was dissolved in 2 m*l* of water, precipitated with acetone, washed, and dried. The substance thus prepared (B) is comparatively stable in air.

Found: C, 19.35; H, 4.70; N, 16.35; Co, 13.64; NH_3, 15.48; Cl, 16.54%. Calcd for $(CoC_7H_{15}N_5O_5)\text{-}Cl_2\cdot 3H_2O$: C, 19.40; H, 4.85; N, 16.16; Co, 13.62; NH_3, 15.73; Cl, 16.38%.

The total nitrogen, carbon, and hydrogen contents were determined with the Yanagimoto C, H, N-Corder, while ammoniacal nitrogen was determined by the distillation method.[9] It was confirmed that no ammonia was evolved on the distillation of an alkaline solution of 5-nitrosalicylic acid. Cobalt was determined gravimetrically by the use of dinitrosoresorcinol.[10]

In order to identify the organic ligand, 3 g of A were heated in a 3 N KOH solution at 60°C for 3 hr. The mixture was filtered and acidified with hydrochloric acid. The ligand thus isolated was extracted with ethyl ether, with subsequent evaporation, to yield the free acid; it was identified as 5-nitrosalicylic acid by a study of the melting point and IR spectra.

Physicochemical Measurements. The electric conductivity of an aqueous solution of A was determined by the use of a conductometer, CM-1DB, Toa Denpa Kogyo.

The magnetic susceptibilities of the complexes were measured by the Gouy method with a magnetic balance YS-22 (Naruse Scientific Instrument) in the temperature range between 100°K and room temperature. The apparatus was calibrated with a nickel chloride solution which had been analyzed with dimethylglyoxime. Pyrex sample tubes 4.2 mm in diameter were used; they were filled with either the sample powder or the nickel chloride solution to 4.5 cm from the bottom. Measurements were carried out at five different field strengths in order to ascertain the absence of ferromagnetic impurities. The values were corrected for both the diamagnetism of the container and the paramagnetism of air, and finally for the diamagnetism of the constituent atoms of the compound itself, in order to obtain the paramagnetic susceptibility.

The visible and ultraviolet absorption spectra were recorded with a recording spectrophotometer, EPS-2, Hitachi, while the infrared spectra were taken with a Nippon Bunko, DS 402-G. The NMR spectra were recorded at 25±2°C with a Varian 60-type instrument, and were quoted for a CF_3COOH solution using tetramethylsilane as an internal standard.

Results and Discussion

The Valency of Cobalt. The authors concluded the formal quadrivalency of cobalt in Compounds A and B from the following findings:

(1) The magnetic susceptibility of B measured in the temperature range between 100°K and room temperature obeyed the Curie-Weiss law with $\mu_{eff}=1.71$ B. M. (Fig. 2). The magnetic susceptibility of A measured at room temperature gave $\mu_{eff}=1.98$ B. M.

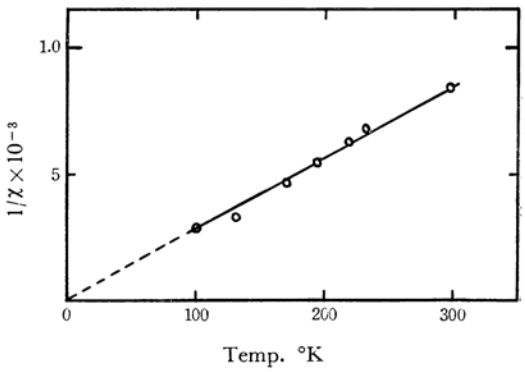
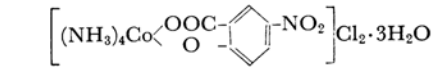
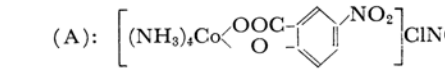


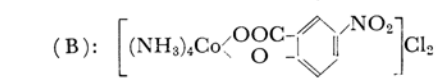
Fig. 2. Magnetic susceptibility *vs.* temperature.



(2) One-mole portions of A and B liberated, respectively, 1.75 and 1.984 equivalents of iodine from an acid solution of potassium iodide, as titrated with sodium thiosulfate. This eliminates the possibility that the paramagnetism might come from Co(II); it could be explained by assuming that Co(IV) was reduced to Co(II).

(3) Electric conductivity of aqueous solutions. The measured conductivity of A was 261.0 $\mho$/cm mol/1450 *l* at 20°C, indicating that the compound has two ionizable anions. On the basis of these data, it seemed reasonable to assume the following structure for Complexes A and B:

(A): 

(B): 

It seems worth noting that the oxidation of Co(III) to Co(IV) in this compound is performed with a common oxidant, such as nitric acid. Thus the nitrosalicylato ligand in this example plays a particular role in the stabilization of Co(IV). Such a stabilization of Co(IV) is explicable on

9) H. A. Horan and H. J. Eppig, *J. Am. Chem. Soc.*, **71**, 581 (1949).

10) Frank J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Company, Inc., New York (1957), p. 293.

TABLE 1. ABSORPTION BANDS OF Co(III)-(IV) AMMINE AND Co(IV) AMMINE

Substance	mμ	ε
$\left[(NH_3)_4Co\langle^{NH_2}_{O_2}\rangle Co(NH_3)_4\right]^{4+}$	477	370
	700	310
in water		
$[(NH_3)_4Co\text{-}O_2\text{-}Co(NH_3)_4]^{5+}$	478	290
in water	670	870
$\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\text{-}NO_2\right]Cl\cdot NO_3\cdot H_2O$	444	3400
	660	10900
in 60% nitric acid		
$\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\text{-}NO_2\right]Cl_2\cdot 3H_2O$	450	3700
	660	12400
in 35% hydrochloric acid		

the basis of the following facts: (1) The extra lone pairs (filled π-orbital) on the coordinating oxygen atoms of the organic ligand should destabilize the Co-dε electrons to facilitate their removal, resulting in the oxidation of Co(III) to Co(IV); (2) The aromatic π-electrons in the ligand should be stabilized by the insertion of an electron negative NO_2 group; such electrons would otherwise move into a hole in the dε level of Co(IV), thus resulting in the oxidation of the organic ligand and in its failure to stabilize the high oxidation state.

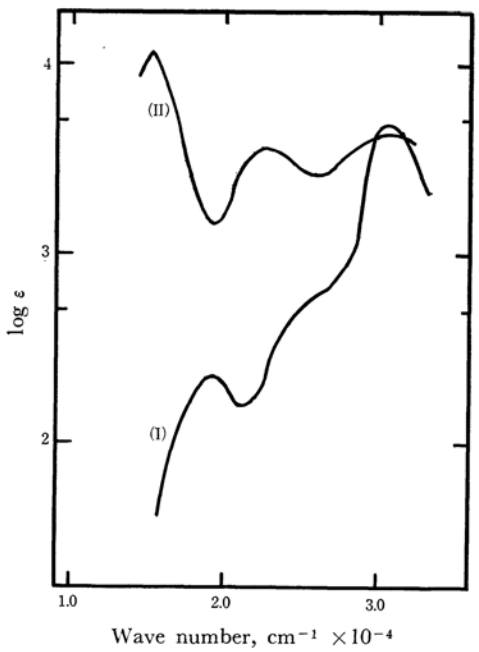


Fig. 3. Absorption spectra of cmplexes.

(I) $\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\right]Cl\cdot H_2O$

(II) $\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\text{-}NO_2\right]Cl_2\cdot 3H_2O$

It also seems remarkable that the salicylato ligand itself is nitrated in the process forming the green complex, for the nitration of salicylic acid in the free state usually requires more drastic conditions.

Absorption Spectra. It is found that both A and B have two strong sbsorption bands, at

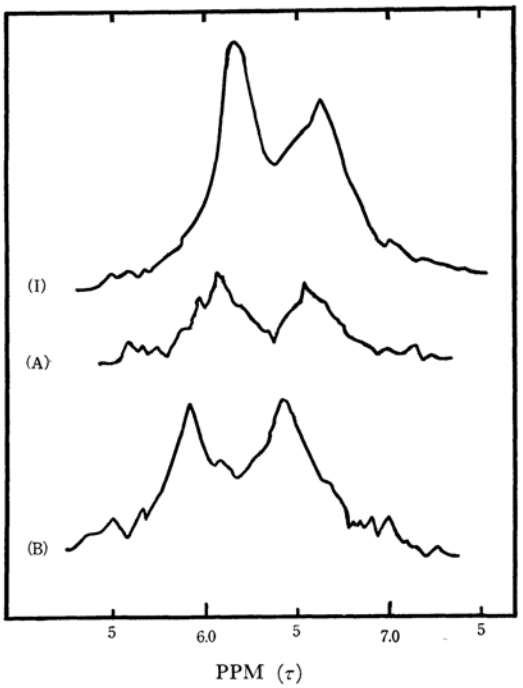


Fig. 4. Proton magnetic resonance spectra of a solution (3/100 mol/l) in CF_3COOH.

(I) $\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\right]Cl\cdot H_2O$

(A) $\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\text{-}NO_2\right]Cl\cdot NO_3\cdot H_2O$

(B) $\left[(NH_3)_4Co\langle^{OOC}_{O}\text{-}C_6H_3\text{-}NO_2\right]Cl_2\cdot 3H_2O$

TABLE 2. THE PROTON MAGNETIC RESONANCE OF NH_3 IN SALICYLATO AMMINE COMPLEXES OF Co(III) AND Co(IV)

Substance	PPM(τ)		The number of NH_3†		
	cis	≠trans	cis	trans	total
$\left[(NH_3)_4Co\langle^{OOC-}_{O}\text{-}C_6H_3\right]Cl\cdot H_2O$	6.143	6.626	2	2	4
$\left[(NH_3)_4Co\langle^{OOC-}_{O}\text{-}C_6H_3(NO_2)\right]Cl\cdot NO_3\cdot H_2O$	5.90	6.40	2	2	4
$\left[(NH_3)_4Co\langle^{OOC-}_{O}\text{-}C_6H_3(NO_2)\right]Cl_2\cdot 3H_2O$	6.058	6.55	2	2	4

≠ NMR studies on cobalt(III) ammine complexes[11] indicate the proton magnetic resonance for ammonia trans to anion appears on the strong field side. We assume that the same relation holds in the present case also.

† Estimated by comparison with the peak of protons in the benzene ring.

444 and 660 mμ with logε=4 (shown in Fig. 3). Table 1 also gives some absorbance data on peroxo dicobalt ammine complexes.

We see that the absorption bands of the 5-nitrosalicylatotetraamminecobalt(IV) ion are at about the same position as those of peroxo dicobaltammine complexes, although the values of ε are largely different.

The State of Coordinated Ammonia as Examined by Means of NMR. The NMR signals of A and B in CF_3COOH could be observed only within a narrow concentration range of 2—3/100 mol/l because of the paramagnetism of the substance. The results are shown in Fig. 4 and Table 2.

From these considerations, it seems reasonable to conclude that some change in the PPM of NH_3 was caused by the change in the oxidation state of cobalt or the kind of the anion, and that the number of ammonia was in conformity with the analytical results.

We express our gratitude to Professor Yasuhide Yukawa, Professor Ryoichi Kiriyama, Professor Souichi Misumi, Dr. Hichio Kawai, Dr. Yoshio Cho and Dr. Mitsuru Sakai for their valuable suggestions. We also wish to thank Mr. Takuzo Fujino for the elemental analyses and Mr. Hideo Naoki for the NMR spectra.

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