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Paramagnetic Cobalt(III) Complexes with Organic Ligands. VII.[1] The Isolation and Properties of Paramagnetic Tetraammine(5-nitrososalicylato)cobalt(III) Complexes

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The title paramagnetic complexes, $[Co(5\text{-}NOsal)(NH_3)_4]X_2 \cdot nH_2O$ (X_2=Cl(NO_3), $Cl_2 \cdot HCl$, and Cl_2), all brown in color, have been isolated and characterized by analytical, spectroscopic, and magnetic methods. The effective magnetic moments of the complexes are 1.6—1.8 BM, and the absorption spectra have two peaks, at 387 and 518 nm. In the XPS of the complex, the cobalt 2p peaks have satellites, and the peak of the nitrogen 1s could be deconvoluted to that of NH_3 nitrogen at 400.2 eV and to that of NO nitrogen at 402.2 eV. This binding energy of the NO nitrogen of the complex is different from that (405.6 eV) of the NO_2 nitrogen of the green Paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) complexes, $[Co(5\text{-}NO_2sal)(NH_3)_4]X_2$, and establishes the difference between these two series of complexes.

In previous papers, we reported several green paramagnetic amine(5-nitrosalicylato)cobalt(III) complexes,[2–7] $[Co(5\text{-}NO_2sal)L]^{2+}$ (L: $(NH_3)_4$, $(en)_2$, $(bpy)_2$, trien), which are prepared from 60% nitric acid and the corresponding diamagnetic amine(salicylato)cobalt(III) complexes, $[Co(sal)L]Cl \cdot nH_2O$.[8,9] Gillard *et al.*[10,11] claimed, however, that the green compounds prepared in this way contain the 5-nitrososalicylato ligand rather than the 5-nitrosalicylato ligand, and the problem has so far remained unsolved. We have, though, recently been able to exclude this latter possibility by isolating a true tetraammine(5-nitrososalicylato)cobalt(III) complexes as $[Co(5\text{-}NOsal)(NH_3)_4]X_2$, which is brown, paramagnetic, and is clearly distinguished from the green paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) complexes, $[Co(5\text{-}NO_2sal)(NH_3)_4]X_2$, especially by the N 1s peaks in the X-ray photoelectron spectra.

Results and Discussion

By the digestion of ammoniacal cobalt(III) chloride with 5-nitrososalicylic acid and the subsequent treatment of the precipitated substance with 60% nitric acid, brown complexes with the constitution $[Co(5\text{-}NOsal)(NH_3)_4]X_2 \cdot nH_2O$ (**1**) (X_2=$Cl \cdot (NO_3) \cdot 2H_2O$ (**1a**), $Cl_2 \cdot H_2O \cdot HCl$ (**1b**), and $Cl_2 \cdot H_2O$ (**1c**); *cf.* Experimental sections) were obtained. They are soluble in water, nitric acid, and hydrochloric acid, but are insoluble in most organic solvents. The magnetic susceptibility obeyed the Curie-Weiss law, with effective magnetic moments of 1.6—1.8 BM, suggesting the presence of one unpaired electron.

The formula conforms to the quadrivalence of cobalt, while the rocking frequency of ligand ammonia was observed at around 830 cm^{-1} in the IR spectrum, which is within the range of those of Co(III) ammine complexes.[12,14] This, like the behavior to be described below, is similar to that of the green paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) complex,[5] $[Co(5\text{-}NO_2sal)(NH_3)_4]X_2$ (**2**), reported previously. Thus, in both complexes, only the proton signals of the ammine ligands appeared in the ^1H NMR spectra in 65% DNO_3, and no proton signals of the substituted salicylato ligand were observable. The ^{13}C NMR spectrum did not show the expected signals because of paramagnetism. Also, the cobalt 2p peaks of XPS of **1** have satellites and have a somewhat greater FWHM (2.6 eV for Co $2p_{3/2}$ at 220 K), as is shown in Fig. 1, and some carbon atoms (estimated to be 17.8% of the total carbon in **1** and 22.2% thereof in **2**)[7] have a higher 1s binding energy (289 eV, sh), as is shown in Fig. 2. This behavior[7] suggests that, in **1** also, the unpaired electron spends its time partly on the cobalt atom and partly on the ring of the substituted salicylato ligand.

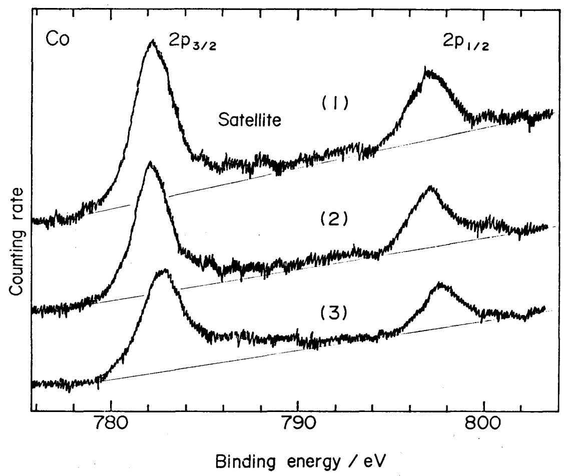
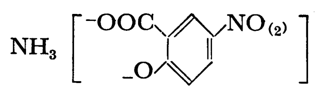


Fig. 1. The XPS in the Co_{2p} region at 220 K of **1b**, **2**, and **3** complexes.
(1): $[Co(5\text{-}NOsal)(NH_3)_4]Cl_2 \cdot H_2O \cdot HCl$, (2): $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl(NO_3) \cdot 3H_2O$, (3): $[Co(5\text{-}NOsal)(NH_3)_4]Cl$.

A clear distinction between **1** and **2** was found in the XPS N 1s spectra (Fig. 3): in the former, the N 1s peak could be deconvoluted to that of NH_3 at 399.5 and 400.2 eV and an NO N 1s peak at 402.0 eV, whereas in the latter, deconvolution gave an NH_3 N 1s peak at 400.2 eV and an NO_2 N 1s peak at 405.6 eV. In the ^1H NMR spectra, the proton signals of the coor-

TABLE 1. SOME PHYSICAL PROPERTIES OF COMPLEXES **1**—**3** AND RELATED LIGANDS

	Absorption bands		^{1}H-NMR spectra	XPS (eV) at 220 K					Magnetic moment	IR spectra
	λ/nm	ε	NH$_3$  δ/ppm	C 1s	N 1s	O 1s	Co $2p_{3/2}$	Co $2p_{1/2}$	μ_{eff}/BM	$\rho_r(NH_3)_r$ cm^{-1}
1a	345 388 520	(9200)[a] (10100) (3500)	2.70 s (3H)[b] 3.63 s (3H) 3.86 s (3H)	285.6 max 289.0 sh	400.2 NH$_3$ 402.0 NO	532.7 max FWHM 3.3	782.2 FWHM 2.6 satellites medium	797.0	1.60[i]	825
1b	342 387 518	(8800)[a] (10300) (3700)	2.70 s (3H)[b] 3.62 s (6H) 3.86 s (3H)	285.6 max 289.0 sh	399.5 400.2 NH$_3$ 402.0 NO	532.7 max FWHM 3.3	782.2 FWHM 2.6 satellites medium	797.0	1.80	838
1c	346 385 522	(8300)[a] (8600) (3000)	2.70 s (3H)[b] 3.63 s (9H)	285.6 max 288.4 sh	399.3 400.4 NH$_3$ 402.2 NO	532.8 max FWHM 2.9	782.6 FWHM 2.6 satellites medium	797.6	1.71	830
2	450 660	(3700) (12400)	3.76 s (6H) 3.30 s (6H)	285.4 max 288.6 sh	400.2 NH$_3$ 405.6 NO$_2$ 407.2 NO$_3$	532.4 max FWHM 3.1	782.2 FWHM 2.4 satellites medium	797.0	1.70	840
3	356	(8500)[c]	2.79 s (6H)[d] 3.46 s (6H) [6.6—7.8m (3H)]	285.1 max	399.8 400.5 NH$_3$ 402.2 NO	532.8 max FWHM 3.1	782.6 FWHM 2.7 satellites strong	797.6	2.84	825
L$_a$[g]	348[e] 710		[6.96 d (1H)[f] 7.67dd(1H) 8.65 d (1H)]	285.1 max 289.0 sh	401.6 NO	533.2 max FWHM 3.0				
L$_b$[h]	320[e]		[7.06 d (1H)[f] 8.32dd(1H) 8.70 d (1H)]	285.1 max 289.0 sh	405.8 NO$_2$	533.0 max FWHM 2.9				

sh: Shoulder. Solvent: a) 60% HNO$_3$. b) 65% DNO$_3$. c) 1.8 mol dm^{-3} H$_2$SO$_4$. d) 11 mol dm^{-3} D$_2$SO$_4$. e) MeOH. f) MeOH-d_4. Standard: Internal DSS for NMR. The maximum of Cl $2p_{3/2}$ has been taken to be at 198.2 eV for XPS. g) L$_a$: 5-Nitrososalicylic acid. h) L$_b$: 5-Nitrosalicylic acid. i) The values obtained varied to some extent and always lower than 1.73 BM. It thus seemed difficult to obtain this chloride nitrate salt in a pure state.

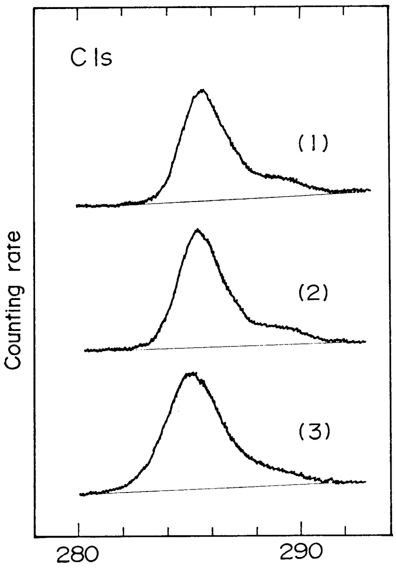


Fig. 2. The XPS in the C_{1s} region at 220 K of **1b**, **2**, and **3** complexes.
(1): $[Co(5\text{-}NOsal)(NH_3)_4]Cl_2 \cdot H_2O \cdot HCl$, (2): $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl(NO_3) \cdot 3H_2O$, (3): $[Co(5\text{-}NOsal\text{-})(NH_3)_4]Cl$.

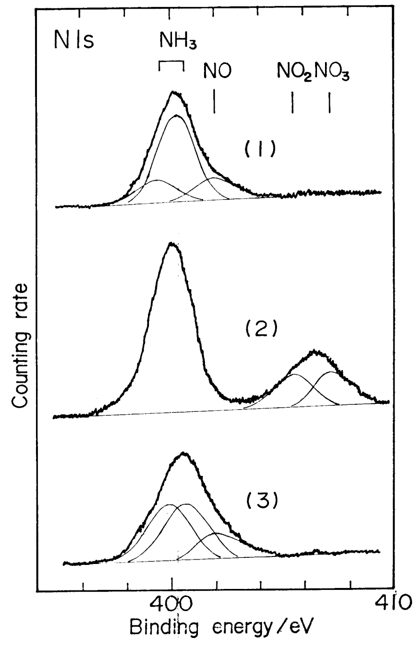


Fig. 3. The XPS in the N_{1s} region at 220 K of **1b**, **2**, and **3** complexes.
(1): $[Co(5\text{-}NOsal)(NH_3)_4]Cl_2 \cdot H_2O \cdot HCl$, (2): $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl(NO_3) \cdot 3H_2O$, (3): $[Co(5\text{-}NOsal)\text{-}(NH_3)_4]Cl$.

dinated ammine ligands of **1** split into three with the intensity ratio of 1:2:1, while those of **2**[5)] split into two with the intensity ratio of 2:2. The chemical shift (δNH_3 at 2.7 ppm) of ammine protons in a position trans[5)] to the carboxyl oxygen of the 5-nitrososalicylato ligand in **1** was at a higher field than that (3.76 ppm) of **2**. Another point of difference was found in the visible and UV absorption spectra reflecting their color differences.[2)]

Paramagnetic tetraammine(5-nitrososalicylato)cobalt(III) complexes of another type, $[Co(5\text{-}NOsal)(NH_3)_4]Cl$ (**3**), has been isolated from the reaction mixture as a much less soluble minor component (*cf.* Experimental section). The formula shows that this compound has an oxidation state less by unity than that of the **1** complexes; it was at first thought to be a simple Co(III) complex. However, the measurement of the magnetic susceptibility of the complex in a solid state from 77.4 K—r.t. gave an effective magnetic moment of 2.84 BM, suggesting the presence of two unpaired electrons, and the cobalt 2p peaks of the XPS have strong satellites, as is shown in Fig. 1. Thus, the compound can be regarded as a sort of biradical complex, two electrons being accomodated in a molecular orbital formed from the ligand orbital and the Co-e_g orbital. The ^1H NMR spectrum of **3** in 11 mol dm^{-3} D_2SO_4 at room temperature showed two singlets of ammine ligands and a multiplet of the 5-nitrososalicylato ligand in the integral ratio of 6:6:3, as is shown in Table 1. The appearance of the latter seems to suggest the absence of any appreciable spin density on the 5-nitrososalicylato ligand in solution, making a marked contrast to the behavior of **1** and **2**. An ESR study which is now going on is expected to give further information as to the electronic state of the complex.

The data of various physicochemical measurements of **1**—**3** are collected in Table 1.

Experimental

Measurements. The NMR spectra were recorded with an FX-60 apparatus (JEOL) for ^{13}C NMR and with an R-40 apparatus (Hitachi) for ^1H NMR. The IR spectra were recorded on potassium bromide disks with an IR-27G apparatus (Shimadzu). The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The magnetic susceptibilities were measured by the Faraday's method using a magnetic balance (Shimadzu) from liq. N_2 to r.t. The XPS were obtained by irradiating the compounds with Mg $K\alpha$ X-rays (120 W) in a vacuum at a pressure of less than 3×10^{-7} Pa and at around 220 K.[7)] The instrument used was a VG ESCA 3 electron spectrometer.

Preparation of 5-Nitrososalicyclic Acid. 5-Nitrososalicyclic acid of a green color was prepared by Gulinov's method.[15)] The absorption spectrum of 5-nitrososalicylic acid in methanol has three peaks, at 268, 348, and 710 nm. The ^1H NMR spectrum of 5-nitrososalicylic acid in methanol-d_4 is different from that of 5-nitrosalicylic acid, as is shown in Table 1.

Preparation of Complex. Tetraammine(5-nitrososalicylato)-cobalt(III) Chloride Nitrate Dihydrate (1a). A 28% ammonia solution (9.6 cm^3) was added to an aqueous solution (12.0 cm^3) of $CoCl_2 \cdot 6H_2O$ (5.71 g, 24.00 mmol). After the mixture has been stirred at room temperature, about 6.4 cm^3 of a 20% hydrogen peroxide solution was slowly added to the solution. 5-Nitrososalicylic acid (4 g, 24.00 mmol) was then added to the solution at 50 °C, and the mixture was concentrated at 60 °C. The precipitate (**A**) thus obtained was filtered off, washed with water, and dried. Yield: 6.88 g. Four cubic centimeters of 60% nitric acid were added to 2 g of **A**. Heat was evolved. The cooled solution was filtered with a glass filter (G 4), and the filtrate was added to ethanol. The brown substance thus separated out was filtered with a glass filter (G 3), washed with ethanol, and dried in a vacuum desiccator. This complex is slightly unstable in nitric acid. Yield: 1.1 g. Found: C, 19.95; H, 4.73; Cl, 8.37%. Calcd for $CoC_7H_{19}N_6O_9Cl$ (MW 425.65) C, 19.75; H, 4.50; Cl, 8.33%. Dec≈172 °C.

*Tetraammine(5-nitrososalicylato)cobalt(III) Dichloride Hydrate Hydrogen Chloride (**1b**).* Two milliliters of 36% hydrochloric acid were added to 1 g (2.35 mmol) of the above complex (**1a**), the brown solution was filtered with a glass filter (G 4), and the filtrate was added to ethanol. The brown complex thus precipitated was filtered with a glass filter (G 3), washed with ethanol, and dried in a silica gel desiccator. Yield: 0.65 g. (66.2%) Found: C, 19.86; H, 4.55; Cl, 24.23%. Calcd for $CoC_7H_{18}N_5O_5Cl_3$ (MW 417.54) C, 20.13; H, 4.35; Cl, 25.47%. Dec≈182 °C.

*Tetraammine(5-nitrososalicylato)cobalt(III) Dichloride Hydrate (**1c**).* This complex was formed when Complex **1b** was dried in a vaccum desiccator over potassium hydroxide. Found: C, 22.49; H, 4.34; Cl, 19.78%. Calcd for $CoC_7H_{17}N_5O_5Cl_2$ (MW 381.08) C, 22.06; H, 4.50; Cl, 18.61%. Dec. ≈180 °C.

*Tetraammine(5-nitrososalicylato)cobalt(III) Monochloride (**3**).* Five and two-tenths grams of A were extracted with 100 cm³ of water at 50 °C. The brown extract was concentrated in a rotary evaporator at 45 °C. The solution was cooled, and the **3** complex thus precipitated was filtered and dried. It was then recrystallized from water. Yield: 0.10 g. Found: C, 25.70; H, 4.58; Cl, 12.50%. Calcd for $CoC_7H_{15}N_5O_4Cl$ (MW 327.61) C, 25.66; H, 4.62; Cl, 10.82%. Dec 160—163 °C.

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1) a) Part VI: Ref. 7; b) Presented at the 43rd National Meeting of the Chemical Society of Japan, Tokyo, April, 1981.

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