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Paramagnetic Cobalt(III) Complexes with Organic Ligands. IX.[1] The Preparation and Properties of Paramagnetic Tetraammine(5-nitrosalicylideneaminato)cobalt(III) Complexes

Yoshihisa YAMAMOTO* and Eiko TOYOTA
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02
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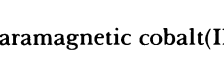
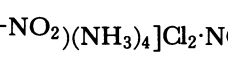
The title paramagnetic cobalt(III) complexes, [Co()$(NH_3)_4$]X_3,(X_3: $Cl_2{\cdot}NO_3$, $(NO_3)_3$), both green color, have been isolated and characterized by analytical, spectroscopic and magnetic methods. The effective magnetic moments are 1.7 BM, suggesting an unpaired spin. The ^{1}H NMR spectra indicate that the unpaired spin on the complexes is localized over the π-orbitals of the chelated ligand. In the XPS, the high binding energy area at 286—289 eV of the C 1s peak of both the complexe is larger than that for the corresponding diamagnetic cobalt(III) complex. The cobalt 2p peaks do not have satellites in the same manner as the usual diamagnetic cobalt(III) complexes. It can be concluded that an unpaired spin on complexes is not located on the cobalt atom, but is located over the π-orbitals of the chelated ligand of complexes.

Previously, we have been concerned with the preparation and properties of several green paramagnetic amine(5-nitrosalicylato)cobalt(III) complexes, [Co(5-NO_2sal)L]$^{2+}$ (L: $(NH_3)_4$,[2] en$_2$,[3] $(bpy)_2$,[4] quadridentate amine[4,5]). Their effective magnetic moments are 1.7—1.9 BM, suggesting an unpaired spin. Until now, the organic ligand in paramagnetic cobalt(III) complexes has been a 5-nitrosalicylato ligand. Therefore, very little is known regarding the isolation and physical properties of paramagnetic cobalt(III) complexes, in contrast to the information on diamagnetic cobalt(III) complexes with various organic ligands.[6—17] The isolation of a new paramagnetic cobalt(III) complex was tried with another organic ligand. As a result, a new paramagnetic cobalt(III) complex has been isolated with a 5-nitrosalicylideneaminato ligand, [Co()$(NH_3)_4$]$Cl_2{\cdot}NO_3$. This paper deals with the preparation and properties of the paramagnetic cobalt(III) complex and with the electronic state of the unpaired spin.

Experimental

Measurements. The NMR spectra were recorded with an FX-60 apparatus (JEOL) for ^{13}C NMR and with an R-40 apparatus (Hitachi) or Varian XL-200 NMR spectrometer for ^{1}H 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) between liq. N_2 and room temperature. The electric conductivities of aqueous solutions were determined by the use of a Shimadzu CM-30 conductometer at room temperature. For the XPS measurements, samples were placed on a gold mesh holder and dispersed with acetone. After evacuating to a vacuum better than 7×10^{-7} Pa(5×10^{-9} Torr), samples were cooled to 200 K and irradiated with Mg $K\alpha$ X rays (120 W). The instrument used was a VG ESCA 3-electron spectrometer. Analyzer energy was set so as to give the half width at half maximum [FWHM] of an Au $4f_{7/2}$ peak of 1.18 eV. The peak separation of N 1s or C 1s spectra was achieved using the Gauss-Newton least-squares method, where a mixed Gaussian-Lorentzian curve shape having a fixed FWHM was utilized. The binding energies of the electrons were calibrated by assigning 285.0 eV to the C 1s peak of the normal benzene-ring carbon.

Preparation of Complexes. Pramagnetic Tetraammine(5-nitrosalicylideneaminato)cobalt(III) Dichloride Nitrate (1a): Three cm^3 of 60% nitric acid were added to tetraammine(salicylideneaminato)cobalt(III) chloride hydrate (**2a**)[16] (2.0 g, 5.95 mmol) of russet color. The color of the complex changed to green. Further, 3 cm^3 of 60% nitric acid was added to the solution and stirred. The solution was filtered using a glass filter (G-4) and the filtrate was added to acetone. The precipitated green complex was filtered, washed with acetone, and dried. The obtained complex was dissolved in 3 cm^3 of 60% nitric acid, the solution was filtrated and the filtrate was added to acetone. A precipitated green complex was filtered, washed with acetone and dried. This process was repeated again. From an orange colored filtrate, the corresponding orange diamagnetic complexes **3** and **5** (see below) were isolated. Yield: 0.85 g (33.6%). Found: C, 19.55; H, 4.24; N, 22.62; Cl, 16.68%. Calcd for $CoC_7H_{17}N_7O_6Cl_2$ (MW 425.10) C, 19.78; H, 4.03; N, 23.06; Cl, 16.68%. Absorption spectrum: 363 nm (ε=5050), 450 nm (ε=2830), and 663 nm (ε=10060) in 60% nitric acid. IR spectrum: 1630 cm^{-1} ($C{=}N_{str.}$) and 830 cm^{-1} ($\rho_r(NH_3)_r$). Λ=371 S cm^2 equiv^{-1} in water.

Paramagnetic Tetraammine(5-nitrosalicylideneaminato)cobalt(III) Trinitrate (1b): This complex was prepared from a reaction mixture of 60% nitric acid (6 cm^3) and tetraammine(salicylideneaminato)cobalt(III) nitrate (**2b**)[16] (2.0 g, 5.39 mmol) with the preparation method of **1a**. Yield: 0.93 g (36.1%). Found: C, 17.13; H, 3.85; N, 25.84%. Calcd for $CoC_7H_{17}N_9O_{12}$ (MW 478.21) C, 17.58; H, 3.58; N, 26.36%. Absorption spectrum: 360 nm (ε=4960), 455 nm (ε=3330) and 667 nm (ε=11000) in 60% nitric acid. IR spectrum: 1630 cm^{-1} ($C{=}N_{str.}$) and 830 cm^{-1} ($\rho_r(NH_3)_r$). Λ=363 S cm^2 equiv^{-1} in water.

Tetraammine(5-nitrosalicylideneaminato)cobalt(III) Dinitrate (3): The orange colored acetone filtrate of **1a** or **1b** was concentrated. After 10 h, a precipitated orange complex was filtered and recrystallized from water. Yield: 0.32 g (12.9%).

Found: C, 19.80; H, 3.76; N, 26.70%. Calcd for $CoC_7H_{17}N_8O_9$ (MW 416.20) C, 20.20; H, 4.12; N, 26.92%. Absorption spectrum: 363 nm (ε=12600) and 480 nm (ε=210) in water. IR spectrum: 1635 cm^{-1} ($C{=}N_{str.}$) and 830 cm^{-1} ($\rho_r(NH_3)_r$). Λ= 226 S cm^2 $equiv^{-1}$ in water.

Tetraammine(3,5-dinitrosalicylideneaminato)cobalt(III) Dinitrate (5): The orange colored acetone filtrate of **1a** or **1b** was permitted to stand for at least 3 d, then, the solution was concentrated. Thus, precipitated complex **5** was filtered and recrystallized from water. Yield: 0.44 g (16.0%). Found: C, 18.59; H, 3.94; N, 26.78%. Calcd for $CoC_7H_{16}N_9O_{11}$ (MW 461.20) C, 18.23; H, 3.50; N, 27.33%. Absorption spectrum: 357 nm (ε=11900) and 480 nm (ε=210) in water. IR spectrum: 1635 cm^{-1} ($C{=}N_{str.}$) and 830 cm^{-1} ($\rho_r(NH_3)_r$). Λ=250 S cm^2 $equiv^{-1}$ in water. ^1H NMR spectrum δ=3.04 (s, 3H), 3.19 (s, 3H), 3.32 (s, 3H), 3.98 (s, 3H) for NH_3; δ=8.29 (d, 1H) for H_4, δ=8.44 (t, 1H) for H_6, δ=8.82 (dd, 1H) for CH=N and δ=10.58 (d, 1H) for C=NH in 1.8 mol dm^{-3} D_2SO_4 solution. The H_3 and H_5 proton signals disappeared by nitration at room temperature.

Solubility. Complexes **1a—b** are soluble in water, 60% nitric acid, DMSO, DMF, and 35% hydrochloric acid, and slightly soluble in methanol but insoluble in the common organic solvents. Complexes **3** and **5** are soluble in water, DMSO, DMF, and insoluble in the common organic solvents. Complex **3** is soluble in 60% nitric acid and 35% hydrochloric acid, but **5** is slightly soluble in 60% nitric acid and 35% hydrochloric aicd.

Results and Discussion

Paramagnetic tetraammine(5-nitrosalicylideneaminato)cobalt(III) complexes, $[Co(HN{=}HC\text{-}C_6H_3(O)\text{-}NO_2)(NH_3)_4]X_3$ (X_3:$Cl_2\cdot NO_3$ (**1a**) and $(NO_3)_3$ (**1b**)), have been isolated from reaction mixtures of diamagnetic tetraammine(salicylideneaminato)cobalt(III) complexes, $[Co(HN{=}HC\text{-}C_6H_4(O))(NH_3)_4]X_2\cdot nH_2O$ (X=Cl, n=1 (**2a**); X=NO_3, n=0 (**2b**)), 60% nitric acid and acetone. The electric conductivity in an aqueous solution was ca. 360 S cm^2 $equiv^{-1}$. The elemental analysis are in agreement with the theoretical values. The magnetic susceptibility obeyed the Curie-Weiss law with effective magnetic moments of 1.7 BM, suggesting the presence of one unpaired spin. The formula conforms to the quadrivalence of cobalt. The rocking frequency of ligand ammonia, however, was observed at 830 cm^{-1} in the IR spectra. This is the range for Co(III) ammine complexes.[18-20] The absorption spectra showed a characteristic strong peak at about 660 nm. In the XPS (Table 1), the nitrogen 1s peaks were separated into four peaks at ca. 399.6 for NH=, at 400.6 for NH_3, at 405.8 for NO_2, and at 407.4 eV for NO_3. The C 1s peaks were separated into four peaks at ca. 285.0, 286.1, 287.1, and 288.5 eV as is shown in Fig. 1. The peak at 285.0 eV is assigned to normal benzene-ring carbon atoms[21] and hydrocarbon contamination. Three peaks in the 286—289 eV region with high binding energies have been assigned to electron-poor carbon atoms, relative to normal ring carbon atoms. The spin orbit separation of Co 2p was 15.0 eV. The ^1H NMR spectra were measured in a 1.8 mol dm^{-3} D_2SO_4 solu-

Table 1. XPS and Magnetic Moments of Complexes

	XPS (eV) at 200 K						Magnetic moments	Curie-Weiss constants
	Co $2P_{3/2}$	Co $2p_{2/1}$	splitting	C 1s	N 1s	O 1s	μ_{eff}/BM	θ/K
1a	782.5	797.5	15.0	285.0(55)	399.6(1) =NH	532.4	1.7	+19
	FWHM 3.0			286.1(28)	400.6(4) NH_3			
	satellites no			287.1(11)	405.8(1) NO_2			
				288.5(6)	407.4(1) NO_3			
				FWHM 2.10	FWHM 2.25			
1b	782.6	797.5	15.1	285.0(51)	399.6(1) =NH	532.6	1.7	+20
	FWHM 2.4			286.5(29)	400.5(4) NH_3			
	satellites no			287.2(13)	405.9(1) NO_2			
				288.4(7)	407.1(3) NO_3			
				FWHM 1.82	FWHM 1.90			
3	782.2	797.1	15.1	285.0(61)	399.3(1) =NH	532.5	dia.	—
	FWHM 2.6			286.4(31)	400.3(4) NH_3			
	satellites no			288.4(8)	405.6(1) NO_2			
				FWHM 2.10	407.1(2) NO_3			
					FWHM 2.13			
4[a]	781.9	796.8	14.9	285.0(75)	399.9(4) NH_3	532.0	1.9	0
	FWHM 2.6			286.8(15)	405.3(1) NO_2			
	medium satellites			288.8(10)	406.6(1) NO_3			
				FWHM 1.82	FWHM 2.10			

a): Ref. 2 and 21. The values of XPS are slightly different from those reported previously,[21] as the data analysis has been carried out more precisely by using a computer and a different reference peak (cf. Experimental section).

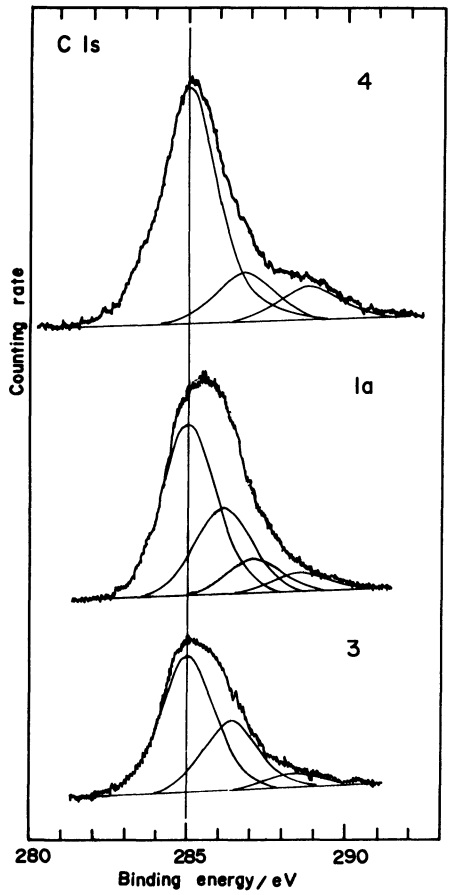


Fig. 1. The XPS in the C 1s region at 220 K of **1a**, **3**, and **4** complexes.

4 : $[Co(^{OOC}_{O}\text{-}NO_2)(NH_3)_4]Cl\cdot NO_3\cdot H_2O$

1a : $[Co(^{HN=HC}_{O}\text{-}NO_2)(NH_3)_4]Cl_2\cdot NO_3$

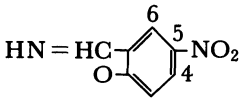
3 : $[Co(^{HN=HC}_{O}\text{-}NO_2)(NH_3)_4](NO_3)_2$

tion but the ^{13}CNMR spectra did not show the expected signals due to of paramagnetism.

In the XPS results for **1a**, the peak of the high binding energy area of C 1s is larger than that of the corresponding orange diamagnetic cobalt(III) complex, $[Co(^{HN=HC}_{O}\text{-}NO_2)(NH_3)_4](NO_3)_2$ (**3**) as is shown in Fig. 1. The peak area of the high binding energy region for **1a** is larger than that for the green paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) complex,[21] $[Co(5\text{-}NO_2sal)(NH_3)_4]X_2$ (**4**). The total intensity ratio (carbon/nitrogen) between seven carbons and five nitrogens (NH_3+NH) is 1.47 for **1a** and 1.31 for **3**, and experimental scattering due to the contamination is about ±15%. The difference in the proportion between **1a** and **3**, however, is always clearly observed. Thus, the electronic state of the chelated ligand of **1a** is different from that of **3**. On the other hand, the Co $2p_{3/2}$ peak at 782.2 eV does not have satellites at 200 K. It is similar to that of diamagnetic cobalt(III) complexes[22,23] and paramagnetic cobalt(III) complexes, e.g., μ-amido-μ-hyperoxobis(ethylenediamine)cobalt(III) tetranitrate,[21] however, shows satellites at 200 K. Then, the unpaired spin on **1a** can be localized over the chelated ligand, but it can not be located on the cobalt atom.

In the ^1H NMR spectrum of **1a**, complex **1a** changed to **3** in 1.8 mol dm^{-3} D_2SO_4 solution at −20 °C,[1] the spectrum showing signals of both **1a** and **3**. An H_5 ring proton signal disappeared due to nitration. The signals at δ=7.28 (d), 7.90 (d), 8.20—8.46 (m) and 11.14 (d) were assigned to the H_3, H_4, H_6 and CH=N and C=NH protons, respectively. Their chemical shifts and coupling constants are very similar to those of **3** (Table 2). Thus, the σ-bonds which are formed from protons and carbon atoms (sp^2 configuration) of a chelated ligand resemble the σ-bond of **3**. The unpaired spin can not be located over the hydrogen of the chelated ligand.[1] Thus, an unpaired spin on **1a**

Table 2. ^1H NMR Spectra of Complexs **1a**, **2a**, and **3**

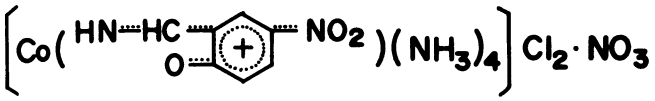


δ

Complex No.	H_3	H_4		H_5	H_6	CH=N	C=NH	NH_3 δ			Temp
	($^3J_{HCCH}$) Hz	($^3J_{HCCH}$) Hz	($^4J_{HCCCH}$) Hz	($^3J_{HCCH}$) Hz	($^4J_{HCCCH}$) Hz	($^3J_{HNCH}$) Hz					°C
1a	7.28 d (9.5)	7.90 d (9.5)	—	—	8.2—8.5 m	8.2—8.5 m	11.14 d	3.26(s)	3.50(s)	4.18(s)	−20
3	6.98 d (9.3)	7.94 dd (9.3)	(3.0)	—	8.30 d (3.0)	8.18 d (11.5)	10.47[a]	3.03(s, 3H)	3.15(s, 6H)	3.93(s, 3H)	+25
2a	7.00 d (8.5)	7.2—7.4 m		6.70 t (7.6)	7.2—7.4 m	8.05 d (11.5)	9.91[a]	3.01(s, 9H)		3.83(s, 3H)	+25

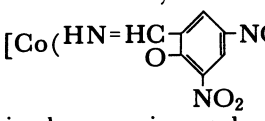
Solvent: 1.8 mol dm^{-3} D_2SO_4; Standard: internal DSS (δ=0). a): broad signal.

has been identified over the π-orbitals of the chelated ligand. Therefore, **1a** is a radical cobalt(III) complex;



A clear distinction between **1a** and **4** was found regarding stability, the Curie-Weiss constant and the XPS of Co 2p. Complex **1a** is more unstable than **4** for ^{1}H NMR measurements. This might be due to a difference in the electronic state of the cobalt atom. The Curie-Weiss constant of **1a** indicates ferromagnetism and the Co 2p peak does not have any satellites.

The absorption spectra of **1a** and **4**[2] have characteristic strong peaks at about 660 nm ($\varepsilon \fallingdotseq 10000$). This strong peak was not observed for **2a** and **3**, the usual diamagnetic cobalt(III) complexes and paramagnetic μ-amido-μ-hyperoxo cobalt(III) complexes[24-26] ($\varepsilon \fallingdotseq 417$ at 687 nm) and the related complexes. Thus, the strong peak is due to the unpaired spin on the complex.

The results for **1b** are listed in Table 1. The results of orange diamagnetic tetraammine(3,5-dinitrosalicylideneaminato)cobalt(III) dinitrate,  (**5**), are given in the experimental section.

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References

1) Part VIII. Y. Yamamoto, S. Shimokawa, and E. Yamada, *Bull. Chem. Soc. Jpn.*, **57**, 1153 (1984).
2) Y. Yamamoto, K. Ito, H. Yoneda, and M. Mori, *Bull. Chem. Soc, Jpn.*, **40**, 2580 (1967).
3) Y. Yamamoto, M. Mori, H. Yoneda, S. Misumi, and K. Ito, *Bull. Chem. Soc. Jpn.*, **42**, 984 (1969).
4) Y. Yamamoto, E. Toyota, and N. Mitsudera, *Bull. Chem. Soc. Jpn.*, **53**, 3517 (1980).
5) Y. Yamamoto and H. Kudo, *Bull. Chem. Soc. Jpn.*, **57**, 287 (1984).
6) A. Ablov, *Bull. Soc. Chim. Fr.*, **53**, 234 (1933).
7) A. C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 1968, 1549.
8) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.
9) A. Nakahara, *Bull. Chem. Soc. Jpn.*, **27**, 560 (1954).
10) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).
11) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).
12) L. J. Zompa, *Chem. Commun.*, 1969, 783.
13) S. Yamada, J. Hidaka, and B. E. Douglas, *Inorg. Chem*, **10**, 2187 (1971).
14) F. P. Dwyer, F. L. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).
15) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **57**, 47 (1984).
16) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **57**, 2650 (1984).
17) Y. Yamamoto, E. Toyota, and S. Tsukuda, *Bull. Chem. Soc. Jpn.*, **58**, 1595 (1985).
18) G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957).
19) L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964).
20) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, **1956**, 3108.
21) Y. Yamamoto, M. Mori, and H. Konno, *Bull. Chem. Soc. Jpn.*, **54**, 1995 (1981).
22) D. C. Frost, C. A. Mcdowell, and I. S. Woolsey, *Molecular Physics*, **27**, 1473 (1974).
23) Y. Okamoto, H. Nakano, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **48**, 1163 (1975).
24) R. Davies and A. G. Sykes, *J. Chem. Soc., A*, **1968**, 2237.
25) R. Davies and A. G. Sykes, *J. Chem. Soc., A*, **1968**, 2831.
26) R. Davies, M. Mori, and A. G. Sykes, *Inorg. Syn.*, Vol. 12, 197.