April, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 1299—1302 (1987) 1299

Paramagnetic Cobalt(III) Complexes with Organic Ligands. X.[1] The Preparation and Properties of Radical Diamminebis(5-nitrosalicylideneaminato)cobalt(III) Complex and Biradical Diamminebis(5-nitrosalicylideneaminato)cobalt(II) Complex

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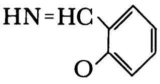
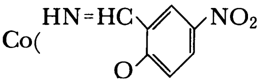
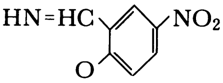
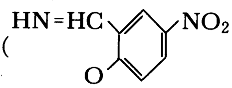
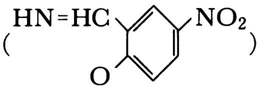
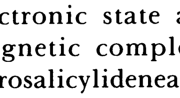
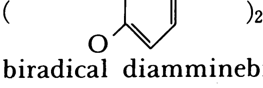
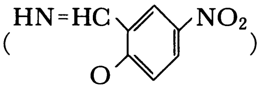
From the reaction mixture of diamminebis(salicylideneaminato)cobalt(III) complex, [Co-( $)_2(NH_3)_2]Cl\cdot H_2O$ (**1**) and 60% nitric acid, radical diamminebis(5-nitrosalicylideneaminato)-cobalt(III) complex, [Co( $)_2(NH_3)_2]Cl\cdot NO_3\cdot 2H_2O$ (**2**), and biradical diamminebis(5-nitrosalicylideneaminato)cobalt(II) complex, [Co( $)_2(NH_3)_2]Cl\cdot NO_3\cdot 2H_2O$ (**3**), have been isolated and characterized by analytical, magnetic, spectroscopic, and XPS methods. The effective magnetic moments of **2** and **3** were 1.7 and 5.5 BM, respectively. In the IR spectrum of **2**, a band due to the rocking deformation vibration of NH_3 was observed at ca. 840 cm^{-1}. The absorption spectra of **2** and **3** showed a strong absorption peak at ca. 690 nm. In the XPS, Co 2p spectra for **3** showed strong satellites, indicating the oxidation number of the cobalt to be +2, whereas no satellites were observed for the other complexes. In comparison with diamagnetic cobalt(III) complex, [Co( $)_2(NH_3)_2]NO_3\cdot H_2O$ (**4**), C 1s spectra for **2** and **3** showed much larger shoulders on the higher binding energy side due to the electron-poor carbons. It suggests the presence of an unpaired spin on ligands in accordance with paramagnetism of the complexes.

Previous paper of this series was concerned with the preparation, properties and electronic state of radical tetraammine(5-nitrosalicylideneaminato)cobalt(III) complex,[2] [Co( $)(NH_3)_4]X_3$ (X_3: $Cl_2\cdot NO_3$, $(NO_3)_3$). The effective magnetic moment is 1.7 BM, suggesting an unpaired spin. An unpaired spin on the complex is not located on the cobalt atom, but is located over the π-orbitals of the chelated ligand of the complex judging from the physicochemical results.

In the same series of experiments, we have already isolated new paramagnetic cobalt complexes from the reaction mixture of 60% nitric acid and diamminebis(salicylideneaminato)cobalt(III) complex, [Co( $)_2(NH_3)_2]Cl\cdot H_2O$. However, the explanation of the electronic states of the new complexes was deferred, because the magnetic properties and XPS data were not parallel to those of the radical tetraammine(5-nitrosalicylideneaminato)cobalt(III) complex. In the present paper, we present the electronic state and structure of the new paramagnetic complexes as radical diamminebis(5-nitrosalicylideneaminato)cobalt(III) complex, [Co-( $)_2(NH_3)_2]Cl\cdot NO_3\cdot 2H_2O$, and biradical diamminebis(5-nitrosalicylideneaminato)-cobalt(II) complex, [Co( $)_2$-$(NH_3)_2]Cl\cdot NO_3\cdot 2H_2O$, and report the preparation and properties of them.

Experimental

Measurements. The ^1H NMR spectra were recorded with an R-40 apparatus (Hitachi). The IR spectra were recorded in potassium bromide disks with an 270-30 apparatus (Hitachi). The visible absorption spectra were recorded with a Shimadzu UV-210 recording spectrophotometer. The magnetic susceptibilities were measured by the Faraday method using a magnetic balance (Shimadzu) from liq. N_2 to room temperature. The electric conductivities of aqueous solutions were determined by the use of a conductometer, CM-30 (Shimadzu) at room temperature. The XPS measurements were carried out in the same manner as described in the previous paper.[2]

Preparation of Complexes. Radical Diamminebis(5-nitrosalicylideneaminato)cobalt(III) Chloride Nitrate Dihydrate (2): Twelve cm^3 of 60% nitric acid were added, drop by drop, to 3 g (7.76 mmol) of trans,trans,trans-diamminebis(salicylideneaminato)cobalt(III) chloride hydrate[5] (**1**). The reaction proceeds with violence. A green crystalline precipitate (complex **2**) was collected by filtration. From the green filtrate, complex **3** (described below) was isolated. The complex **2** on a filter funnel was washed with 60% nitric acid (about 3 cm^3), with acetone and ether, and dried. Yield: 1.42 g (32.9%). Found: C, 30.42; H, 3.43; N, 18.05; Cl, 5.81%. Calcd for $CoC_{14}H_{20}N_7O_{11}Cl$ (MW 556.75) C, 30.20; H, 3.62; N, 17.61; Cl, 6.37%. Color: green. D_p=185 °C. Λ=250 S cm^2 mol^{-1} in water. IR spectrum: 1620 cm^{-1} (C=N), 840 cm^{-1}

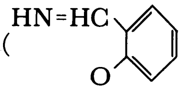
($\rho_r(NH_3)_r$).

Biradical Diamminebis(5-nitrosalicylideneaminato)cobalt(II) Chloride Nitrate Dihydrate (3): The green filtrate (described above) was added to acetone-ether (1 : 1) solution and stirred. The green complex **3** thus precipitated was filtered, washed with acetone-ether (1 : 1) solution and with ether, then dried. From the brown filtrate, complex **4** (described below) was isolated. Yield: 1.48 g (34.3%). Found: C, 29.92; H, 3.68; N, 17.23; Cl, 5.08%. Calcd for $CoC_{14}H_{20}N_7O_{11}Cl$ (MW 556.75) C, 30.20; H, 3.62; N, 17.61; Cl, 6.37%. Color: green. D_p=183 °C. Λ=250 S cm^2 mol^{-1} in water. IR spectrum: 1625 cm^{-1} (C=N).

Diamagnetic Diamminebis(5-nitrosalicylideneaminato)cobalt(III) Nitrate Hydrate (4): The brown colored filtrate (described above) was concentrated and the precipitated brown complex was recrystallized from water. Yield: 0.22 g (5.6%). Found: C, 33.29; H, 3.42; N, 19.65%. Calcd for $CoC_{14}H_{18}N_7O_{10}$ (MW 503.28) C, 33.41; H, 3.61; N, 19.48%. Color: brown. D_p=238 °C. Λ=95 S cm^2 mol^{-1} in water at 50 °C. IR spectrum: 1625 cm^{-1} (C=N), 835 cm^{-1} ($\rho_r(NH_3)_r$). ^{1}H NMR spectrum: The H_5[5] ring proton signal disappeared due to nitration. The H_3, H_4, H_6 ring proton, CH=N and C=NH proton signals were observed at δ 6.79 (d, 2H), 7.96 (dd, 2H), 8.41 (d, 2H), 8.51 (d, 2H), and 11.10 (d, 2H), respectively in DMSO-d_6 solution.

Solubility. Complex **2** is soluble in DMSO, DMF, and slightly soluble in water and 60% nitric acid, but insoluble in the common organic solvents such as alcohols, acetone, and ether. Complex **3** is soluble in DMSO, DMF, water, and 60% nitric acid, and slightly soluble in acetone and methanol, but insoluble in the common organic solvents such as ethanol and ether.

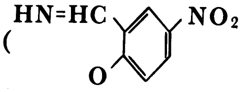
Results and Discussion

Previously, we reported on the preparation, properties, and structure of diamagnetic trans,trans,trans-diamminebis(salicylideneaminato)cobalt(III) chloride hydrate,[5] [Co()$_2$(NH$_3$)$_2$]Cl·H$_2$O (**1**).

$[\mathrm{Co}(\mathrm{HN{=}HC}\text{-}C_6H_4\text{-}O)_2(NH_3)_2]Cl\cdot H_2O$

trans,trans,trans-configuration (abbreviation: t,t,t-) denotes the positions for the two ammine ligands, two phenoxyl groups and two CH=NH groups of the coordinated chelate ligands, respectively.

Radical diamminebis(5-nitrosalicylideneaminato)-cobalt(III) chloride nitrate dihydrate (**2**) and biradical diamminebis(5-nitrosalicylideneaminato)cobalt(II) chloride nitrate dihydrate (**3**) were isolated from a reaction mixture of complex (**1**) and 60% nitric acid.

Radical Diamminebis(5-nitrosalicylideneaminato)-cobalt(III) Chloride Nitrate Dihydrate, [Co-()$_2$(NH$_3$)$_2$]Cl·NO$_3$·2H$_2$O (2):

$[\mathrm{Co}(\mathrm{HN{=}HC}\text{-}C_6H_3(NO_2)\text{-}O)_2(NH_3)_2]Cl\cdot NO_3\cdot 2H_2O$

The electric conductivity in an aqueous solution was 250 S cm^2 mol^{-1}. The magnetic susceptibility obeyed the Curie-Weiss law, with effective magnetic moment of 1.7 BM, suggesting the presence of an unpaired spin. A band due to the rocking deformation vibration of the ammine ligand was observed at 840 cm^{-1} in the IR spectrum. This is in the range for Co(III) ammine complexes.[6–10] The ^{1}H NMR spectrum of **2** could not be measured in 1.8 mol dm^{-3} D_2SO_4 solution because of the insolubility.

In the XPS, two N 1s spectra were observed at ca. 400 eV and ca. 406 eV. The lower binding energy peak was separated to two peaks which were assigned to -NH= and NH_3 nitrogens. The higher binding energy peak was also separated into two peaks which were assigned to NO_2 and NO_3 nitrogens[2–4] as shown in Table 1.

Table 1. XPS, Magnetic Moments, and Absorption Spectra of Complexes

Complex No.	Binding energies of electrons, E_B/eV						Magnetic moments μ_{eff}/BM	Curie-Weiss constants θ/K	Absorption bands in 60% nitric acid nm (ε)
	Co 2p$_{3/2}$	Co 2p$_{1/2}$	splitting	C 1s	N 1s	O 1s			
2	782.1 FWHM 2.4 satellites no	797.4	15.3	285.0 (45.2)[a] 286.1 (34.0) 287.4 (16.5) 289.4 (4.3)	399.4 =NH 400.3 NH$_3$ 405.7 NO$_2$ 406.8 NO$_3$	532.7	1.7	+23	380 (18890) 700 (6600)
3	782.2 FWHM 3.5 satellites very strong	797.3	15.1	285.0 (38.9) 286.3 (27.9) 287.7 (14.5) 289.1 (15.2) 291.2 (3.5)	399.8 =NH 400.2 NH$_3$ 405.8 NO$_2$ 406.9 NO$_3$	532.4	5.5	+10	363 (13500) 696 (12700)
4	782.1 FWHM 2.5 satellites no	797.0	14.9	285.0 (61.6) 286.3 (33.9) 288.9 (4.5)	399.4 =NH 399.9 NH$_3$ 405.5 NO$_2$ 406.7 NO$_3$	532.6	dia.		370 (19900)
5[b]	782.5 FWHM 3.0 satellites no	797.5	15.0	285.0 (55) 286.1 (28) 287.1 (11) 288.5 (6)	399.6 =NH 400.6 NH$_3$ 405.8 NO$_2$ 407.4 NO$_3$	532.4	1.7	+19	363 (5050) 450 (2830) 667 (10060)

a) Relative intensities in % after peak separation. The peak less than 1% was neglected. b) Ref. 2.

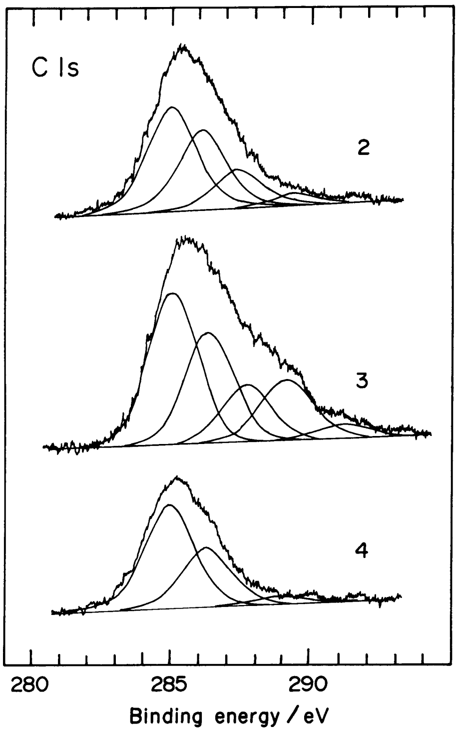
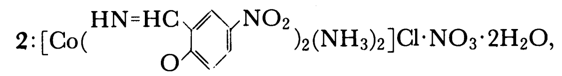
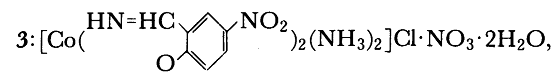
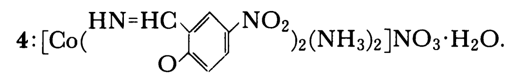


Fig. 1. The XPS in the C 1s region of **2**—**4** complexes.


$\mathbf{2}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{Cl}\cdot\mathrm{NO_3}\cdot 2\mathrm{H_2O}$,


$\mathbf{3}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{Cl}\cdot\mathrm{NO_3}\cdot 2\mathrm{H_2O}$,


$\mathbf{4}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{NO_3}\cdot\mathrm{H_2O}$.

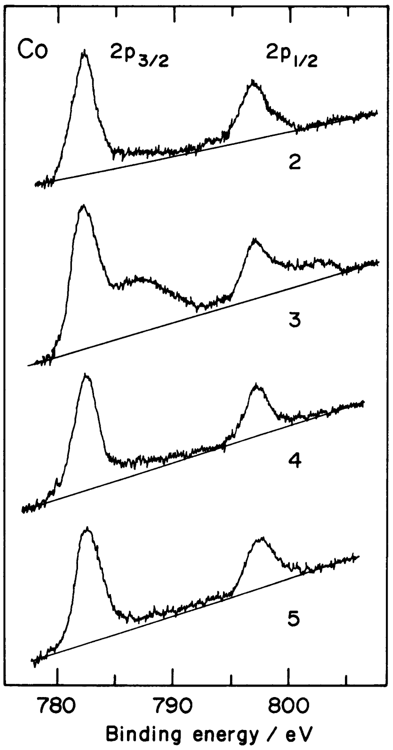
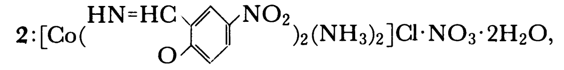
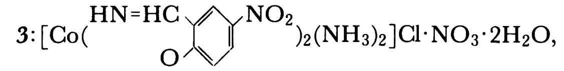
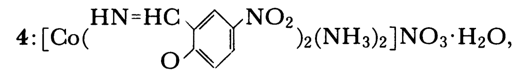
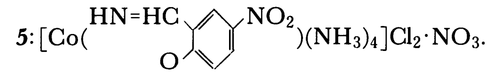


Fig. 2. The XPS in the Co 2p region of **2**—**5** complexes.

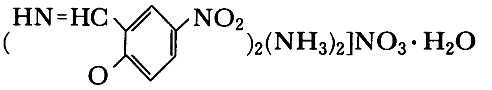

$\mathbf{2}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{Cl}\cdot\mathrm{NO_3}\cdot 2\mathrm{H_2O}$,

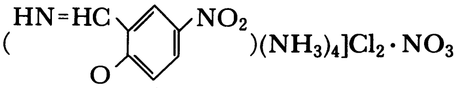

$\mathbf{3}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{Cl}\cdot\mathrm{NO_3}\cdot 2\mathrm{H_2O}$,


$\mathbf{4}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{NO_3}\cdot\mathrm{H_2O}$,

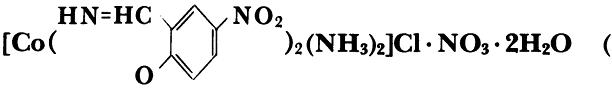

$\mathbf{5}{:}\,[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})(\mathrm{NH_3})_4]\mathrm{Cl_2}\cdot\mathrm{NO_3}$.

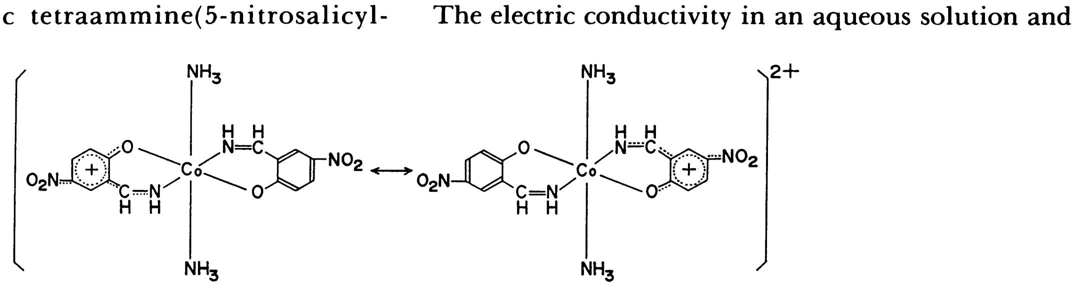
The C 1s peak was separated into four peaks having a full width at half maximum [FWHM] of 2.1 eV. The peaks that appeared in the higher binding energy region are assigned to electron-poor carbons relative to normal ring carbons at 285.0 eV. As is shown in Fig. 1 and Table 1, the proportion of the electron-poor carbons in the higher binding energy region relative to normal carbons is larger than that of the corresponding diamagnetic cobalt(III) nitrate hydrate, [Co-


$(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{NO_3}\cdot\mathrm{H_2O}$ (**4**). The Co $2p_{3/2}$ peak at 782.1 eV in the XPS does not have satellites. The absorption spectrum showed a strong peak at 700 nm. The above results and the magnetic moment are closely similar to those of the green paramagnetic tetraammine(5-nitrosalicylideneaminato)cobalt(III) chloride nitrate, [Co-


$(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})(\mathrm{NH_3})_4]\mathrm{Cl_2}\cdot\mathrm{NO_3}$ (**5**), previously reported.[2] Thus, an unpaired spin on **2** is not located on the cobalt atom but is located over the chelated ligands. Therefore, complex **2** is a radical cobalt(III) complex such as Scheme 1.

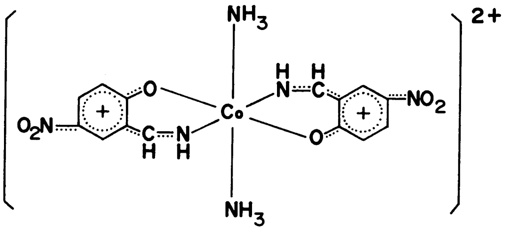
Biradical Diamminebis(5-nitrosalicylideneaminato)cobalt(II) Chloride Nitrate Dihydrate,


$[\mathrm{Co}(\mathrm{HN{=}HC}\ \mathrm{NO_2}\ \mathrm{O})_2(\mathrm{NH_3})_2]\mathrm{Cl}\cdot\mathrm{NO_3}\cdot 2\mathrm{H_2O}$ **(3):** The electric conductivity in an aqueous solution and



Scheme 1.

the analytical results were both similar to those for **2**. However, the results of the magnetic susceptibility, XPS, and absorption spectra were very different from those of **2**. The ^{1}H NMR spectrum of **3** in 1.8 mol dm^{-3} D_2SO_4 solution did not show the signal because of the paramagnetism. The magnetic susceptibility obeyed the Curie–Weiss low, with effective magnetic moment of 5.5 BM, suggesting the presence of five unpaired spins. The Co 2p peaks in the XPS showed strong satellites. This spectrum is very different from those of **2**, **4**, and **5** as shown in Fig. 2. The strong satellites are due to either Co(II) ions or high spin Co(III) ions. A number of Co(II) compounds are reported to show strong satellites in Co 2p spectra.[11–17] As a high spin Co(III) ion, only CoF_3 is reported to show strong satellites.[11,12] A distinction between Co(II) and high spin Co(III) ions is difficult to evaluate from the Co 2p spectrum alone, however, together with the following experimental results, the cobalt in complex **3** is considered to be Co(II). In the C 1s peak, the proportion of the electron-poor carbons in the higher binding energy region relative to a normal carbon is larger than that of complex **2** as shown in Fig. 1. In addition, the absorption peak (ε=12700) at 696 nm due to the unpaired spin[2] on the complex is much stronger than that (ε=6600) of complex **2**. All these results suggest that two unpaired spins are located over the chelated ligand, and three unpaired spins are located on the cobalt atom. Accordingly, complex **3** is considered to be a biradical diamminebis(5-nitrosalicylideneaminato)cobalt(II) complex such as Scheme 2.



Scheme 2.

The results for complex **4** are collected in Table 1 and in the Experimental section.

In the XPS data, the relative peak intensity of C 1s to N 1s did not show larger scattering than ±10% by complexes and for each measurement, indicating that the level of carbonaceous contamination was almost constant (Note that the atomic ratio between carbon and nitrogen is the same for complex **2**—**4**). Quantitative conclusions, however, were not drawn from the XPS data, as, with our data and a calculation system, E_{B} assignment for each carbon atom could not be performed. The probability that the higher E_{B} fraction in C 1s spectra is due to shake up phenomena is very low, since the known shake up satellites are observed at least 6 eV higher than the main peak and the intensity is less than 8% that of the main peak.[18] The higher E_{B} fraction in C 1s spectra increases in the order of complex **4**<**2**<**3**, as is clearly seen in Fig. 1, and no significant differences were observed for the N 1s spectra. Therefore taken together with the magnetic susceptibility and absorption spectra data, it is definite that one electron is missing per one ligand in complex **3**. Probably, it is on the carbon skeleton, but the location or detailed electronic configulations cannot be specified at present.

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