Cobalt(IV) Amine Complexes with Organic Ligands. XI.[1] The Preparation and Properties of Tetraammine(7-chloro-5-nitro- or 5,7-dinitro-8-quinolinolato)cobalt(IV) Complexes and the Corresponding Cobalt(III) Complexes

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Synopsis. Tetraammine(7-chloro-5-nitro- or 5,7-dinitro-8-quinolinolato)cobalt(IV) complexes and the corresponding cobalt(III) complexes have been isolated, and characterized by analytical, spectroscopic, magnetic, and XPS methods. The effective magnetic moments of cobalt(IV) complexes were ca. 1.6 BM, suggesting an unpaired spin. An unpaired spin on the complex is located over the π-orbitals of the 7-chloro-5-nitro- or 5,7-dinitro-8-quinolinolato ligand (abbreviation: chelated ligand) and on the cobalt atom from the results of the C 1s and Co 2p spectra by XPS. The Cl 2p binding energy of the chloride ion suggests that the valence electrons of the chloride ions may have some interaction with the π-orbitals of the chelated ligand.

In this series, the preparation, properties, and electronic states of cobalt(IV) complexes, $[Co(5\text{-}NO_2sal)L]Cl(NO_3)\cdot nH_2O$ (L: $(NH_3)_4$, $(bpy)_2$, quadridentate amine),[2] radical cobalt(III) complexes, $[Co(5\text{-}NO_2salam)(NH_3)_4]Cl_2(NO_3)$[3] and $[Co(5\text{-}NO_2salam)_2(NH_3)_2]Cl(NO_3)\cdot 2H_2O$,[1] and biradical cobalt(II) complex, $[Co(5\text{-}NO_2salam)_2(NH_3)_2]Cl(NO_3)\cdot 2H_2O$,[1] have been reported. The electronic states of the above mentioned complexes have been solved by physicochemical and XPS methods. Through the above studies, there was an implication that free chloride ions in the complexes may contribute to their stability. So far, the electronic state of the chloride ions has remain unsolved, since no measurement of the chloride ions by XPS was carried out. The present paper deals with the preparation and properties of the title cobalt(IV) complexes, and with the role of the chloride ions in the complexes.

Experimental

Measurements. The XPS measurements were carried out with a VG ESCALAB Mk-II electron spectrometer by irradiating Mg $K\alpha$ X-rays (60—150 W). Sample was placed either on a nickel holder with a copper mesh adhesive or on a indium foil with a gold mesh, and then introduced into the spectrometer. After evacuation to a vacuum of better than 3×10^{-6} Pa, the sample was cooled to ca. 200 K. Sample cooling was initiated within 10 min of the introduction to the spectrometer. Spectra were analysed using a VGS-5000 data system: Peak separation was carried out by a nonlinear least squares method using a mixed Gaussian-Lorentzian curve shape; background level was determined by a method proposed by Shirley,[4] and the contribution from X-ray satellites was subtracted. The electron-binding energies, E_B, were calibrated by assigning either 285.0 eV to the C 1s peak of 8-quinolinol or 407.0 eV to the N 1s peak of the nitrate free anion. The latter value was an average of the values from previous studies;[1,2b,5] the 90% confidence limits of the average are ±0.15 eV. The ^1H NMR spectra were recorded with an FX-90Q apparatus (JEOL). 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 liquid 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.

Preparation of Complexes. Tetraammine(5,7-dinitro-8-quinolinolato)cobalt(III) Dinitrate (2a) and Tetraammine(5,7-dinitro-8-quinolinolato)cobalt(IV) Trinitrate (3a): Eight cm^3 of 60% HNO_3 were added, drop by drop, to 2.0 g (5.06 mmol) of $[Co(oxin)(NH_3)_4](NO_3)_2$ (**1a**).[6] Soon, a crystalline precipitate (complex **2a**) separates out, and was collected by filtration, and recrystallized from water. The green filtrate was added to acetone (150 cm^3) and stirred at 5 °C. The green cobalt(IV) complex (**3a**), thus precipitated, was filtered, washed with acetone and ether at 5 °C, and dried. Yields: 0.68 g (27.7%) for **2a**, 0.91 g (32.8%) for **3a**. Found **2a**: C, 22.06; H, 3.54; N, 25.77%. Calcd for $CoC_9H_{16}N_9O_{11}$: (MW 485.22) C, 22.28; H, 3.32; N, 25.98%. Found **3a**: C, 19.47; H, 3.09; N, 25.32%. Calcd for $CoC_9H_{16}N_{10}O_{14}$: (MW 547.25) C, 19.75; H, 2.95; N, 25.60%. Absorption spectra **2a** (H_2O): 383 (ε 13800), 398 nm^{sh} (12500); **3a** (60% HNO_3): 384 (5000), 398^{sh} (4600), 670 (1100). Λ=240 $S\,cm^2\,mol^{-1}$ for **2** in water. ^1H NMR (DMSO-d_6) **2a**: δ=3.60 (3H, NH_3), 3.75 (6H, NH_3), 4.18 (3H, NH_3); δ=8.25 (q, H_3), 8.74 (d, H_2), 9.15 (s, H_6), 9.40 (d, H_4).

Tetraammine(7-chloro-5-nitro-8-quinolinolato)cobalt(III) Dinitrate (2b), Tetraammine(7-chloro-5-nitro-8-quinolinolato)cobalt(IV) Dichloride Nitrate (3b), and Tetraammine(5,7-dinitro-8-quinolinolato)cobalt(IV) Chloride Dinitrate (3c): Eight cm^3 of 60% HNO_3 were added, drop by drop, to 2.0 g (5.55 mmol) of $[Co(oxin)(NH_3)_4]Cl_2\cdot H_2O$ (**1b**).[7] The precipitated yellowish-brown crystalline complex **2** (mixture of **2a** and **2b**) was collected by filtration and recrystallized from water. The green filtrate was added to acetone (200 cm^3) and stirred. Thus, the precipitated green cobalt(IV) complex **3** (mixture of **3b** and **3c**) was filtered, washed with acetone and ether, and dried. Complex **2b** was isolated from an orange-colored acetone filtrate of **3**. The ratio of **2b** and **2a** in **2** was 7 to 3, according to the results of elemental analyses and ^1H NMR spectra, and the ratio of **3b** and **3c** in **3** was 7 to 3 from the results of elemental analyses. Yields **2b**: 0.32 g (12.15%); **2**: 0.91 g (34.3%); **3**: 0.56 g (20.4%). Found **2b**: C, 22.56; H, 3.61; N, 23.52; Cl, 7.19%. Calcd for $CoC_9H_{16}N_8O_9Cl$: (MW 474.66) C, 22.77; H, 3.40; N, 23.61; Cl, 7.47%. Found **2**: C, 22.24; H, 3.62; N, 24.12, Cl, 5.61%. Calcd for $CoC_9H_{16}N_{8.3}O_{9.6}Cl_{0.7}$: (MW 477.85) (**2b**:**2a**=7:3) C, 22.62; H, 3.38; N, 24.33, Cl, 5.19%. Found **3**: C, 22.15; H, 3.55; N, 21.81; Cl, 16.88%. Calcd for $CoC_9H_{16}N_{7.6}O_{7.5}Cl_{2.4}$: (MW 494.70) (**3b**:**3c**=7:3) C, 21.85; H, 3.26; N, 21.52, Cl, 17.20%. Absorption spectra **2b** (H_2O): 412 nm (ε 11800); **2** (H_2O): 407 (12800); **3** (60% HNO_3): 405 (3340), 720 (1500). Λ=240 for **2b** and 410 $S\,cm^2\,mol^{-1}$ for **3**

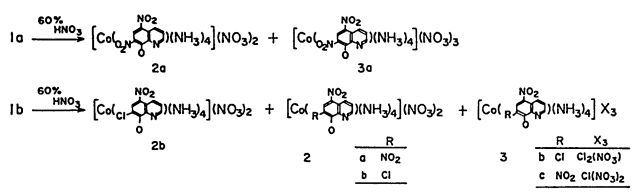
in water. ^{1}H NMR (DMSO-d_6) **2b**: δ=3.54 (3H, NH_3), 3.65 (6H, NH_3), 4.11 (3H, NH_3); δ=8.10 (q, H_3), 8.64 (d, H_2), 8.69 (s, H_6), 9.40 (d, H_4).

Results and Discussion

Complexes **2a** and **3a** have been obtained from a reaction mixture of **1a** and 60% HNO_3. Complexes **2b**, **2**, and **3** have been obtained from a reaction mixture of **1b** and 60% HNO_3 (Scheme 1). The colors of **2a**, **2b**, and **2** are yellowish-brown, yellowish-orange, and yellowish-orange, respectively and those of **3a** and **3** are green. Complexes **2a**, **2b**, and **2** were soluble in DMSO, and slightly soluble in water and methanol. Complexes **3a** and **3** were soluble in 60% HNO_3 and DMSO.

In the ^{1}H NMR spectra in DMSO-d_6, the signals at δ=3.5—4.2 (12H) and at δ=8.1—9.4 (4H) of **2a**, **2b**, and **2** were assigned to the ammine protons and the coordinated 8-quinolinolato ligand, respectively. The signals at δ=8.25, 8.74, 9.15, and 9.40 of **2a** were very close to those of 5,7-dinitro-8-quinolinol,[8] while those at δ=8.10, 8.64, 8.69, and 9.40 of **2b** were very close to those of 7-chloro-5-nitro-8-quinolinol.[8] This indicates that **2a** and **2b** contain the coordinated 5,7-dinitro-8-quinolinolato and 7-chloro-5-nitro-8-quinolinolato ligands, respectively. A proportion between **2b** and **2a** in **2** was estimated to be 7 to 3 from the intensity ratio of the H_6 proton signals of **2** (Fig. 1). The electric conductivities of **2a**, **2b**, and **2** in the aqueous solutions are ca. 240 S cm^2 mol^{-1}. Complexes **2a**, **2b**, and **2** were diamagnetic by the magnetic susceptibility. Absorption bands at 383—412 nm in water of **2a**, **2b**, and **2** were assigned to the charge-transfer band.[6] In XPS, the Cl 2$p_{3/2}$ spectra of **2b** and **2** were observed at 200.4—200.5 eV (Fig. 2). The peak at 200.4—200.5 eV was assigned to the chlorine atom of the coordinated 7-chloro-5-nitro-8-quinolinolato ligand, since the E_B of the peak was close to that (201.0 ev) of chlorobenzene,[9] but was different from that (197.6 ev) of **1b**. The N 1s spectra of **2a**, **2b**, and **2** were observed at ca. 400 and ca. 406 eV. The lower E_B peak was separated to two peaks which were assigned to -NH= and NH_3 nitrogens. The higher E_B peak was also separated into three peaks which were assigned to 5-NO_2, 7-NO_2, and NO_3 nitrogens (Table 1).[1,2b,3]

The magnetic susceptibilities of **3** and **3a** obeyed the Curie-Weiss law, with an effective magnetic moment of 1.58 BM for **3** and 1.50 BM for **3a**, suggesting the presence of an unpaired spin. The absorption spectra in 60% HNO_3 of **3** and **3a** showed two peaks at 405 and 720 nm for **3** and three peaks at 384, 398(sh), and 670 nm for **3a**. The peaks at 720 and 670 nm are due



Scheme 1.

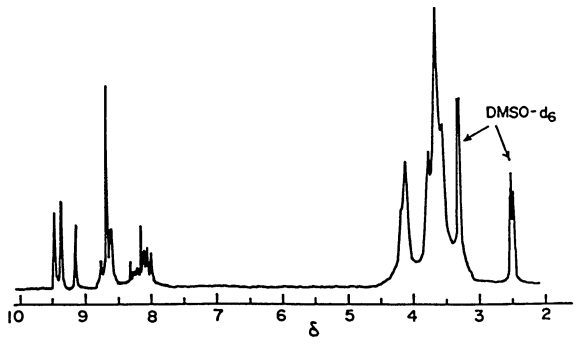


Fig. 1. The ^{1}H NMR spectrum of complex **2**.
2: [Co(5-NO_2-7-R-oxin)(NH_3)$_4$](NO_3)$_2$ (R: Cl, NO_2).

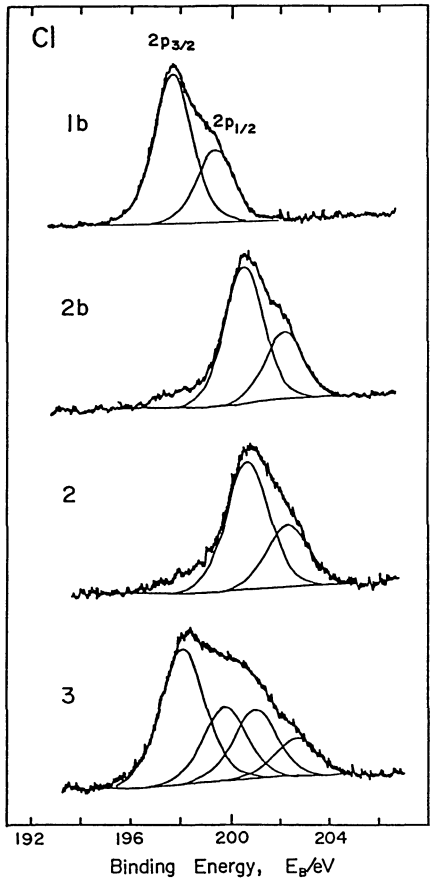


Fig. 2. The XPS in the Cl 2p region of complexes.
1b: [Co(oxin)(NH_3)$_4$]$Cl_2 \cdot H_2O$
2b: [Co(7-Cl-5-NO_2-oxin)(NH_3)$_4$](NO_3)$_2$
2: [Co(5-NO_2-7-R-oxin)(NH_3)$_4$](NO_3)$_2$ (R: Cl, NO_2)
3: [Co(5-NO_2-7-R-oxin)(NH_3)$_4$]X_3 (R: Cl, NO_2; X_3: $Cl_2(NO_3)$, $Cl(NO_3)_2$).

to the unpaired spin.[3] The ^{1}H NMR spectra of **3** and **3a** did not show the expected signals, because of paramagnetism. The electric conductivity in an aqueous solution of **3** was 410 S cm^2 mol^{-1}. In the XPS of **3**, the N 1s spectrum was observed at ca. 400 and ca. 406 eV. Each peak was separated into two (-N= and NH_3) or three peaks (5-NO_2, 7-NO_2, and NO_3) (Table 1). The C 1s peak was separated into two peaks at 285.6 and 288.2 eV. The peak that appeared in the higher E_B region was assigned to the electron-

Table 1. XPS of Complexes

Complex No.	Binding energies of electrons, E_B/eV					
	Co $2p_{3/2}$	Co $2p_{1/2}$	Splitting	C 1s	N 1s	Cl $2p_{3/2}$
2a	782.3(±0.2) FWHM 2.74 (±0.28)	797.3(±0)	15.0	285.6(±0.1) Broad[a] [Weak]	399.5(±0.4) -N= 400.5(±0.2) NH_3 404.9(±0.5) 5-NO_2 406.3(±0.1) 7-NO_2 407.0[b] NO_3^- FWHM 2.13(±0.19)	
2b	782.2(±0.2) FWHM 2.20 (±0.28)	797.2(±0.2)	15.0	285.5(±0.2) Broad[a] [Weak]	399.4(±0.5) -N= 400.3(±0) NH_3 405.5(±0.3) 5-NO_2 407.0[b] NO_3^- FWHM 1.74(±0.03)	200.4(±0.1) -Cl FWHM 1.90(±0.11)
2	782.3(±0.1) FWHM 2.20 (±0.08)	797.3(±0.2)	15.0	285.5(±0.2) Broad[a] [Weak]	399.4(±0) -N= 400.3(±0.2) NH_3 404.6(±0.2) 5-NO_2 406.0(±0.2) 7-NO_2 407.0[b] NO_3^- FWHM 1.86(±0)	200.5(±0.1) -Cl FWHM 2.06(±0.09)
3	782.2(±0.2) FWHM 2.58 (±0.48)	797.3(±0.1)	15.1	285.6(±0.2) 288.2(±0.3)	399.4(±0.3) -N= 400.3(±0.2) NH_3 404.7(±0.4) 5-NO_2 406.0(±0.1) 7-NO_2 407.0[b] NO_3^- FWHM 1.99(±0.16)	198.0(±0.2) Cl^- 200.8(±0.1) -Cl FWHM 2.11 (±0.13)
1b	782.0(±0.3) FWHM 2.13 (±0.35)	797.0(±0)	15.0	285.0[c] Broad[a] [Weak]	399.5(±0.1) -N= 400.2(±0.1) NH_3 FWHM 1.70(±0.01)	197.6(±0.2) Cl^- FWHM 1.86(±0.05)
5				285.0	402.2 $=N^+=$	196.7 Cl^-
6				285.4	402.3	197.1 Cl^-

a): In higher E_B region. b): An average E_B [N 1s] for NO_3^- calculated from the previous data,[1,3,7] 407.00±0.15 eV, was used to the energy calibration. c): An average E_B [C 1s] for carbons in 8-quinolinol was taken to be 285.0 eV. Uncertainties in parentheses are 90% confidence limits.

poor carbons[1,3] relative to the normal ring carbons at 285.5 eV. The proportion of electron-poor carbons in the higher binding energy region was about 2-times larger than that of **2**. The Co $2p_{3/2}$ peak at 782.2 eV showed satellites. These results are in agreement with those of tetraammine(5-nitrosalicylato)cobalt-(IV) complexes,[2b] $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl(NO_3)\cdot H_2O$ (**4**), previously reported. Thus, an unpaired spin is located over the π-orbitals of the chelated ligand and on the cobalt atom. The Cl $2p_{3/2}$ spectrum of **3** was observed at 198.0 and 200.8 eV (Table 1 and Fig. 2). The peak at 198.0 eV was assigned to a free chloride ion (Cl^-), and the peak at 200.8 eV was assigned to the chlorine atom of the coordinated 7-chloro-5-nitro-8-quinolinolato ligand. The intensity ratio between the lower E_B and higher E_B peaks was about 2 to 1. The E_B (198.0 eV) of the chloride ion is higher than those (196.7—197.6 eV) of **1b**, hexadecyltrimethylammonium chloride, $[(C_{16}H_{33})(CH_3)_3N]Cl$ (**5**), and tetramethylammonium chloride,[10] $[(CH_3)_4N]Cl$ (**6**) (Table 1). The higher E_B suggests that the valence electrons of the chloride ions in **3** may have some interaction with the π-orbitals of the chelated ligand and a part of electrons of the chloride ion may flow over the π-orbitals of the chelated ligand, since such a shift to higher E_B is not observed for compounds without a localized spin on the π-orbitals, which is the case in **2**. Further, **3a**, which has an unpaired spin but no chloride ions as a free anion, is unstable under X-ray irradiation and in an aqueous solution. These experimental results indicate that the interaction between the chloride ions and the π-orbitals of the chelated ligand contributes to the stability of **3**.

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