1186 © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***60***, *1186—1188 (1987)* [Vol. 60, No. 3

Cobalt(III) Complexes with [$N_{6-n}X_n$]-Type Ligands. VI.1) The Preparation and Properties of Tetraammine(salicylamidato)cobalt(III) Complexes

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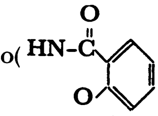
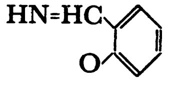
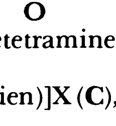
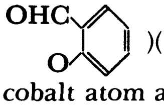
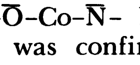
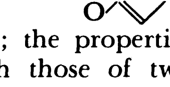
Synopsis. Tetraammine(salicylamidato)cobalt(III) complexes, [Co()$(NH_3)_4$]$X\cdot nH_2O$ (X: Cl, NO_3 and picrate), have been isolated and characterized by means of analytical, spectroscopic, and magnetic methods. The bond between the cobalt atom and the chelated ligand in the complex is expressed in the form of $-\overline{\mathrm{O}}-\mathrm{Co}-\overline{\mathrm{N}}-$. The properties of the title complexes are intermediate between those of the tetraammine(salicylideneaminato)cobalt(III) complex, which has the $-\overline{\mathrm{O}}-\mathrm{Co}-\mathrm{N}-$ bond, and the tetraammine(salicylato)cobalt(III) complex, which has the $-\overline{\mathrm{O}}-\mathrm{Co}-\overline{\mathrm{O}}-$ bond.

The previous papers were concerned with the preparation and properties of many mixed-ligand ammine cobalt(III) complexes, such as the tetraammine(salicylideneaminato)cobalt(III) complexes, [Co()$(NH_3)_4$]X_2 (**A**),2) the tetraammine(8-quinolinolato)cobalt(III) complexes, [Co()$(NH_3)_4$]X_2 (**B**),3—5) the salicylato(triethylenetetramine)cobalt(III) complexes, [Co()(trien)]X (**C**),6) and the salicylaldehydato(triethylenetetramine)cobalt(III) complexes, [Co()(trien)]X_2 (**D**).7) The bonds between the cobalt atom and the chelated ligands in the complexes are expressed in the form of $-\overline{\mathrm{O}}-\mathrm{Co}-\mathrm{N}-$, $-\overline{\mathrm{O}}-\mathrm{Co}-\overline{\mathrm{O}}-$, and $-\overline{\mathrm{O}}-\mathrm{Co}-\mathrm{O}-$. A few metal complexes for a $-\overline{\mathrm{O}}-\mathrm{Co}-\overline{\mathrm{N}}-$ bond were isolated, and the structure was confirmed by X-ray diffraction for the bis(glycylglycinato)cobaltate(III) ion, [Co(gly-gly)$_2$]$^-$.8,9) However, no mixed-ligand ammine metal complex for a $-\overline{\mathrm{O}}-\mathrm{M}-\overline{\mathrm{N}}-$ bond has yet been reported, especially concerning its preparation and properties. The present paper deals with the preparation and properties of tetraammine(salicylamidato)cobalt(III) complexes, [Co()$(NH_3)_4$]X (X: Cl, NO_3 and picrate); the properties of the complex are compared with those of two related complexes, **A** and **C**.

Experimental

Measurements. The IR spectra were recorded as potassium bromide disks with an IR-27G apparatus (Shimadzu). The visible absorption spectra were recorded with a Shimadzu UV-210 recording spectrophotometer. The electric conductivities of aqueous solutions were determined by the use of a conductometer, CM-30 (Shimadzu), at room temperature. The magnetic susceptibilities were measured by Faraday's method using a magnetic balance (Shimadzu) at room temperature. The NMR spectra were recorded with an R-40 apparatus (Hitachi) for ^1H and with an FX-60 apparatus (JEOL) for ^{13}C.

Preparation of Complexes. Tetraammine(salicylamidato)cobalt(III) Chloride Hydrate (1): A 28% aqueous ammonia (30 cm^3) was added to an aqueous solution (20 cm^3) of $CoCl_2\cdot 6H_2O$ (9.52 g, 40.0 mmol), and the mixture was stirred. To the solution was added slowly 6 mol dm^{-3} H_2O_2 solution (11 cm^3) in an ice bath. The color of the solution turned from brown to red. A methanol solution (60 cm^3) of salicylamide (5.48 g, 40.0 mmol) was added to the solution, and the solution was stirred at 55 °C for 22 h. Then, the solution was filtered, and the filtrate was concentrated with a rotary evaporator at 30—40 °C to ca. 50 cm^3. The precipitated salicylamide was filtered off. The filtrate was cooled to 0—5 °C. After 1 or 2 d, the precipitated russet crystals were filtered, washed with ethanol and ether, and recrystallized twice from water. Yield: 3.5 g (27.7%). Found: C, 26.57; H, 6.34; N, 22.13; Cl, 11.18%. Calcd for $CoC_7H_{19}N_5O_3Cl$ (MW 315.65): C, 26.64; H, 6.07; N, 22.19; Cl, 11.23%. Λ=113 S cm^2 mol^{-1} in water. IR spectrum: 850 cm^{-1} ($\rho_r(NH_3)_r$). ^1H NMR spectrum (cf. Fig. 1): δ 3.00 (3H, N(2)H_3), 3.15 (6H, N(1)H_3+N(4)H_3), 3.71 (4H, N(3)H_3+NH proton of salicylamidato), 6.6—7.9 (4H, ring protons of salicylamidato). ^{13}C NMR spectrum2): δ 120.0 (C-1), 165.8 (C-2), 117.1 (C-3), 133.2 (C-4), 123.7 (C-5), 130.7 (C-6), 171.7 (C-7). Decomp: 160 °C.

Tetraammine(salicylamidato)cobalt(III) Nitrate Hydrate (2): To an aqueous solution (9 cm^3) of **1** (1.0 g, 3.17 mmol) was added an aqueous solution (2 cm^3) of silver nitrate (0.538 g, 3.17 mmol). The mixture was stirred, and the precipitated silver chloride was filtered off. The filtrate was concentrated with a rotary evaporator at 30 °C to ca. 2 cm^3. The deposit of Complex **2** was filtered and recrystallized from water–methanol–ether (ca. 1:1:2) twice. Yield: 0.31 g (28.6%). Color: russet. Found: C, 24.78; H, 5.82; N, 24.72%. Calcd for $CoC_7H_{19}N_6O_6$ (MW 342.20): C, 24.57; H, 5.60; N, 24.56%. Λ=112 S cm^2 mol^{-1} in water. IR spectrum: 855 cm^{-1} ($\rho_r(NH_3)_r$). ^1H NMR spectrum: δ 2.97 (3H, N(2)H_3), 3.15 (6H, N(1)H_3+N(4)H_3), 3.70 (4H, N(3)H_3+NH proton), 6.6—7.9 (4H, ring protons) in 1.8 mol dm^{-3} D_2SO_4 solution. ^{13}C NMR spectrum: δ 120.0 (C-1), 165.8 (C-2), 117.0 (C-3), 133.2 (C-4), 123.6 (C-5), 130.7 (C-6), 171.7 (C-7) in D_2O. Decomp: 170 °C.

Tetraammine(salicylamidato)cobalt(III) Picrate (3): An aqueous solution of **1** (0.5 g, 1.58 mmol) was added to an aqueous solution of picric acid (0.363 g, 1.58 mmol), and the mixture was stirred. The precipitated Complex **3** was filtered, washed with water and ethanol, and dried. Yield: 0.76 g (97.4%). Color: yellowish-brown. Found: C, 31.73; H, 4.23; N, 22.60%. Calcd for $CoC_{13}H_{19}N_8O_9$ (MW 490.28): C, 31.85; H, 3.91; N, 22.85%. IR spectrum: 840 cm^{-1} ($\rho_r(NH_3)_r$). ^{1}H NMR spectrum: δ 2.93 (3H, N(2)H$_3$), 3.10 (6H, N(1)H$_3$+N(4)H$_3$), 3.63 (4H, N(3)H$_3$+NH proton), 6.3—7.7 (4H, ring proton), 8.53 (2H, picrate proton) in DMSO-d_6. Absorption band in methanol: 550 nm (ε=170). Decomp: 220 °C.

Solubility. Complexes **1** and **2** are soluble in water, 35% hydrochloric acid, acetic acid, and DMSO, and are slightly soluble in methanol, but are insoluble in the common organic solvents. Complex **3** is soluble in tetrahydrofuran, DMSO and DMF, and is slightly soluble in water, alcohols, acetonitrile, and dioxane, but is insoluble in chloroform, dichloromethane, and diethyl ether.

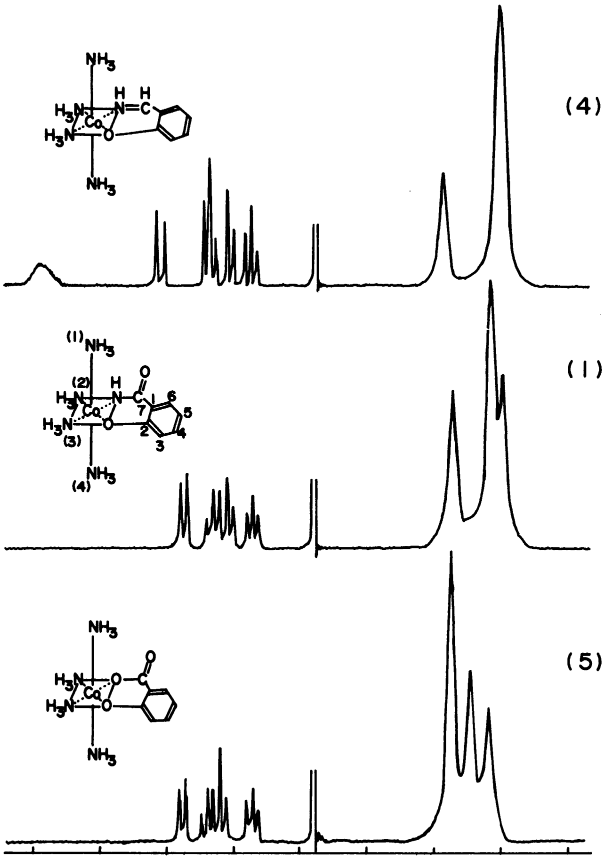


Fig. 1. The ^{1}H NMR spectra of **1**, **4**, and **5** complexes in 1.8 mol dm^{-3} D_2SO_4, internal DSS (δ=0)

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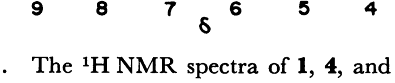
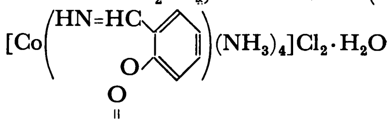


1:


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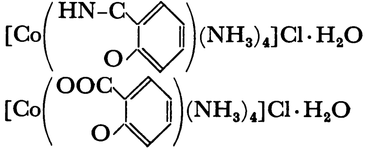
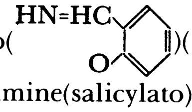


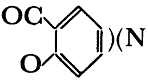
Results and Discussion

Tetraammine(salicylamidato)cobalt(III) chloride hydrate, (**1**), was isolated from a reaction mixture of $CoCl_2\cdot6H_2O$, 28% aqueous ammonia, 6 mol dm^{-3} H_2O_2, and salicylamide. The corresponding nitrate (**2**) and picrate (**3**) were prepared from **1** and silver nitrate or picric acid, respectively.

Complex **1** is a diamagnetic cobalt(III) complex of the low-spin type, judging from the magnetic susceptibility. The aqueous solution was neutral. The absorption spectrum in methanol showed four bands at 328, 378 (shoulder), 512 and 550 nm (Table 1). The absorption band at 378 nm is assigned to the charge-transfer band,[1—3] while the bands at 512 nm and 550 nm are assigned to the split first band.[10,11] In the ^{1}H NMR spectrum for **1** (Fig. 1), the multiplet signals at 6.6—7.9 ppm (4H) are assigned to the ring protons of the salicylamidato ligand, while the signals at 3.0—3.7 ppm (13H) are assigned to the ammine protons of $(NH_3)_4$ and the NH proton of the salicylamidato ligand. The assignment (cf. the Experimental section) of N(1)H$_3$, N(2)H$_3$, N(3)H$_3$, and N(4)H$_3$ for ammine protons was attempted by means of a consideration of the assignment of tetraammine(salicylideneaminato)cobalt(III) chloride hydrate, [Co(



)$(NH_3)_4]Cl_2\cdot H_2O$ (**4**),[2] and tetraammine(salicylato)cobalt(III) chloride hydrate, [Co-(



)$(NH_3)_4]Cl\cdot H_2O$ (**5**).[12]

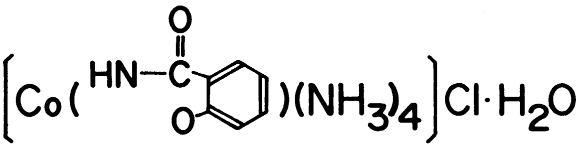
The structure of **1** is identified by means of the study of the absorption spectrum, the ^{1}H NMR spectrum, the IR spectrum, the property of the $-CONH_2$ group of salicylamide, the results of elemental analysis, and electric conductivity in an aqueous solution. The absorption spectrum showed two bands at 512 and 550 nm in the 450—550 nm region. The spectral feature is similar to that (two bands at 475 and 550 nm) for **4**, but is different from that (one band at 532 nm) of **5** (Table 1); i.e., the cobalt atom in **1** may be bonded to the oxygen and nitrogen of the chelated ligand. In the NMR spectrum, the chemical shifts (δ 3.00(3H), 3.15(6H), and 3.71(4H)) for ammine protons are close to those (δ 3.01(9H) and 3.83(3H)) for **4**, but different from those (δ 3.21(3H), 3.48(3H), and 3.78(6H)) for **5** (Fig. 1); i.e., the cobalt atom may also be bonded to the oxygen and nitrogen of the chelated ligand. The signal at 3.71 ppm due to the -NH proton of the

Table 1. Absorption Bands of Complexes **1**, **2**, **4**, and **5**

Complex No.	Absorption bands in methanol λ/nm (ε/cm^{-1} mol^{-1} dm^3)			
1	328 (3020)	378 sh (495)	512 (150)	550 (150)
2	327 (3160)	380 sh (510)	512 (150)	550 (150)
4[a]		378 (2750)	475 sh (185)	550 (110)
5	331 (3200)	380 sh (260)		532 (150)

a) Ref. 2.

salicylamidato ligand is very different from that at 9.91 ppm of **4**; i.e., the electronic state of the -NH proton must be different from that of the =NH proton. Further, the ring-proton signals of the chelated ligand are similar to those of **5** (Fig. 1), and the chemical shift (δ 7.73) for the H_6 proton is very close to that (δ 7.75) for **5**, but different from that (δ 7.35) for **4**; i.e., the electronic and steric effects between the oxygen and H_6 proton of the chelated ligand of **1** may be similar to those of carbonyl oxygen and the H_6 proton for **5**. The IR spectrum of **1** did not show the -C=N stretching signal in the 1620—1630 cm^{-1} region. In addition, the $-\mathrm{CONH_2}$ group of salicylamide changes to $-\mathrm{CO\bar{N}H}$ because of the electron-attracting of the carbonyl group, such as glycylglycinecobalt(III) complexes.[8,9] Thus, Complex **1** is a tetraammine(salicylamidato)cobalt(III) chloride hydrate, as is shown in Scheme 1. The structure is supported by the results of the elemental analysis and electric conductivity in an aqueous solution.



Scheme 1.

The properties of **1** are intermediate between those of Complexes **4** and **5**, judging from the results of ^{1}H NMR, their absorption spectra, and their stability is solutions. The ammine proton signals for **1** are close to those of **4**, but the ring-proton signals are close to those of **5** (Fig. 1). The spectral features in the 450—550 nm region for **1** are similar to those of **4**, but the ε at 550 nm is similar to that of **5** (Table 1). Complex **1** is more unstable than both Complexes **4** and **5** in a solution such as water and methanol, though the decomposition temperature (160 °C) of **1** is close to that of **4** (163 °C) and **5** (158 °C) in the solid state.

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