Cobalt(III) Complexes with Quadridentate Ligands. V.1) The Preparation and Properties of Paramagnetic and Diamagnetic *cis*-β_2-Isomer of the 5-Nitrosalicylato(quadridentate amine)cobalt(III) Complexes

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(Received April 15, 1983)

Synopsis. Several green paramagnetic 5-nitrosalicylato(quadridentate amine)cobalt(III) chloride nitrate hydrates, $[Co(5\text{-}NO_2sal)L]Cl\cdot NO_3\cdot nH_2O$ (L: 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet) and the corresponding orange diamagnetic nitrate hydrates, $[Co(5\text{-}NO_2sal)L]NO_3\cdot nH_2O$, have been isolated and characterized by analytical, spectroscopic, and magnetic methods.

The preparation and properties of paramagnetic metal complexes with the quadridentate amine ligands such as 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet, as is shown in Fig. 1, have not previously been described, except for iron(III) complexes2) with sexadentate ligands derived from salicylaldehyde and 3,2,3-tet or 3,3,3-tet. The present paper deals with the preparation and properties of the green paramagnetic 5-nitrosalicylato(quadridentate amine)cobalt(III) complexes, $[Co(5\text{-}NO_2sal)L]^{n+}$ (L: 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet; n=2) and of the corresponding orange diamagnetic cobalt(III) complexes (n=1).

Results and Discussion

The green paramagnetic *cis*-β_2-5-nitrosalicylato(quadridentate amine)cobalt(III) chloride nitrate hydrates, $[Co(5\text{-}NO_2sal)L]Cl\cdot NO_3\cdot nH_2O$ (L: 2,3,2-tet (**1a**), 3,2,3-tet (**1b**), 3,3,3-tet (**1c**)), have been isolated from a reaction mixture of the diamagnetic *cis*-β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrates,3) $[Co(sal)L]Cl\cdot nH_2O$ (L: 2,3,2-tet (**2a**), 3,2,3-tet (**2b**), 3,3,3-tet (**2c**)), 60% HNO_3 and acetone. From the orange acetone filtrate, the orange diamagnetic *cis*-β_2-5-nitrosalicylato(quadridentate amine)cobalt(III) nitrate hydrates, $[Co(5\text{-}NO_2sal)L]NO_3\cdot nH_2O$ (L: 2,3,2-tet (**3a**), 3,2,3-tet (**3b**), 3,3,3-tet (**3c**)) have been isolated. Their colors in the solid state are green (**1a**—**c**), organge (**3a** and **3b**), and pink-russet (**3c**). The effective magnetic moments of **1a**—**c** are 1.7—1.8 BM,† suggesting one unpaired electron. Complexes **3a**—**c** are diamagnetic. In the ^1H NMR spectra, the signals of the methylene protons, amine protons, and salicylato protons of **1a**—**c** and **3a**—**c** have been assigned by the comparison with those3) of **2a**—**c**. Their form is *cis*-β_2-form from their ^1H NMR spectra, because both signals of the NH_2-side methylene protons (*cf.* Table 1) and the NH-side methylene protons (*cf.* Table 1) of the coordinated quadridentate ligands of **1a**—**c** and **3a**—**c** are distinguishable.3,7)

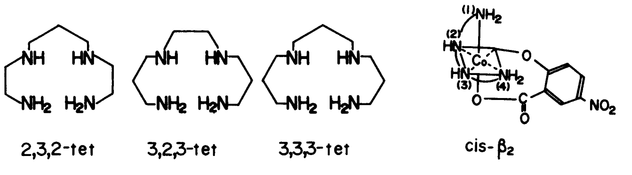

Fig. 1. The quadridentate amine ligands of 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet, and the *cis*-β_2-form of complexes.

The properties of IR, ^1H-, ^{13}C NMR spectra, and magnetic moments of **1a**—**c** are similar to those of the green paramagnetic 5-nitrosalicylato(amine)cobalt(III) complexes, $[Co(5\text{-}NO_2sal)L]X_2\cdot nH_2O$ (L: trien (**4a**), en_2 (**4b**), $(bpy)_2$ (**4c**), and $(NH_3)_4$ (**4d**)), *i.e.*, an unpaired electron of **4a**—**d** is delocalized over the chelate ring containing the cobalt atom and the 5-nitrosalicylato ligand from the results of the IR spectra,4) ^1H-, ^{13}C NMR spectra,4) magnetic susceptibility,5) the electric resistivity,5) ESR,5) and XPS.6) Thus, an unpaired electron of **1a**—**c** is also delocalized over the chelate ring containing the cobalt atom and the 5-nitrosalicylato ligand.

A clear distinction between **1a**—**c** and **4a**7) was found in the absorption spectra in 60% HNO_3. The ε's of the absorption bands at around 350 nm of **1a**—**c** are larger than those at 460 nm. The absorption bands at around 350 nm of **1a**—**c** show a hypsochromic shift from that (360 nm) of **4a** as is shown in Table 1. These properties have been ascribed to the coordinated quadridentate ligands.

The properties of **3a**—**c** are similar to those of the orange diamagnetic 5-nitrosalicylato(trien)cobalt(III) complex,7) $[Co(5\text{-}NO_2sal)trien]NO_3\cdot 3H_2O$ (**5**), in the IR, NMR spectra, and magnetic susceptibility. Both signals of the center methylene protons (*cf.* Table 1) and NH_2-side methylene protons of the coordinated quadridentate ligand in **3a**—**b** are distinguishable, but those of **1a**—**b** are indistinguishable, because of the paramagnetism. The first absorption bands of **3a**—**c** shift to 503 nm (**3a**) from 535 nm (**3c**). This shift is similar to that3) of **2a**—**c**. Some physical properties of **1a**—**c**, **3a**—**c**, **4a**, and **5** are collected in Table 1.

Experimental

Measurements. The NMR spectra were recorded with an R-40 apparatus (Hitachi) for ^1H NMR. The IR spectra were recorded in potassium bromide disks with an IR-27G spectrophotometer (Shimadzu). The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The magnetic susceptibilities were measured by the Faraday method using a mag-

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† $1\ \mathrm{BM}=9.274\times10^{-24}\ \mathrm{A\ m^{-2}}$.

Table 1. Some physical properties of complexes **1a—c** and **3a—c**

	Center methylene protons $NHCH_2C\underline{H}_2CH_2NH_2$ $NHCH_2C\underline{H}_2CH_2NH$ δ	NH_2-side methylene protons $NHCH_2C\underline{H}_2NH_2$ $NHCH_2CH_2C\underline{H}_2NH_2$ δ	NH-side methylene protons $-C\underline{H}_2NHC\underline{H}_2CH_2NH_2$ $-C\underline{H}_2NHC\underline{H}_2CH_2CH_2NH_2$ δ
4a[b]		2.33—2.82(3H)	2.82—3.84(9H)
1a	1.63—2.70(5H)		2.70—3.78(9H)
1b	1.31—2.38(7H)		2.38—3.21(9H)
1c	1.32—2.37(9H)		2.37—3.37(9H)
5[b]		2.56(3H)	3.14(9H)
3a	1.99(2H)	2.04—2.54(3H)	2.89(9H)
3b	2.02(4H)	2.24—2.46(3H)	2.46—3.28(9H)
3c	1.60—2.40(9H)		2.40—3.26(9H)

	$N(1)H_2$ δ	$N(4)H_2$ δ	N(3)H δ	N(2)H δ	Salicylato δ	Absorption bands λ/nm (ε)			Magnetic moments μ_{eff}/BM
4a[b]	4.48(2H)	5.14(1H) 5.38(1H)	6.35(1H)	a)	—[1]	360 (3240)	455 (3300)	663 (11800)	1.7
1a	4.46(3H)	5.34(2H)		6.07(1H)	—[2]	355 (5500)	460 (3100)	670 (8600)	1.7
1b	3.55(1H) 4.25(1H)	4.48—5.65(3H)		a)	—[1]	352 (5300)	460 (3100)	670 (8100)	1.7
1c	3.37—4.39 (2H)	4.67(3H)		5.47(1H)	—[1]	346 (5500)	453 (3200)	657 (10500)	1.8
5[b]	4.53(2H)	4.97(1H) 5.35(1H)	6.34(1H)	6.87(1H)	7.1—8.9 (3H)[3]	378 (13600)	498 (316)		dia
3a	4.42(2H)	4.96(2H)	5.24(1H)	6.34(1H)	7.1—8.6 (3H)[1]	375 (13200)	503 (337)		dia
3b	3.28—3.70 (1H) 3.83(1H)	4.52(2H)	5.16(1H)	5.91(1H)	7.2— a)[3]	370 (13000)	510 (254)		dia
3c	3.48—4.11 (2H)	4.63(3H)		5.38(1H)	7.2—8.8 (3H)[1]	375 (14100)	535 (246)		dia

Solvents and Standard: 1) 3.6 mol dm^{-3} D_2SO_4, internal DSS; 2) 65% DNO_3, internal DSS; 3) 1.8 mol dm^{-3} D_2SO_4, internal DSS. a) This signal is overlapped with the solvent. b) Ref. 7.

netic balance (Shimadzu) from liquid nitrogen to room temperature.

Materials. The quadridentate amine ligands of 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet were purchased from Strem Chemicals Inc.

Preparation of Complexes. Diamagnetic *cis*-β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrates, $[Co(sal)L]Cl\cdot nH_2O$ (L: 2,3,2-tet, n=2 (**2a**), L: 3,2,3-tet, n=3 (**2b**), and L: 3,3,3-tet, n=1 (**2c**)) were prepared from the reaction mixture of salicylic acid or sodium salicylate and $[CoCl_2L]Cl\cdot nH_2O$ (L: 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet) according to the previous paper.[3]

Paramagnetic β_2-5-Nitrosalicylato(3,7-diazanonane-1,9-diamine)cobalt(III) Chloride Nitrate Dihydrate (1a), Paramagnetic β_2-5-Nitrosalicylato(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride Nitrate Dihydrate (1b), and Paramagnetic β_2-5-Nitrosalicylato(4,8-diazaundecane-1,11-diamine)cobalt(III) Chloride Nitrate Dihydrate (1c): One cubic centimeter of 60% nitric acid was added to **2a** (1.0 g, 2.34 mmol), **2b** (1.0 g, 2.18 mmol), and **2c** (1.0 g, 2.29 mmol), respectively. After the reaction, 60% nitric acid (1 cm^3) was added to the reaction mixture and stirred. Then the green solution was filtered using a glass filter (G-4), and the filtrate was added to acetone. The green complex thus precipitated was filtered off, washed with acetone, and dried. It was then precipitated twice more by dissolution in 60% nitric acid and by the addition of acetone. Complexes **1a—c** are soluble in water, DMSO, DMF, and acid solvents and slightly soluble in MeOH, though insoluble in common organic solvents. Yields: 0.28 g (22.4%) for **1a**, 0.15 g (12.6%) for **1b**, 0.29 g (22.5%) for **1c**. Found **1a**: C, 31.67; H, 5.42; N, 15.51; Cl, 6.61%. **1b**: C, 32.83; H, 5.23; N, 15.91; Cl, 6.79%. **1c**: C, 34.55; H, 5.95; N, 15.12; Cl, 6.69%. Calcd for **1a**: C, 31.50; H, 5.10; N, 15.74; Cl, 6.64%. **1b**: C, 32.89; H, 5.34; N, 15.34; Cl, 6.47%. **1c**: C, 34.20; H, 5.56; N, 14.96; Cl, 6.31%. Decomp 184 °C for **1a**, 183 °C for **1b** and 160 °C for **1c**. IR spectra, **1a**: 3050, 3080, and 3180 cm^{-1}; 1030(s), 1050(sh), 1055(s), and 1080(m) cm^{-1}. **1b**: 3050, 3100, and 3200 cm^{-1}; 1015(m), 1040(s), 1045(s), and 1080(m) cm^{-1}. **1c**: 3080, 3120, and 3200 cm^{-1}; 1025(sh), 1035(s), 1050(s), and 1080(s) cm^{-1}.

β_2-5-Nitrosalicylato(3,7-diazanonane-1,9-diamine)cobalt(III) Nitrate (3a), β_2-5-Nitrosalicylato(4,7-diazadecane-1,10-diamine)cobalt(III) Nitrate Hydrate (3b), and β_2-5-Nitrosalicylato(4,8-diazaundecane-1,11-diamine)cobalt(III) Nitrate Hydrate (3c): The **1a**, **1b**, or **1c** complex was precipitated by the addition of acetone to a 60% nitric acid solution of the **2a**, **2b**, or **2c** (above section). From the orange acetone solution of the filtrate, complexes **3a**, **3b**, or **3c** crystallized directly on standing. Then, the orange complex thus separated was filtered off, washed with water and dried. Complexes **3a—c** isolated were recrystallized from water, twice and dried. Complexes **3a**, **3b** are soluble in DMSO and somewhat soluble in water, though complex **3c** is soluble in water, DMSO, DMF, and MeOH. Yields: 0.36 g (33.3%) for **3a**, 0.43 g (39.9%) for **3b**, 0.30 g (25.8%) for **3c**. Found **3a**: C, 36.27; H, 4.72; N, 18.65%. **3b**: C, 36.57; H, 5.54; N, 17.40%. **3c**: C, 38.16; H, 5.39; N, 17.05%. Calcd for **3a**: C, 36.37; H, 5.01; N, 18.18%. **3b**: C, 36.45; H, 5.50; N, 17.00%. **3c**: C, 37.80; H, 5.75; N, 16.53%. Decomp 233 °C for **3a**, 195 °C for **3b**, 208 °C for **3c**. IR spectra, **3a**: 3080, 3160, and 3220 cm^{-1}; 1005(sh), 1012(m), 1025(s), 1040(s), 1060(vs), and 1070(vs) cm^{-1}. **3b**: 3120, 3190, and 3230 cm^{-1}; 1015(m), 1040(sh), 1050(vs), 1070(vs), and 1080(sh) cm^{-1}. **3c**: 3080, 3120, and 3200 cm^{-1}; 1025(sh), 1035(s), 1050(s), 1070(sh), and 1080(s) cm^{-1}.

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