Cobalt(IV) Ammine Complexes with 5-Nitrosalicylato or Similar Ligands. IV.[1] Preparation, ^{1}H-NMR, ^{13}C-NMR, and IR Spectra

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The ^{1}H-NMR spectrum of the 5-nitrosalicylatotetraamminecobalt(IV) complex did not show the signals of phenyl protons of the salicylato ligand, but did show those of ammine protons at 3.7 (s, 6H) and 3.3 ppm (s, 6H). The ^{13}C-NMR peaks could not be observed because of the paramagnetism. The ^{1}H-NMR spectra of the salicylatotetraamminecobalt(III) complexes showed peaks at 3.96 (s, 6H), 3.65 (s, 3H), and 3.38 ppm (s, 3H) for the ammine protons and at 6.7—8.1 ppm (m, 4H) for the phenyl protons of the salicylato ligand. Their ^{13}C-NMR spectra showed seven signals for the salicylato ligand. The IR peaks assignable to the rocking deformation vibration were observed at 830—855 cm^{-1} for the ammine ligands of 5-nitrosalicylatotetraamminecobalt(IV) complexes and at 820—840 cm^{-1} for those of salicylatotetraamminecobalt(III) complexes, in conformity with the view that the former complexes are actually cobalt(III) complexes of a free radical nature.

The previous papers have been concerned with the preparation[2,3] and some physical properties[4] of cobalt(IV) ammine complexes with 5-nitrosalicylato and similar ligands. The delocalization of an electron hole over the cobalt and 5-nitrosalicylato ligand system of the "cobalt(IV)" ammine complex ion with 5-nitrosalicylato or similar ligands was inferred from the magnetic susceptibility[4] and the electrical resistivity.[4] The present paper will deal with the results of measurements of the ^{1}H-NMR, ^{13}C-NMR, IR-spectra and the isolation of 5-nitrosalicylatotetraamminecobalt(IV) dinitrates and 5-nitrosalicylatotetraamminecobalt(III) nitrate.

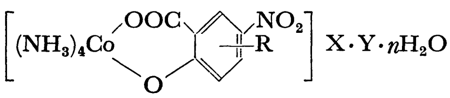
Results and Discussion

Formation of the Complexes. The salicylatotetraammine cobalt complexes studied in this research, together with the abbriviations adopted in this paper, are listed in Table 1. The **2a**—**2c** complexes are oxidized and changed to the **1a**—**1c** complexes respectively, but the **2d** complex is not oxidized with 60% nitric acid. The **1g** and **1h** complexes have been synthesized for the first time. The **1h** complex has been prepared only from the **1g** complex by metathesis. The **1g** and **1h** complexes are green and paramagnetic. Their absorption spectra show a characteristic peak at 660 nm (log $\varepsilon \approx 4$) as do other cobalt(IV) ammine complexes with 5-nitrosalicylato or similar ligands. The **1g** complex has the electrical resistivity of 10^{11} Ω cm.

The **3a** and **3b** complexes are orange and are insoluble in most organic solvents, but are soluble in water and dimethyl sulfoxide. Neither the **3a** complex nor the **3b** complex changes to a green, paramagnetic complex, **1h** and **1a** with 60% nitric acid respectively. The **3a** and **3b** complexes were characterized by the measurement of the magnetic susceptibility (diamag.), the absorption spectra (510 nm, $\varepsilon \approx 190$), the ^{1}H-NMR spectra [ammine protons (12H), and the 5-nitrosalicylato ligand protons (3H)] and equivalent conductance (114 S cm^2 for the **3a** complex). These data show that the **3a** and **3b** complexes are cobalt(III) complexes of the low-spin type.

NMR Spectra. The ^{1}H-NMR spectrum of the **1d** complex was measured in 1.8 M deuteriosulfuric acid at room temperature. The spectrum, as is shown in Fig. 1, did not show peaks of the phenyl protons of the salicylato ligand, but did show those of the ammine protons, the chemical shifts of which are close to those of the **2a** complex. The chemical shift of the methyl

TABLE 1. LIST OF SALICYLATOTETRAAMMINE COBALT COMPLEXES



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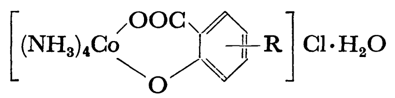

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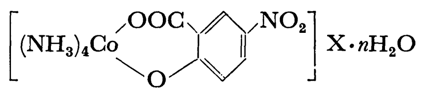

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	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**
R	H	3-CH_3	4-CH_3	H	3-CH_3	4-CH_3	H	H	H	3-CH_3	4-CH_3	5-CH_3		
X	Cl	Cl	Cl	Cl	Cl	Cl	pic[a]	NO_3					NO_3	Cl
Y	NO_3	NO_3	NO_3	Cl	Cl	Cl	pic[a]	NO_3						
n	1	1	1	3	3	3	2	1/2					1	2

a) pic:

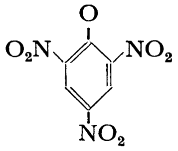

TABLE 2. THE ^{1}H-NMR AND IR SPECTRA OF COBALTAMMINE COMPLEXES

No.	Ammine			(CH$_3$)-salicylato		Solvents	IR spectra $\rho_r(NH_3)_r$ cm^{-1}
		[δ(^{2}NH$_3$-Co-^{3}NH$_3$)]					
	δ(^{1}NH$_3$-Co-^{4}NH$_3$)	δ(^{2}NH$_3$-Co)	δ(^{3}NH$_3$-Co)	δ(CH$_3$-Sal)	δ(C$_6$H$_{3-4}$)		
1a	3.73, s, 6H	[3.23, s, 6H]		—		1	835
1d	3.76, s, 6H	[3.30, s, 6H]		—		1	840
1e	3.53, s, 6H	[3.20, s, 6H]		1.73, s, 3H		2	840
1f	3.75, s, 6H	[3.20, s, 6H]		2.0, s, 3H		2	855
2a	3.96, s, 6H	3.65, s, 3H	3.38, s, 3H	—	6.7—8.1, m, 4H	1	
2a	3.63, s, 6H	3.40, s, 3H	3.07, s, 3H	—	6.4—7.7, m, 4H	2	840
2b	3.63, s, 6H	3.44, s, 3H	3.18, s, 3H	2.02, s, 3H	6.4—7.7, m, 3H	2	830
2c	3.68, s, 6H	3.43, s, 3H	3.13, s, 3H	2.16, s, 3H	6.4—7.7, m, 3H	2	820
2d	3.60, s, 6H	3.33, s, 3H	3.0, s, 3H	2.03, s, 3H	6.9—7.4, m, 3H	2	820
3a	3.63, s, 6H	[3.16, s, 6H]		—	6.7—8.3, m, 3H	3	828
3b	3.87, s, 6H	3.47, s, 3H	3.30, s, 3H	—	7.0—8.9, m, 3H	1	840
L$^{\mathrm{a}}$				—	6.8—8.0, m, 4H	4	
L$^{\mathrm{b}}$				2.26, s, 3H	6.9—7.8, m, 3H	4	

Abbreviations: **L$^{\mathrm{a}}$**: salicylic acid, **L$^{\mathrm{b}}$**: 3-methylsalicylic acid. Standards: **L$^{\mathrm{a}}$** and **L$^{\mathrm{b}}$** were used with the internal TMS in the CDCl$_3$ and the other complexes were used with the external TMS in the CDCl$_3$. Solvents: 1: 1.8 M D$_2$SO$_4$, 2: D$_2$O and CF$_3$COOH, 3: 0.2 M DCl, 4: CDCl$_3$. ρ_r (NH$_3$)$_r$: 855 for the **1b** complex, 830 for the **1g** complex, and 835 cm^{-1} for the **1h** complex.

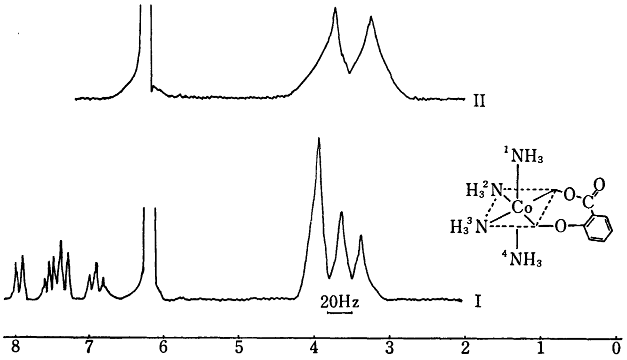

Fig. 1. The ^{1}H-NMR spectra of complexes **2a** and **1d**.

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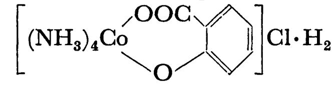
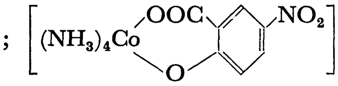

Cl·H$_2$O in 1.8M D$_2$SO$_4$.

II;

Cl$_2$·3H$_2$O in 1.8M D$_2$SO$_4$.

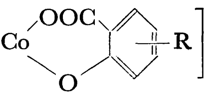
Standard: External TMS in CDCl$_3$.

protons of the salicylato ligand in the **1e**, **1f**, and **2b**—**2d** complexes did not show any appreciable change, either, as is shown in Table 2. The measurements of the ^{13}C-NMR spectra of the **1a**, **1c**, and **1d** complexes were attempted in several solvents, at varying concentrations at low and at room temperature. The spectra did not show the expected signals because of the paramagnetism of those complexes. These results lead to the conclusion that, in the **1a**—**1h** complexes, the electron hole is not distributed over the ammine ligands and the methyl group of substituted 5-nitrosalicylato ligand, though it seems to be delocalized over the chelate ring containing the cobalt atom and the benzene ring of the 5-nitrosalicylato ligand.

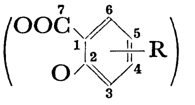
^{1}H-NMR spectrum of the **2a** complex showed three singlets of ammine groups and a multiplet of the salicylato ligand in the expected integral ratio (3:3:6:4) at room temperature, as is shown in Fig. 1. The singlet (3.38 ppm) at the highest field was assigned to the protons of the ammine ligand in a position *trans* to the carboxyl oxygen of the salicylato ligand in the **2a** complex. The singlet at 3.65 ppm is assigned to the protons of the ammine ligand in a position *trans* to the phenolic oxygen, which is less electronegative than the carboxyl oxygen, while that at 3.96 ppm is assigned to the protons of two ammine ligands in positions *cis* to the salicylato ligand. The multiplet (6.7—8.1 ppm) at the lowest field was assigned to the protons of the salicylato ligand. The above assignment was made in view of the following: studies of pentaammineaniono-cobalt(III) ions, [Co(NH$_3$)$_5$X]$^{n+}$ (X: Cl, Br, OH ···), have been reported by Buckingham,[5] Jolly,[6] and Clifton,[7] who described that the chemical shift of the NH$_3$ group in a position *trans* to the electronegative atom (X) is at higher fields than those of NH$_3$ groups in a position *cis* to the electronegative atom. The chemical shift of the NH$_3$ group in a position *trans* to the electronegative atom (HSO$_4^-$) is at higher field than that of the NH$_3$ group in a position *trans* to other electronegative atoms (H$_2$O, Cl, ···).[6] Marzilli[8] and Hawkins[9] also reported the case of sarcosinatotriethylenetetraminecobalt(III) ions in which the proton signals of the NH$_2$ group in a position *trans* to the coordinated carboxyl oxygen of sarcosinato ligand appeared at higher fields than those of the NH$_2$ group in a position *cis* to the coordinated carboxyl oxygen.

The ^{13}C-NMR spectra of the **2a** complex were measured in heavy water at room temperature. The assignment of the salicylato ligand of the complex was attempted by means of a consideration of the assignment of salicylaldehyde[10] and methylsalicylate.[10] Two signals, C-1 and C-3, of the salicylato ligand overlapped, as is shown in Table 3, but they split when the pH was

Table 3. $^{13}C\ \{^1H\}$-NMR of the complexes,



Cl·H_2O, and ligands



No.	δ (R) (H), CH_3	δ C-1	C-2	C-3	C-4	C-5	C-6	C-7	Solvents and standards
2a	(−)	117.5	167.5	117.5	134.6	124.1	132.7	174.1	$D_2O^{a)}$
2b	17.5	116.8	166.7	133.2	134.6	116.4	130.2	174.7	$D_2O^{a)}$
2c	21.2	114.6	167.4	118.9	145.8	123.8	132.5	174.0	$D_2O^{a)}$
2d	20.3	117.2	165.3	124.0	135.8	126.9	130.0	174.1	$D_2O^{a)}$
3a	(−)	118.0	166.5	123.4	134.9	125.4	129.9	175.5	DMSO-$d_6^{b)}$
3b	(−)	114.6	169.8	124.2	135.0	126.8	129.6	175.8	DMSO-$d_6^{b)}$
$\mathbf{L^a}$	(−)	113.8	162.7	118.0	136.6	120.2	131.5	173.6	MeOH$^{c)}$
$\mathbf{L^b}$	15.6	112.9	161.0	127.2	137.2	119.7	129.0	174.3	MeOH$^{c)}$
$\mathbf{L^c}$	21.8	111.1	162.7	118.1	148.3	121.5	131.4	173.6	MeOH$^{c)}$
$\mathbf{L^d}$	20.4	113.3	160.2	117.9	137.6	129.7	131.1	173.6	MeOH$^{c)}$
$\mathbf{L^e}$	(−)	121.0	161.4	117.4	136.6	119.6	133.6	196.7	—
$\mathbf{L^f}$	(−)	114.6	168.5	119.9	141.7	128.4	131.9	172.5	MeOH-$d_4^{d)}$

Standards: a) MeOH (δ=49.8 ppm), b) DMSO-d_6 (δ=39.5 ppm), c) Internal TMS (δ=0ppm), measured in methanol and heavy water. d) MeOH-d_4 (δ=49.8 ppm). Abbreviations: $\mathbf{L^a}$: salicylic acid, $\mathbf{L^b}$: 3-methylsalicylic acid, $\mathbf{L^c}$; 4-methylsalicylic acid, $\mathbf{L^d}$: 5-Methylsalicylic acid, $\mathbf{L^e}$: salicylaldehyde,[10] and $\mathbf{L^f}$: 5-nitrosalicylic acid.

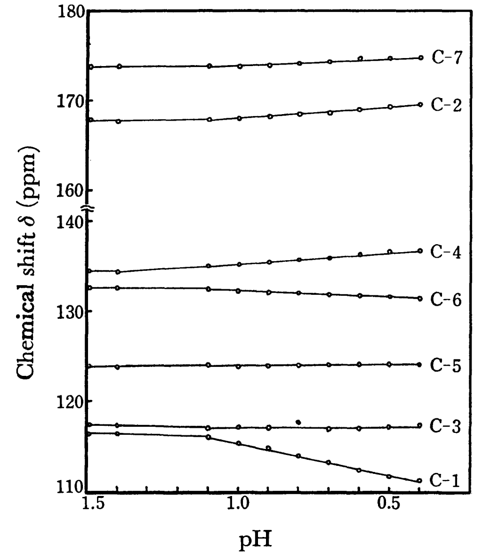
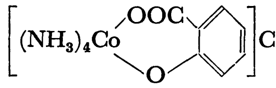


Fig. 2. ^{13}C-NMR chemical shift *vs.* pH of the complex **2a.**



$[(NH_3)_4Co(OOC\text{-}C_6H_4\text{-}O)]$Cl·$H_2O$ in D_2O and HCl.

Standard: MeOH (δ=49.8 ppm).

lowered below 1.1 by the addition of hydrochloric acid. In hydrochloric acid, the carbon signal of C-5 did not shift, that of C-3 shifted slightly to a higher field, C-6 shifted to a higher field, and those of C-2, C-4, and C-7 shifted to a lower filed, as is shown in Fig. 2. This observation seems to be due to the hydrogen bonding[11,12] between the lone pairs of the carbonyl oxygen atom of the salicylato ligand and proton of hydrochloric acid.

The ^{1}H-NMR spectra of the **3a**—**3b** complexes are similar to those of the **2a**—**2d** complexes. The ^{13}C-NMR spectra of the **3a**—**3b** complexes in DMSO-d_6 are shown in Table 3. The chemical shifts of the substituted carbon atom of the salicylato ligand both in the **2b**—**2c** complexes and in the free ligands, L^b-L^d, L^f, move to a lower field upon the substitution of methyl and nitro groups. These shifts are coincident with the data reported by Levy and Nelson.[13,14] The exceptions are the carbon signals of the C-5 position of the 5-methyl- or 5-nitrosalicylato ligands in the **2d** and **3a**—**3b** complexes which do not shift to a lower field.

IR Spectra. It was reported by Nakamoto,[15] Wilmshuist[16] and Svatos[17] that the rocking deformation vibration of metal ammine complexes, which appears as a broad band, is influenced by the oxidation state of the metal in the ammine complex. Thus, it appears at 650 cm^{-1} in hexaamminecobalt(II) chloride[17—19] and at 827 cm^{-1} in hexaamminecobalt(III) chloride.[17—19] The rocking deformation vibration was observed as a broad band at 830—855 cm^{-1} for the **1a**—**1f** complexes, at 820—840 cm^{-1} for the **2a**—**2d** complexes, and at 828—840 cm^{-1} for the **3a**—**3b** complexes, showing little difference among these complexes. From the above facts, the most reasonable conclusion seems that the ammine ligands in the **1a**—**1f** complexes are similar to those of the **2a**—**2d** complexes and that the **1a**—**1f** complexes have a free radical nature in which the electron hole is delocalized over the 5-nitrosalicylato ligand and the cobalt ion in agreement with magnetic susceptibility,[4] the electrical resistivity[4] and the NMR spectra of the **1a** and **1d**—**1f** complexes. The situation might be similar to the cases of μ-peroxo and μ-hyperoxo dicobalt complexes, both of which have the rocking deformation band of ammine at around 800 cm^{-1} and are considered to contain trivalent cobalt.[20,21]

Experimental

Measurements. The NMR spectra were measured with a FX-60 (JEOL) for ^{13}C-NMR and JNM-PMX-60 (JEOL), R-40 (Hitachi) for ^{1}H-NMR. The IR spectra were measured with a JASCO spectrophotometer, DS 402-G, and an EPI 238 Hitachi apparatus in potassium bromide disks for the **1a**—**1h** and **2a**—**2d** complexes and in Nujol mulls for the **3a**—**3b** complexes. The visible absorption spectra were recorded with Shimadzu MPS-5000 recording spectrophotometer. The electrical resistivity was measured with a Toa Denpa Kogyo Microvolt ammeter. The magnetic susceptibilities were measured by the Gouy method with a magnetic balance (Shimadzu) at room temperature. The pH was measured with a Toa Electronics pH-meter, HM-5B.

Preparation of Complexes. *The **1a**, **1b**, **1c**, **1d**, **1e**, and **1f** complexes* were prepared as has been described in previous papers.[2,3] *The **2a**, **2b**, **2c**, and **2d** complexes* were prepared by Morgan and Smith's method.[22]

*5-Nitrosalicylatotetraamminecobalt(IV) Picrate Dihydrate (**1g**).* An aqueous solution of 0.8 g (1.89 mmol) of the **1a** complex was slowly added to an aqueous solution of 0.87 g (3.79 mmol) of picric acid, and mixture was stirred. The precipitated green complex was filtered off, washed with water, and dried. Yield: 0.94 g (62.3%), Found: C, 28.49; H, 2.87; N, 19.41%. Calcd for $CoC_{19}H_{23}N_{11}O_{21}$ (*MW*: 800.39) C, 28.51; H, 2.90; N, 19.25%. The absorption maximum in the visible spectrum was at 660 nm (ε=12700) in water.

*5-Nitrosalicylatotetraamminecobalt(IV) Nitrate Hemihydrate(**1h**).* 0.5 g (0.62 mmol) of the **1 g** complex was dissolved in 60% nitric acid, and some picric acid was precipitated. The solution was then filtered with a glass filter (G4), and the filtrate was added to acetone. The precipitated green complex was filtered off, washed and dried. Yield: 0.20 g (72.7 %), Found: C, 19.47; H, 3.80; N, 21.66%. Calcd for $CoC_7H_{16}N_7O_{11.5}$: (*MW*: 441.18) C, 19.06; H, 3.65; N, 22.22%. Visible absorption peaks: 450 nm (ε=3700) and 660 nm (ε=14100) in 60% nitric acid.

*5-Nitrosalicylatotetraamminecobalt(III) Nitrate Monohydrate(**3a**).* The **1a** complex was precipitated by the addition of acetone to a 60% nitric acid solution of 3.0 g (9.5 mmol) of the **2a** complex according to the method presented in a previous paper.[2] The **3a** complex was isolated from this orange-colored acetone solution, recrystallized from water, and dried. Yield: 0.96 g (18.5%), Found: C, 21.82; H. 4.53; N, 21.90%. Calcd for $CoC_7H_{17}N_6O_9$: (*MW*: 387.52) C, 21.70; H, 4.42; N, 21.69 %. The visible absorption peak was 510 nm (ε=196) in water.

*5-Nitrosalicylatotetraamminecobalt(III) Chloride Dihydrate Hydrochloric Acid (**3b**).* 0.4 g (1.03 mmol) of the **3a** complex was dissolved in 30% hydrochloric acid. The precipitate formed by the addition of acetone was filtered off, washed, and dried. Yield: 0.26 g (58.2%), Found: C, 20.34; H, 4.85; N, 16.27; Cl, 17.62%. Calcd for $CoC_7H_{20}N_5O_7Cl_2$: (*MW*; 416.12) C, 20.21; H, 4.84; N, 16.83; Cl, 17.04%. The visible absorption peak was 512 nm (ε=185) in 35% hydrochloric acid.

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