Paramagnetic Cobalt(III) Complexes with Organic Ligands. V. The Isolation and Properties of Salts of the Paramagnetic Bis(2,2'-bipyridine)(5-nitrosalicylato)cobalt(III) and of the Paramagnetic "β_1 and β_2"-Isomers of the 5-Nitrosalicylato(triethylenetetramine)cobalt(III) and Their Derivatives[1)]

Yoshihisa YAMAMOTO,* Eiko TOYOTA, and Naoto MITSUDERA
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02
(Received February 4, 1980)

The picrate of the paramagnetic, $[Co(5\text{-}NO_2sal)(bpy)_2]^{2+}$, has been isolated from a reaction mixture of picric acid, 60% nitric acid, and bis(2,2'-bipyridine)(salicylato)cobalt(III) chloride trihydrate, $[Co(sal)(bpy)_2]Cl\cdot 3H_2O$, which had been prepared from salicylic acid and *cis*-bis(2,2'-bipyridine)dichlorocobalt(III) chloride dihydrate. The absorption spectrum and the stability of an aqueous solution of the picrate of the paramagnetic, $[Co(5\text{-}NO_2sal)(bpy)_2]^{2+}$, were somewhat different from those of complexes of the paramagnetic, $[Co(5\text{-}NO_2sal\text{-}R)(NH_3)_4]^{2+}$ (R: H, CH_3). Several complexes of the paramagnetic, β_1-5-nitrosalicylato-, β_2-5-nitrosalicylato-, and β_2-3-methyl (and 4-methyl)-5-nitrosalicylato(triethylenetetramine)cobalt(III) have, analogously, been isolated from reaction mixtures of 60% nitric acid and β_1-salicylato-, β_2-salicylato, or β_2-methylsalicylato(triethylenetetramine)cobalt(III) chloride hydrate respectively. Their β_1 and β_2-isomeric forms were proved by a study of their IR and ^{1}H-NMR spectra. From the IR, NMR, and the magnetic susceptibility measurement results, these compounds are considered to have the paramagnetic complex, $[Co(5\text{-}NO_2sal)L]^{2+}$ (L: $(NH_3)_4$, $(en)_2$, $(bpy)_2$, and trien), and the electron hole is considered to delocalize over the chelate ring containing the cobalt atom and the 5-nitrosalicylato ligand.

Previously we have reported on several green paramagnetic cobalt(III) complexes with organic ligands, which are formally tetravalent. Various physicochemical measurements have showed, however, that the compounds contain radical cations and that the cobalt is trivalent.[2)] In the paramagnetic cobalt(III) complexes, the paramagnetic cobalt(III) complex of an aromatic amine ligand such as bipyridine and the isomers of the paramagnetic cobalt(III) complex such as the triethylenetetramine ligand have not yet been described.

The present paper deals with the isolation and properties of complexes of the paramagnetic bis(2,2'-bipyridine)(5-nitrosalicylato)cobalt(III) and of the isomers of the paramagnetic β_1 and β_2-5-nitrosalicylato(triethylenetetramine)cobalt(III); also, their properties are compared with those of 5-nitrosalicylato(tetraammine)cobalt(III) complexes.[2)]

Results and Discussion

Bis(2,2'-bipyridine)(salicylato)cobalt(III) Chloride Trihydrate, $[Co(sal)(bpy)_2]Cl\cdot 3H_2O$ (1) and Paramagnetic Bis(2,2'-bipyridine)(5-nitrosalicylato)cobalt(III) Picrate, $[Co(5\text{-}NO_2sal)(bpy)_2](pic)_2$ (2). Although many studies of bis(2,2'-bipyridine)cobalt(III) complexes with aliphatic organic ligands[3-6)] or inorganic ligands[5-8)] have already been reported, the bis(2,2'-bipyridine)cobalt(III) complex with an aromatic organic ligand has never been described. Complex **1** was prepared by the reaction of the salicylic acid and *cis*-$[CoCl_2(bpy)_2]Cl\cdot 2H_2O$. Complex **1** can also be prepared from the corresponding *trans* dichloro complex. It is soluble in water, methanol, or dimethyl sulfoxide and is insoluble in most organic solvents. The color of an aqueous solution of **1** is reddish brown, while that of a methanolic solution is green. This color change is reversible.[9)] Complex **1** decomposes in an aqueous solution. Complex **2** has been isolated from the reaction mixture of Complex **1**, 60% nitric acid, and picric acid. In an aqueous solution, **2** is much more unstable than paramagnetic 5-nitrosalicylato(tetraammine)cobalt(III) complexes, $[Co(5\text{-}NO_2sal\text{-}R)(NH_3)_4]^{2+}$ (R: H, CH_3) (**3**).

The absorption spectrum of **1** in methanol has three absorption bands at 301, 313, and 587 nm. The absorption bands at 301 and 313 nm are the specific absorption bands[3c)] of **1**. The absorption band at 587 nm is based on the d-d transition ($^1T_{1g}\leftarrow{}^1A_{1g}$) of the cobalt ion. The absorption spectrum of **2** in 65% nitric acid has two absorption bands, at 577 and 645 nm, in the 450—700 nm region. The ε at 645 nm of **2** is much weaker than that[10)] at 660 nm of **3**, while the peak at 577 nm is stronger than that at 587 nm of **1**.

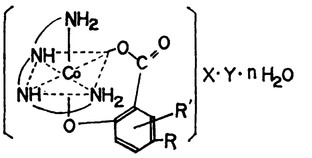
In the ^{1}H-NMR spectra, the signals (6.1—7.5 ppm) of the salicylato protons of the coordinated salicylato ligand of **1** were observed in dimethyl-d_6 sulfoxide, but those of **2** were not observed.[2)] The signals (7.3—9.1 ppm) of the bipyridine protons of the coordinated bipyridine ligand of **1** and **2** were observed. In the ^{13}C-NMR spectrum of **1** in heavy water we observed fifteen signals for the bis(2,2'-bipyridine) ligand and seven signals for the salicylato ligand, which were assigned on the basis of the chemical shifts of salicylato(tetraammine)cobalt(III) chloride monohydrate,[2)] $[Co(sal)(NH_3)_4]Cl\cdot H_2O$ (**4**). The spectrum of **2** did not show the expected signals because of paramagnetism.[2)]

The effective magnetic moment was 1.6 B.M., and the Curie-Weiss constant was -10 K for **2**.

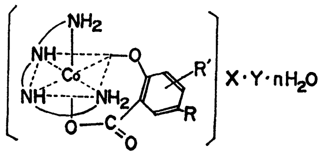
In the IR spectra, the rocking deformation vibration was observed at 764 cm^{-1} for **1** and at 766 cm^{-1} for **2**. The cobalt atom of these complexes is considered to contain trivalent cobalt.[2)]

From the IR, ^{1}H- and ^{13}C-NMR spectra and the magnetic susceptibility, an aromatic amine complex (**2**) was found to show the same properties as those of the

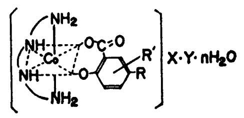
TABLE 1. THREE ISOMERIC FORMS AND THE ABBREVIATIONS OF THE SALICYLATO (TRIETHYLENETETRAMINE)COBALT COMPLEXES



β_1



β_2



α

Complex	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Form	β_1	β_1	β_2	β_2	β_1	β_2	β_2	β_2	β_2	β_1	β_2	β_2	β_2	β_1	β_2
R	H	H	H	H	H	H	NO_2	NO_2	NO_2	NO_2	NO_2	NO_2	NO_2	NO_2	NO_2
R′	3-CH_3	4-CH_3	3-CH_3	4-CH_3	H	H	H	3-CH_3	4-CH_3	H	H	3-CH_3	4-CH_3	H	H
X	Cl	Cl	Cl	Cl	Cl	Cl	NO_3	NO_3	NO_3	Cl	Cl	Cl	Cl	Cl	Cl
Y	—	—	—	—	—	—	—	—	—	NO_3	NO_3	NO_3	NO_3	Cl	Cl
n	2	2	1	1	1	1	3	2	2	2	2	2	2	3	3

TABLE 2. SOME PHYSICAL PROPERTIES OF COMPLEXES **3**—**6** AND **9**—**15**

Complex No.	IR spectra 3000—3300 cm^{-1}	IR spectra 990—1100 cm^{-1}	$\rho_r(NH_2)_r$ cm^{-1}	Absorption bands λ/nm	Absorption bands ε	Magnetic moments μ_{eff}(B.M.)	Mp [dec] °C	Electro conductivity of aqueous solutions $S \cdot cm^2\ eq^{-1}$
5	2950, 3100, 3220	995, 1030	860	335	3330[1)]		238—240	110
	3250, 3270	1062(vs), 1080		524	291			
6	2950, 3080, 3180	998, 1030	857	328	3100[1)]		236—239	105
	3230, 3270	1058(vs), 1072		525	287			
7	2880, 2940, 3055	993, 1033	860	338	3370[1)]		245—247	106
	3150, 3220, 3270	1055, 1078(vs)		510	288			
8	2880, 2940, 3060	990, 1035	860	331	3060[1)]		247—248	104
	3150, 3240, 3270	1052, 1078(vs)		511	275			
11	2870, 3100	995, 1030,	830	378	13550[1)]		[229—231]	91
	3200, 3270	1050, 1070(vs)		498	316			
12	2870, 3120	995, 1030	835	382	15000[1)]		[255—258]	120
	3230, 3270	1053, 1078(vs)		496	340			
13	2870, 3120	995, 1028	830	374	13450[1)]		[249—251]	107
	3230, 3270	1050, 1070(vs)		500	307			
14	2900, 3100	1000, 1035	835	345	4100[2)]	1.68	[124—125]	283
	3200, 3250	1070, 1090		460	4250			
				660	12900			
15	2870, 3080	995, 1030	835	360	3240[2)]	1.70	[183—184]	254
	3180, 3260	1055, 1078		455	3300			
				663	11800			
16	2880, 3120	995, 1030	838	340	3980[2)]	1.66	[182—183]	271
	3180, 3260	1052, 1075		455	2900			
				667	7850			
17	2880, 3120	996, 1030	830	360	3600[2)]	1.64	[182—183]	272
	3200, 3260	1055, 1075		452	3940			
				633	7400			

Mp: **9**; 238—241, **10**; 240—243 °C. Solvents: 1) H_2O, 2) 60% HNO_3.

aliphatic amine complexes (**3**) except for the absorption spectra and the stability of the aqueous solutions.

β-Salicylato(triethylenetetramine)cobalt(III) Complexes and Paramagnetic β-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Complexes. The paramagnetic properties of these isomers have been the subject of little research. We expect that the delocalization of a radical cation of these isomers will differs from that of **3**. Three isomeric forms and the abbreviations of the salicylato (triethylenetetramine)cobalt(III) complexes studied in this paper are listed in Table 1. The color and solubility of **5**—**8** are similar to those of **9**[11)] and **10**.[11)] Complexes **14**—**19** are insoluble in most organic solvents, but are soluble in nitric acid, hydrochloric acid, and dimethyl sulfoxide. Aqueous solutions of the **14**—**19** complexes are somewhat more unstable than that of **3**, while that of **14** is more unstable than that of **15**.

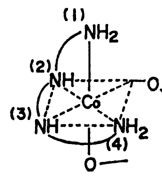
The IR spectra of the **5**—**7** and **11**—**17** complexes have four strong peaks in the 990—1100 and 3000—3300 cm^{-1} regions respectively, as is shown in Table 2;

TABLE 3. ^{1}H-NMR SPECTRA OF COMPLEXES **3**—**6** AND **9**—**15**

Complex No.	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$[a)] CH$_2$ δ/ppm	N(1)H$_2$ δ/ppm	N(4)H$_2$ δ/ppm	N(3)H δ/ppm	[N(2)H+salicylato] N(2)H δ/ppm	salicylato δ/ppm	CH$_3$ δ/ppm
5	2.38—3.87(12H)	4.34(1H) 4.53(1H)	4.70(1H) 5.20(1H)	b)	6.49(1H)	6.50—7.80(3H)	2.26(3H)[1)]
6	2.39—3.86(12H)	4.34(1H) 4.48(1H)	4.69(1H) 5.21(1H)	6.12(1H)	6.52(1H)	6.52—7.81(3H)	2.30(3H)[1)]
7	2.38—2.85 (3H) 2.85—3.75 (9H)	4.35(2H)	4.60(1H) 5.18(1H)	6.12(1H)	[6.40—7.83(4H)]		2.30(3H)[1)]
8	2.37—2.82 (3H) 2.82—3.74 (9H)	4.32(2H)	4.62(1H) 5.13(1H)	6.05(1H)	[6.37—7.78(4H)]		2.29(3H)[1)]
11	2.35—2.85 (3H) 2.85—3.85 (9H)	4.53(2H)	4.97(1H) 5.35(1H)	6.34(1H)	6.87(1H)	7.13—8.85(3H)	— [1)]
12	2.47—2.81 (3H) 2.81—3.88 (9H)	4.47(2H)	4.89(1H) 5.34(1H)	6.31(1H)	6.85(1H)	7.96—8.67(2H)	2.30(3H)[1)]
13	2.42—2.87 (3H) 2.87—3.87 (9H)	4.52(2H)	4.92(1H) 5.39(1H)	6.35(1H)	6.89(1H)	7.29—8.74(2H)	2.25(3H)[1)]
14	2.42—3.92(12H)	4.40(1H) 4.70(1H)	5.27(1H) 5.48(1H)	6.52(1H)	b)		— [2)]
	2.45—3.98(12H)	4.43(1H) 4.70(1H)	c)	6.60(1H)	7.00(1H)		— [1)]
15	2.33—2.82 (3H) 2.82—3.84 (9H)	4.48(2H)	5.14(1H) 5.38(1H)	6.35(1H)	b)		— [2)]
	2.34—2.83 (3H) 2.83—3.88 (9H)	4.54(2H)	c)	6.36(1H)	7.13(1H)		— [1)]
16	2.46—2.90 (3H) 2.90—3.88 (9H)	4.60(2H)	c)	6.51(1H)	7.21(1H)		2.25(3H)[1)]
17	2.46—2.84 (3H) 2.84—3.92 (9H)	4.56(2H)	c)	6.45(1H)	7.15(1H)		2.27(3H)[1)]

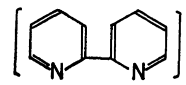
Solvents: 1) 1.8 mol dm^{-3} D_2SO_4. 2) 3.6 mol dm^{-3} D_2SO_4. Standard: internal DSS.

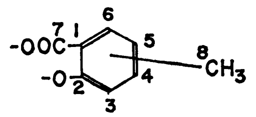
a) N(1), N(2), N(3), and N(4) of the coordinated triethylenetetramine ligand.



b) This signal overlapped with the solvent. c) This signal overlapped with the side band of the solvent.

TABLE 4. ^{13}C-NMR SPECTRA OF COMPLEXES **1**, **5**—**8**, AND **11**





Complex No.	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ δ/ppm	c-1	c-2	c-3	c-4	c-5	c-6	c-7	c-8
1	[123.1 125.6 125.8 125.9 129.3 129.5 142.7 142.8 143.5 151.4 152.0 152.2 157.1 157.4 157.9]	118.1	165.9	117.8	134.8	124.5	132.1	173.2	—
5	56.3 53.8 52.4 52.1 45.9 43.7	115.3	167.0	133.1	135.1	116.4	129.9	175.1	17.3
6	56.3 53.9 52.3 52.0 45.9 43.7	115.3	168.0	119.0	146.1	124.1	132.3	174.8	21.2
7	52.7 51.9 50.1 48.5 47.6 42.0	116.2	167.0	133.0	134.4	115.7	130.0	174.7	17.9
8	52.8 52.2 49.7 48.3 47.4 42.0	118.8	168.3	118.4	145.7	124.0	132.4	174.2	21.1
11	52.9 52.3 50.1 48.5 47.8 42.4	116.0	172.3	125.1	136.8	128.5	130.7	176.1	—

Solvent: D_2O. Standard: internal dioxane (δ=67.4 ppm).

therefore, they are assigned the β-form.[12)] The rocking deformation vibrations[2)] of these complexes were observed at 830—860 cm^{-1}.

The absorption spectra of the **14**—**17** complexes in 60% nitric acid showed three absorption bands at about 345, 460, and 660 nm. In the **14** and **15** complexes, although these spectra show similar forms, the second absorption band of **14** is shorter than that of **15**. The ε at 660 nm of these complexes is similar to that[10a)] at 660 nm of **3**. In the **15**—**17** complexes, the second absorption band of **16** is shorter than that of **15**, while the ε at 667 nm of **16** and that at 633 nm of **17** are weaker than that at 663 nm of **15**. These properties seem to be due to the substituent effect of the methyl group.[10b)] In the **11**—**13** complexes, the second absorption bands are longer than those of **7**, **8**, and **10** respectively, while the ε's of those bands of the **11**—**13** complexes are much stronger than those of **7**, **8**, and **10** respectively. Those properties seem to be due to the substituent effect of the nitro group. The first absorption bands of **7**, **8**, and **10** shift to a shorter wavelength area than those of **5**, **6**, and **9** respectively. The absorption spectra of **18** and **19** could not be obtained because they turned dark green in 35% hydrochloric acid.

In the ^{1}H-NMR spectra, the protons of the coordinated triethylenetetramine and methylsalicylato ligands of these complexes were assigned on the basis of the results in earlier papers,[11,13)] as is shown in Table 3. The signals of the 5-nitrosalicylato protons of the coordinated 5-nitrosalicylato ligands of **14** and **15**—**17** were not observed, either. The spectra of **5**, **6**, and **14** are similar to that of β_1-complex[11)] (**9**) while those of **7**, **8**, and **15**—**17** are similar to that of the β_2-complex[11)] (**10**). They are assigned the β_1 and β_2-forms respectively. The chemical shifts of the NH and NH_2 protons of coordinated trien in **11**, **14**, and **15** shifted to a lower field than those of **9** and **10**. This could be due to the nitro group in the coordinated 5-nitrosalicylato ligand. In the ^{13}C-NMR spectra of **5**—**8** and **11** in heavy water, we observed eight signals for the methylsalicylato ligand and six signals for the triethylenetetramine ligand. The chemical shifts of the methylsalicylato ligand are assigned on the basis of the chemical shift of **4**.[2)] Those of the trien ligand are difficult to assign to the individual carbon atom. The ^{13}C-NMR spectra of **14**—**19** did not show the expected signals because of paramagnetism.

The effective magnetic moments of the **14**—**19** complexes were 1.7 B.M.

The above data show that the paramagnetic properties of the **14** and **15** isomers are little different from each other, while their properties are in agreement with those of **3**. The properties of **16** and **17** are only a little different from those of **15**. They can thus be grouped together as paramagnetic 5-nitrosalicylato(amine)cobalt(III) complexes, $[Co(5\text{-}NO_2sal)L]^{2+}$ (L: $(NH_3)_4$, $(en)_2$, $(bpy)_2$, trien), with a radical cation delocalized over the chelate ring containing the cobalt atom and the 5-nitrosalicylato ligand, from the results of the IR spectra,[2)] ^{1}H-, and ^{13}C-NMR spectra,[2)] the magnetic susceptibility,[14)] and the electric resistivity.[14)] The properties of these complexes are collected in Tables 2—4.

Experimental

Measurements. The NMR spectra were recorded with an FX-60 apparatus (JEOL) for ^{13}C-NMR and an R-40 apparatus (Hitachi) for ^{1}H-NMR. The IR spectra were recorded on potassium bromide disks with a IR-27G apparatus (Shimadzu). The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The magnetic susceptibilities were measured by the Gouy method using a magnetic balance (Shimadzu) from liq.N_2 to r.t. The pH was measured with a Corning pH-meter M-125. The electro conductivity of an aqueous solution was determined by the use of a conductometer, CM-30 (Shimadzu) at room temperature.

Preparation of Complexes. Bis(2,2'-bipyridine)(salicylato)cobalt(III) Chloride Trihydrate (1): *cis*-Bis(2,2'-bipyridine)-dichlorocobalt(III) chloride dihydrate[15)] (2.0 g, 3.89 mmol dm^{-3}) was added to AgOH, which had been made from silver nitrate (1.33 g, 7.83 mmol dm^{-3}) and potassium hydroxide. The mixture was stirred for about 30 min at 60 °C and then filtered. To the filtrate we then added salicylic acid (0.53 g, 3.84 mmol dm^{-3}) in a 10% ammonia solution of 5 ml. The mixture was concentrated at 60 °C. The black complex thus precipitated was filtered off, washed with a 3% ammonia solution, dried, and recrystallized from a 2—3% ammonia solution. Complex **1** was dried in a desiccator over diphosphorus pentaoxide. Yield: 1.70 g (73.2%). Found: C, 54.56; H, 4.07; N, 9.82; Cl, 5.23%. Calcd for $CoC_{27}H_{26}N_4O_6Cl$ (MW 596.91) C, 54.33; H, 4.39; N, 9.39; Cl, 5.94%. mp 240—243 °C. IR spectrum: ρ_r(Co–N)$_r$: 764 cm^{-1}. Absorption bands: 301 (ε=25600), 313 (ε=24200), and 587 nm (ε=330) in MeOH.

Paramagnetic Bis(2,2'-bipyridine)(5-nitrosalicylato)cobalt(III) Dipicrate (2): About 1 cm^3 of 60% nitric acid was added to **1** of 1.0 g (1.68 mmol dm^{-3}). The color of the solution was thus changed to green. Then several cm^3 of 60% nitric acid were added to it. An aqueous solution of picric acid (0.77 g, 3.36 mmol dm^{-3}) was added to the green solution, and it was stirred. The yellowish-green complex (**2**) thus precipitated was filtered off, washed with ice water, and dried. Yield: 1.34 g (79.1%). Found: C, 46.82; H, 2.40; N, 14.94%. Calcd for $CoC_{39}H_{23}N_{11}O_{19}$ (MW 1008.61) C, 46.44; H, 2.30; N, 15.28%. Dec 163—167 °C. IR spectrum: ρ_r(Co–N)$_r$: 766 cm^{-1}. Absorption bands: 577 (ε=867) and 645 nm (ε=675) in 65% DNO_3.

β-Salicylato(triethylenetetramine)cobalt(III) Chloride Monohydrate, β-3-Methylsalicylato(triethylenetetramine)cobalt(III) Chloride Monohydrate, and β-4-Methylsalicylato(triethylenetetramine)-cobalt(III) Chloride Monohydrate: These complexes were prepared by the reaction of the α-dichloro(triethylenetetramine)-cobalt(III) chloride[16)] and salicylic acid, 3-methylsalicylic acid, or 4-methylsalicylic acid at pH 10—11 by Morgan's method.[17)] Yields: 3-methylsalicylato(triethylenetetramine)-cobalt(III) chloride monohydrate, 64.4%; 4-methylsalicylato-(triethylenetetramine)cobalt(III) chloride monohydrate, 67.1%.

Separation of β_1-3-Methylsalicylato(triethylenetetramine)cobalt(III) Chloride Dihydrate (5), β_1-4-Methylsalicylato(triethylenetetramine)-cobalt(III) Chloride Dihydrate (6), β_2-3-Methylsalicylato(triethylenetetramine)cobalt(III) Chloride Monohydrate (7), and β_2-4-Methylsalicylato(triethylenetetramine)cobalt(III) Chliorde Monohydrate (8): The separation of β_1 and β_2 complexes was achieved by the use of ion-exchange resin.[18)] Complexes **5** and **6** are changed to the corresponding β_2-complexes in an alkali solution. Yields: 0.033 g (6.6%) for **5**; 0.028 g (5.6%) for **6**; 0.43 g (86%) for **7**; 0.42 g (84%) for **8**. Found **5**: C, 39.88; H, 6.66; N, 13.48; Cl, 9.08%. **6**: C, 39.10; H, 6.39; N, 12.89; Cl, 8.95%. **7**: C, 41.35; H, 6.68; N, 13.59; Cl, 9.16%. **8**: C, 40.81; H, 6.14; N, 13.80; Cl, 9.39%. Calcd for **5** and **6**: $CoC_{14}H_{28}N_4O_5Cl$ (MW 426.79) C, 39.40; H, 6.61; N, 13.13; Cl, 8.31%. **7** and **8**: $CoC_{14}H_{26}N_4O_4Cl$ (MW 408.78) C, 41.14; H, 6.41; N, 13.71; Cl, 8.67%.

β_2-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Nitrate Trihydrate (11): Complex **11** was prepared according to the procedure of a previous paper.[2)] An orange-colored solution of **11**, acetone, and 60% nitric acid was set aside to crystallize at room temperature for several days. The orange complex thus separated was filtered off, washed with ice-water, and

dried. It was recrystallized several times from water, while it did not turn green in the 60% nitric acid. Yield: 0.54 g (14.1%). Found: C, 30.87; H, 5.07; N, 17.16%. Calcd for $CoC_{13}H_{27}N_6O_{11}$ (MW 502.33) C, 31.08; H, 5.42; N, 16.73%.

β_2-3-Methyl-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Nitrate Dihydrate (12) and β_2-4-Methyl-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Nitrate Dihydrate (13): Complexes **12** and **13** were prepared according to the procedure used for Complex **11**. Yields: 0.26 g (21.3%) for **12**; 0.20 g (16.4%) for **13**. Found **12**: C, 33.54; H, 5.22; N, 17.26%. **13**: C, 33.47; H, 5.26; N, 16.86%. Calcd for $CoC_{14}H_{27}N_6O_{10}$ (MW 498.34) C, 33.74; H, 5.46; N, 16.86%.

Paramagnetic β_1-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Chloride Nitrate Dihydrate (14): Three cm^3 of 60% nitric acid were added to **9** (1.0 g, 2.53 mmol dm^{-3}). After the reaction,[10b] the solution was filtered using a glass filter (G-4), and the green filtrate was added to acetone. The green complex thus precipitated was filtered off, washed with acetone, and dried. It was then reprecipitated twice more by dissolution in 60% nitric acid and by the addition of acetone. Yield: 0.46 g (35.5%). Found: C, 30.64; H, 5.18; N, 15.90; Cl, 6.86%. Calcd for $CoC_{13}H_{25}N_6O_{10}Cl$ (MW 519.77) C, 30.04; H, 4.85; N, 16.17; Cl, 6.82%.

Paramagnetic β_2-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Chloride Nitrate Dihydrate (15): Complex **15** was prepared from **10** (3.0 g, 7.60 mmol dm^{-3}) and 60% nitric acid (9 cm^3), according to the procedure used for Complex **14**. Yield: 1.87 g (47.3%). Found: C, 30.23; H, 5.03; N, 16.02, Cl, 7.25%. Calcd for $CoC_{13}H_{25}N_6O_{10}Cl$ (MW 519.77) C, 30.04; H, 4.85; N, 16.17; Cl, 6.82%.

Paramagnetic β_2-3-Methyl-5-Nitrosalicylato(triethylenetetramine)-cobalt(III) Chloride Nitrate Dihydrate (16) and Paramagnetic β_2-4-Methyl-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Chloride Nitrate Dihydrate (17): Complexes **16** and **17** were prepared from **7** (1 g, 2.45 mmol dm^{-3}) or **8** (1 g, 2.45 mmol dm^{-3}) and 60% nitric acid (3 cm^3), according to the procedure used for Complex **14**. Yields: 0.56 g (42.8%) for **16**; 0.44 g (33.6%) for **17**. Found **16**: C, 31.11; H, 5.40; N, 16.01; Cl, 6.19%. **17**: C, 31.82; H, 5.15; N, 16.09; Cl, 6.70%. Calcd for **16** and **17** $CoC_{14}H_{27}N_6O_{10}Cl$ (MW 533.80) C, 31.50; H, 5.10; N, 15.74; Cl, 6.64%.

Paramagnetic β_1-5-Nitrosalicylato(triethylenetetramine)cobalt(III) Chloride Trihydrate (18) and Paramagnetic β_2-5-Nitrosalicylato-(triethylenetetramine)cobalt(III) Chloride Trihydrate (19): Complexes **18** and **19** were prepared from **14** (0.30 g, 0.52 mmol dm^{-3}) or **15** (0.50 g, 0.96 mmol dm^{-3}) and 35% hydrochloric acid (1 cm^3 for **14** and 1.5 cm^3 for **15**) respectively. Yields: 0.17 g (62.9%) for **18**; 0.31 g (63.1%) for **19**. Found **18**: C, 30.56; H, 5.52; N, 13.50; Cl, 13.10%. **19**: C, 29.97; H, 5.27; N, 13.42; Cl, 13.46%. Calcd for $CoC_{13}H_{27}N_5O_8Cl_2$ (MW 511.23) C, 30.54; H, 5.32; N, 13.70; Cl, 13.87%. Magnetic moments, μ_{eff}: 1.66 for **18**, 1.70 B.M. for **19**.

The authors wish to express their gratitude to Professor Masayasu Mori of Osaka City University for his discussions.

References

1) Part IV; Ref. 2. Presented at the 29th Symposium on Coordination Chemistry of the Chemical Society of Japan, Hamamatsu, 1979.

2) Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2894 (1978).

3) a) M. Murakami, S. Senoh, N. Matsusato, H. Itatani, and J-W Kang, *Nippon Kagaku Zasshi.*, **83**, 734 (1962); b) M. Murakami, S. Senoh, N. Matsusato, H. Itatani, and J-W Kang, *ibid.*, **83**, 737 (1962); c) M. Murakami, S. Senoh, N. Matsusato, H. Itatani, and J-W Kang, *ibid.*, **83**, 741 (1962); d) M. Murakami, S. Senoh, N. Matsusato, H. Itatani, and J-W Kang, *ibid.*, **83**, 819 (1962); e) M. Murakami, S. Senoh, N. Matsusato, H. Itatani, and J-W Kang, *ibid.*, **83**, 823 (1962)

4) D. A. Palade and T. N. Volokh, *Zh. Neorg. Khim.*, **15**, 1872 (1970).

5) "Advances in Inorganic Chemistry and Radiochemistry," ed by H. J. Emeleus and A. G. Sharpe, Academic Press, New York and London (1969), Vol. 12, p. 135.

6) a) D. M. Palade, *Ukr. Khim. Zh.* (*Russ. Ed.*), **37**, 319 (1971); b) D. M. Palade, *Zh. Neorg. Khim.*, **14**, 3029 (1969).

7) D. M. Palade, A. V. Ablov, and V. N. Zubarev, *Zh. Neorg. Khim.*, **14**, 445 (1969).

8) M. P. Hancock, J. Josephsen, and C. E. Schaffer, *Acta. Chem. Scand.*, **A30**, 79 (1976).

9) "Shin Jikken Kagaku Koza," ed by T. Tachibana Maruzen, Tokyo (1976), Vol. 8 (III), p. 1470; b) S. Herzog, R. Klausch, and J. Lantos, *Z. Chem.*, **4**, 150 (1964).

10) a) Y. Yamamoto, K. Ito, H. Yoneda, and M. Mori, *Bull. Chem. Soc. Jpn.*, **40**, 2580 (1967); b) Y. Yamamoto, M. Mori, H. Yoneda, S. Misumi, and K. Ito, *ibid.*, **42**, 984 (1969).

11) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **52**, 2540 (1979).

12) a) D. A. Buckingham, M. Dwyer, G. J. Gainsford, V. Janson Ho, L. G. Marzilli, Ward T. Robinson, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **14**, 1739 (1975); b) L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967); c) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

13) Y. Yamamoto and E. Toyota, *Chem. Pharm. Bull.*, **26**, 2275 (1978).

14) Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **42**, 999 (1969).

15) a) F. M. Jaeger and J. A. van Dijk, *Z. Anorg. Allg. Chem.*, **227**, 273 (1936); b) F. M. Jaeger and J. A. van Dijk, *Proc. Acad. Sci. Amsterdam.*, **39**, 164 (1936).

16) A. M. Sargeson and G. H. Searle, *Inorg, Chem.*, **6**, 787 (1967).

17) G. T. Morgan and J. D. M. Smith, *J. Chem. Soc.*, **1956**, 1922.

18) D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, M. Dwyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, Ward T. Robinson, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **96**, 1713 (1974).