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Cobalt(IV) Ammine Complexes with 5-Nitrosalicylato or Similar Ligands. III. Electric Resistivity, Magnetic Susceptibility, and ESR*1

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The electric and magnetic properties of a series of 5-nitrosalicyclato ammine cobalt(IV) complexes (paramagnetic), the salicylato ammine cobalt(III) complex (diamagnetic), μ-superoxodicobalt ammine complexes (paramagnetic), and the μ-peroxodicobalt ammine complex were studied. The resistivity(ρ) at room temperature and the energy gap(ε) for paramagnetic complexes were in the range of, $\rho = 7.6 \times 10^{10}$—$1.5 \times 10^{11}$ Ω cm and $\varepsilon = 0.7$—1.1 eV, whereas those for diamagnetic complexes were in the range of $\rho = 10^{12}$—10^{14} Ω cm and $\varepsilon = 0.75$—1.2 eV. The magnetic susceptibilities of the paramagnetic complexes obeyed the Curie-Weiss law, with comparatively large Curie-Weiss constants (-18—26°K). The g-values and line widths (ΔH_{msl}) in the ESR signals at room temperature were determined for powdered samples of 5-nitrosalicylatotetraamminecobalt(IV) complexes and their derivatives. The ESR parameters obtained were in the range of $g = 2.0030$—2.0070 and $\Delta H_{\mathrm{msl}} = 22.0$—$30.6$ Oe for powders.

Previous papers have reported on the preparation of cobalt(IV) ammine complexes with 5-nitrosalicylato[1] or similar ligands[2]. Inasmuch as these compounds contain cobalt in the unusual valence state (IV, d^5 in the low spin state), various anomalies are expected in their physical properties. The present paper deals with the results of measurements of the solid electric conductivities, magnetic susceptibilities, and ESR of these compounds.

Experimental

Preparation. *5-Nitrosalicylatotetraamminecobalt(IV) Complexes, 5-Nitrosalicylatobis(ethylenediamine)cobalt(IV) Complexes, 3-Methyl-5-Nitrosalicylatotetraamminecobalt(IV) Complexes, and 4-Methyl-5-Nitrosalicylatotetraamminecobalt-(IV) Complexes.* These complexes were prepared by the methods reported in Papers I[1] and II[2].

The salicylatotetraamminecobalt(III) Complex and its Derivatives and the Salicylatobis(ethylenediamine)-cobalt(III) Complex. These complexes were prepared by Morgan's method.[3]

[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Suita, 1968.

1) Y. Yamamoto, the Late K. Ito, H. Yoneda and M. Mori, This Bulletin, **40**, 2580, (1967).

2) Y. Yamamoto, M. Mori, H. Yoneda, S. Misumi and the Late K. Ito, submitted to this Bulletin.

3) G T. Morgan and J. D. Smith, *J. Chem. Soc.*, **1922**, 1956; G. T. Morgan and J. D. Smith, *ibid.*, **1924**, 1924.

The μ-Amido-μ-superoxo-bis(tetraamminecobalt)(4+) Complex. This complex was prepared according to the method of Mori, Weil and Ishiguro.[4]

The μ-Superoxo-bis(pentaamminecobalt)(5+) Complex. This complex was prepared according to the method of Gleu and Rehm.[5]

The μ-Peroxo-bis(pentaamminecobalt)(4+) Complex. This complex was prepared by Werner's method.[6]

Measurements of Electrical Conductivities. The measurements were made with a Toa Denpa Kogyo Microvolt Ammeter, Model PM-18 (for the range 10^{-4}—10^{-12} A), and a Takeda Riken Vibrating Reed Electrometer, Model TR-81 (10^{-7}—10^{-15} A). A fine powder of each complex was compressed into a disk (12 mm in diameter and 1—2 mm thick) under a pressure of about 3×10^2 kg/cm^2. Silver-paste was used as the electrode. The D.C. conductivity was measured in the temperature range from −50 to +120°C. The conductivity vessel, as shown in Fig. 1[7], was evacuated down to 10^{-2} mmHg.

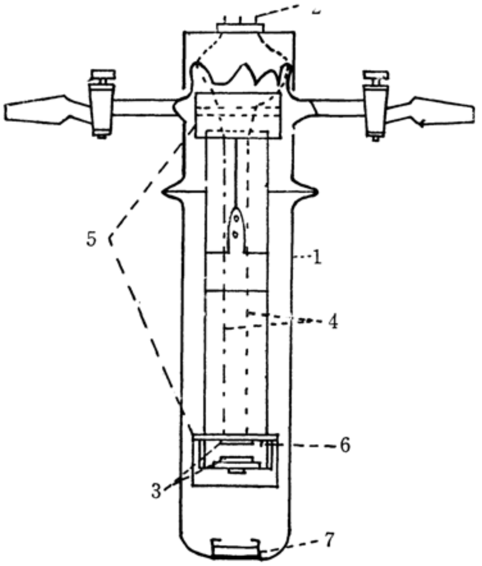


Fig. 1. The apparatus used in measurement of current through powdered sample.

1. Pyrex glass tube
2. Connector of lead line
3. Electrodes
4. Lead line
5. Teflon insulator
6. Thermocouple
7. Dryer

Measurements of Magnetic Susceptibilities. The measurements were made by the Gouy method with a magnetic balance (Shimadzu Seisaku Sho) in the temperature range between 80°K and room temperature. The magnetic susceptibility of 5-nitro-4-methylsalicylatotetraamminecobalt(IV) chloride nitrate was also measured by the AC method, using a Hartshorn bridge in the temperature range between 4.22°K and 1.21°K. The accuracy was ±0.1%.

Electron Spin Resonance. The spectra were recorded at room temperature with a TMF-20305 Tokyo Denki Seiki. Quartz sample tubes 1.5 mm in diameter were used; they were filled with solutions in several kinds of solvent to about 4 cm from the bottom.

Results and Discussion

Electrical Resistivities. An almost linear relationship was observed between the current and the applied voltage up to 15V in the temperature range from −50—+120°C. In most cases the tempera-

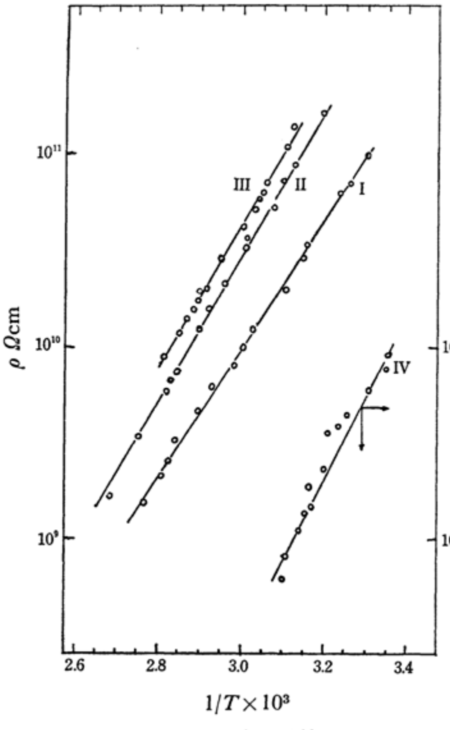
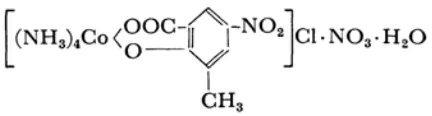


Fig. 2. Resistivity *vs.* $1/T\times10^3$.

(I)


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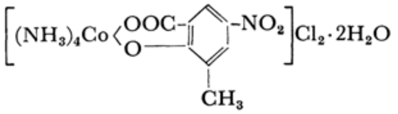

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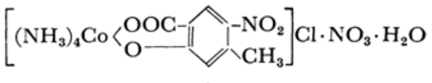

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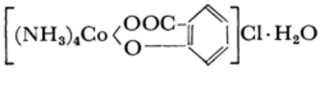

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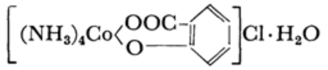
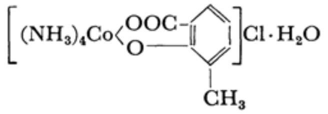
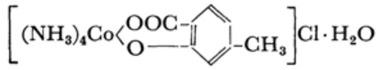
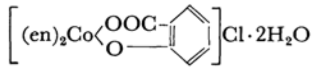
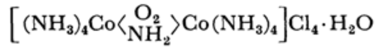
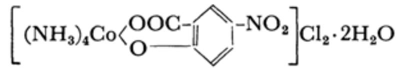
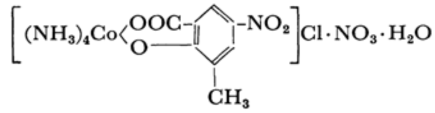
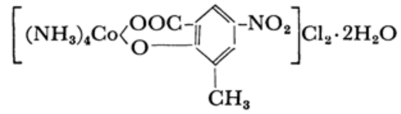
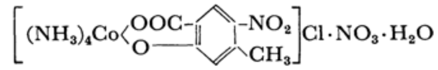
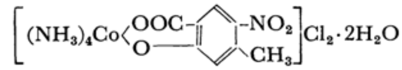
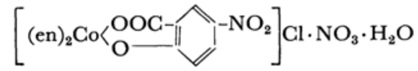
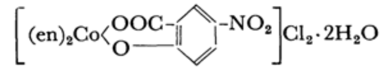
[4] M. Mori, J. A. Weil and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).

[5] K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, **237**, 79 (1938).

[6] A. Werner and A. Mylius, *ibid.*, **16**, 262 (1898).

[7] S. Kawai, S. Ito, F. Kanamaru and R. Kiriyama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 1757 (1962).

TABLE 1. ELECTRIC PROPERTIES OF COBALTAMMINE COMPLEXES

Compound	Specific resistivity at room temperature ρ_{20}, Ωcm	ε, eV (Temp.)
	5.7×10^{12}	1.24
	8.7×10^{14}	0.77
	3.5×10^{14}	0.8
	4.1×10^{12}	0.75
$[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]\cdot(SO_4)_2\cdot3H_2O$	5.7×10^{11}	1.66
 $\left[(NH_3)_4Co\langle{}^{O_2}_{NH_2}\rangle Co(NH_3)_4\right]Cl_4\cdot H_2O$	5.2×10^{9}	1.42 (−40—−5°C) 0.34 (−5—+50°C) 0 (+50°C∼)
$[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]\cdot(SO_4)_2\cdot HSO_4\cdot3H_2O$	1.9×10^{7}	
	7.55×10^{10}	0.48
	9.8×10^{10}	0.67
	1.5×10^{11}	0.78
	9.6×10^{10}	1.10
	7.5×10^{10}	0.8
	5.2×10^{11}	0.95
	1.5×10^{11}	0.75

ture dependence of the resistivity obeyed the $\rho=\exp(\varepsilon/2\boldsymbol{k}T)$ equation (Fig. 2). The resistivity at 25°C (ρ_{25}) and the apparent energy gap (ε) as calculated from the above equation are tabulated in Table 1.

It should be noted that most of these complexes have the water of crystalliaztion; the influence of this water must be considered in analysing the results of these electric measurements. For the μ-amido-μ-superoxo-bis(tetraamminecobalt) complex, measurement was made in the −40—+80°C range. An almost linear relationship between ρ and $1/T$ was observed between −40 and −10°C, and also between −10°C and +50°C, but the linear relation was not observed above +55°C (Fig. 3). This change in the conductivity behavior is thought to be due to such water molecules. On the other hand, the resistivity of cobalt(IV) complexes showed an almost linear relationship with $1/T$ up to 120°C (*cf.* Fig. 2). This seems to indicate that, in this compound, the water is bound tightly to the carbonyl group of the salicylato ligand. This idea of tightly-bound water was presented by Morgan and Smith[3] for their salicylatotetraamminecobalt(III) salts and was proved by the X-ray analysis of the chloride monohydrate by Hosoo, Kushi, and Kuroya.[8]

Next, let us consider the effect of the number of d-electrons in the cetral metal ion on the electric resistivities of the complexes. Balto and Weiss[9]

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[8] T. Hosoo, Y. Kushi and H. Kuroya, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo 1967, *Collection of Résumés,* **2B** 223.

[9] B. A. Balto and D. E. Weiss, *Aust. J. Chem.,* **15**, 653 (1962).

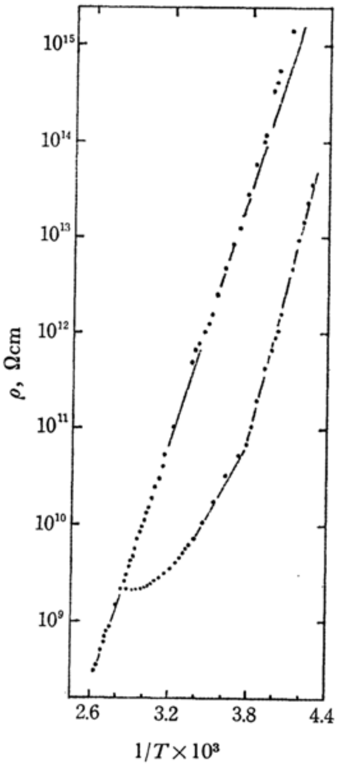
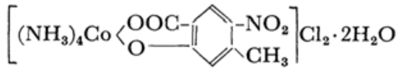
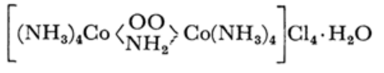


Fig. 3. Resistivity *vs.* $1/T\times10^3$.

(I)



(II)



$$\left[(NH_3)_4Co\langle\begin{smallmatrix}OO\\NH_2\end{smallmatrix}\rangle Co(NH_3)_4\right]Cl_4\cdot H_2O$$

reported the preparation and the resistivity measurements of the iron(III) complex (d^5, 4.7×10^5 Ωcm) and the iron(II) complex (d^6, 3.8×10^4 Ωcm), both with a pentacyclic ligand which had been prepared from chloranil and o-phenylenediamine. Inoue, Hayashi, Takiuchi and Imoto[10] reported on the organic polymer-tin(IV) complex (d^{10}, 3.8×10^{10} Ωcm) and the organic polymer-tin(II) complex ($d^{10}s^2$, 1.76×10^9 Ωcm). Thus, both these groups of investigations found that the number of d or s-electrons in the central metal ion does not have much effect on the electric resistivity, provided that the relevant orbital is sufficiently localized on the central metal ion.

Consequently, if our cobalt compounds contained true tetravalent cobalt atoms, *i.e.*, if the hole produced as the result of oxidation were localized on the cobalt atom, the resistivity should not be much different from that of the normal cobalt(III) ammine complex. Actually, the resistivities of our paramagnetic cobalt(IV) ammine complexes with 5-nitrosalicylato or similar ligands are lower than those of cobalt(III) complexes with similar ligands by factors of 10^2—10^4. Such large differences in the electrical resistivities seem to suggest that the distribution of the electron hole is spread over the entire molecule, or that our green compounds might preferably be regarded as containing free radial complex ions. We might, for comparison, refer to the electrical resistivity of violanthrone-B (a free radical, $\rho_{15}=6.9\times10^6$ Ωcm[11]) and that of violanthrone (with no unpaired spin, $\rho_{15}=1.1\times10^{11}$ Ω·cm[11] or 2.3×10^{10} Ωcm[12]). These results indicate that the radical formation has much effect on the electrical resistivity.

A similar relationship holds between the electrical resistivities of diamagnetic peroxo dicobalt complexes and those of paramagnetic superoxo dicobalt (formerly called peroxo cobalt(III) cobalt(IV)) complexes. The electrical resistivities of paramagnetic μ-superoxo compounds are lower than those of diamagnetic peroxo complexes by factors of 10^2—10^4 (Table 1).

Fielding[13] had reported the resistivity of μ-speroxobis(pentaamminecobalt)(5+) hydrogen trisulfate trihydrate to be $\rho=2\times10^7$ Ωcm at 20°C, which is almost in complete agreement with the measurements made by the present author (Table 1).

Electron Spin Resonance. In the case of superoxo dicobalt complexes, Ebsworth and Weil[14] observed a hyperfine structure with 15 equally-spaced components in the paramagnetic resonance spectra of aqueous solutions: this structure clearly indicated that the unpaired electron spends equal fractions of time on the two cobalt nuclei. Recently, Weil and Kinnaird[15] reported that the ESR spectra of O^{17}-labeled $[(NH_3)_4\ Co\langle\begin{smallmatrix}OO\\NH_2\end{smallmatrix}\rangle Co(NH_3)_4]^{4+}$ dissolved in very dilute nitric acid showed a hyperfine structure of oxygen-17 in addition to 15 hyperfine lines of cobalt. These ESR spectra show that the unpaired electron is located on the molecular orbital extending over cobalt-oxygen-cobalt.

The present research has revealed that ESR signals are also observable in the green 5-nitrosalicylato cobalt ammine complexes at room temperature. This proves that the complex is actually in a high oxidation state, because coblt(II) compounds known to have too short a relaxation time to allow any ESR signal to appear at room temperature.

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[10] H. Inoue, S. Hayashi, S. Takiuchi and E. Imoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 1622 (1962).

[11] H. Akamatu, T. Maekawa, Y. Iida and M. Kinoshita, This Bulletin **37**, 849 (1964).

[12] H. Inokuchi, *ibid.*, **24**, 222 (1951).

[13] P. E. Fielding, *J. Chem. Phys.*, **22**, 1153 (1954); P. E. Fielding and D. P. Mellor, *J. Chem. Phys.*, **22**, 1155 (1954).

[14] E. V. A. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

[15] J. A. Weil and J. K. Kinnaird, *ibid.*, **71**, 3341 (1967).

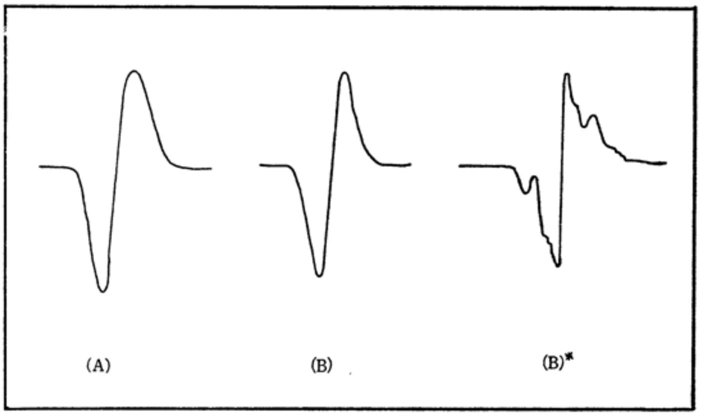
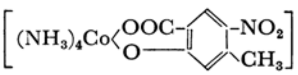
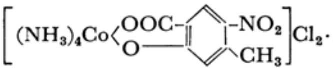
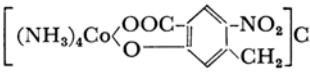


Fig. 4. The ESR spectra of  X_2 of powders at 22°C.

(A) :  $Cl_2 \cdot 2H_2O$;

(B) and (B*) :  $Cl \cdot NO_3 \cdot H_2O$ (B*) : 30 min after preparation.

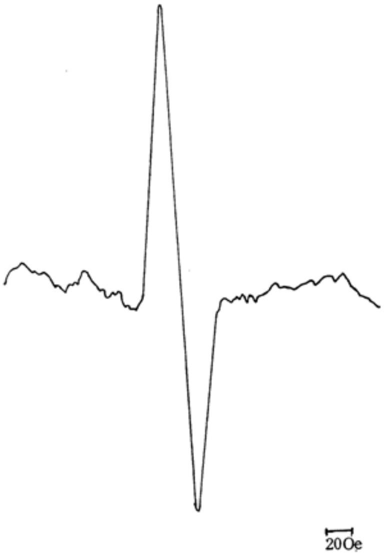
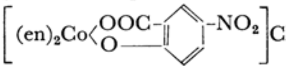


Fig. 5. ESR spectrum of
 $Cl \cdot NO_3 \cdot H_2O$
in aqueous solution at 22°C (about 10^{-1} mol/l).

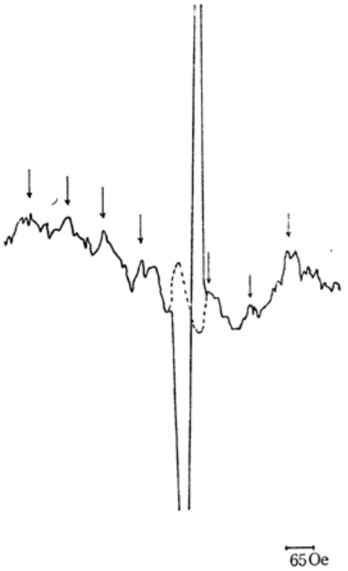
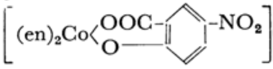


Fig. 6. ESR spectrum of
 $Cl \cdot NO_3 \cdot H_2O$
in aqueous solution at 22°C (about 10^{-2} mol/l).

The powder ESR of 5-nitrosalicylatotetraamminecobalt(IV) salts, 3-methyl or 4-methyl-5-nitrosalicylatotetraamminecobalt(IV) salts (Fig. 4), and 5-nitrosalicylatobis(ethylenediammine) cobalt (IV) salts gave symmetrical spectra; the obtained values of *g*-factor and line width (between points of maximum slope)are given in Table 1.

As has been stated in Paper II,[2] the 5-nitrosalicylatobis(ethylenediamine)cobalt(IV) complex is more stable than the 5-nitrosalicylatotetraamminecobalt(IV) complex and its methyl derivatives, hence, it is more suitable for the ESR study of solutions.

The solution of 5-nitrosalicylatotetraamminecobalt(IV) salts in water gave spectra without any hyperfine structure and were slightly asymmetric, the high field side being slightly broader. The spectra could be observed for only about an hour after the dissolution of the samples. Solutions in 35% hydrochloric acid, 20—60% phosphoric acid, and 100% methanol gave no observable spectra.

A solution of 5-nitrosalicylatobis(ethylenediamine)cobalt(IV) complexes in mthanol or 35% hydrochloric acid gave spectra without any hyperfine structure, and the line slope was asymmetric, the high-field side being broader. The aqueous ESR spectra of 5-nitrosalicylatobis(ethylenediamine)-cobalt(IV) salts showed no hyperfine structure, except in a limited range of concentration of about 10^{-1}—10^{-3} mol/l (Fig. 5). At the sample concentration of about 10^{-2}—10^{-3} mol/l, a hyperfine structure of eight lines developed on both field sides of one strong line (Fig. 6). At present, however, it is difficult to assign these hyperfine structures.

One thing that can be said about the obtained spectra described above is that the *g*-value is always close to the free electron value (Table 2), This seems to be in line with the afore-mentioned assumption of the free-radical nature of the green paramagnetic 5-nitrosalicylatc ammine cobalt complexes.

Magnetic Susceptibilities. The susceptibilities of the compounds were found to be independent of the temperature. $\chi_{\rm mol}^{\rm cor}$ was obtained by correcting the observed molar magnetic susceptibility, $\chi_{\rm mol}$, for the diamagnetic contribution of the molecule, which was taken to be 0.000200—0.000220 c.g.s.e. m.u. The effective magnetic moment of the molecule in Bohr magnetons, $\mu_{\rm eff}$, was obtained using the formula:

$$\mu_{\rm eff} = 2.84\sqrt{\chi_{\rm mol}^{\rm cor}(T-\theta)}$$

The Curie-Weiss plots and some related parameters are given in Fig. 7 and Table 2 respectively. The comparatively large Curie-Weiss constants again seem to conform with the free radical nature of the substance as assumed in the foregoing discussion of the electric resistivities. These values might be compared with the Curie-Weiss constants of such free radical as diphenylpicrylhydrazyl (−10°K[16)]), diphenylpicrylhydrazyl (in CS_2, −22°K[17)]), and violanthron-B (−45°K[11)]).

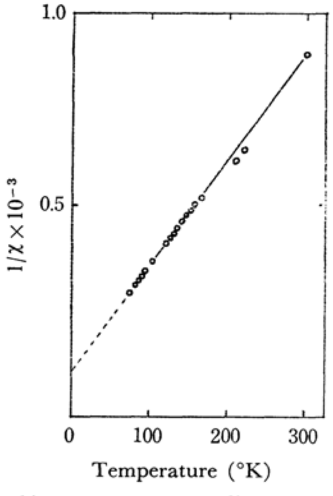
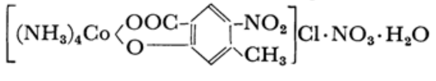


Fig. 7. $1/\chi$ *vs.* temperature diagram.



In the case of 5-nitro-4-methylsalicylatotetraamminecobalt(IV) chloride nitrate, the susceptibility measurements were also made at the temperatures of liquid helium; these measurements gave the Curie-Weiss constant of 0°K(Fig. 8) and the effective Bohr magneton number of 1.05±0.05, in contrast to the values above the temperature of liquid nitrogen, (−18°K, 1.7 B.M., Table 2). This discrepancy between results in different temperature ranges is doubtless due to the bending of the Curie-Weiss plot in the region of very low temperatures.

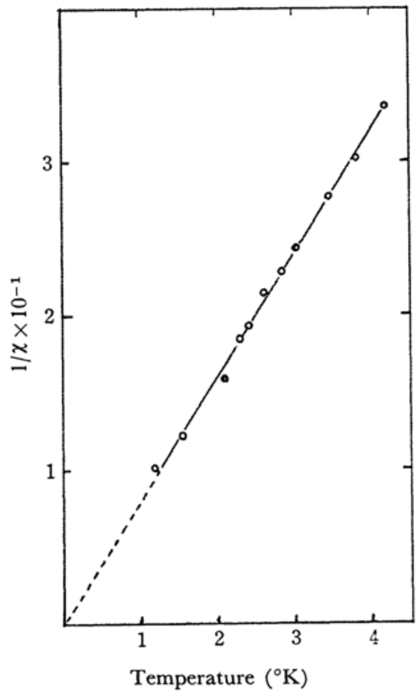
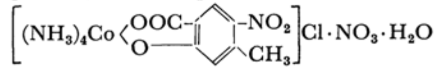


Fig. 8. $1/\chi$ *vs.* Temperature diagram.



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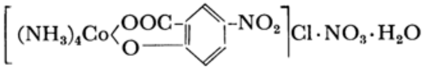
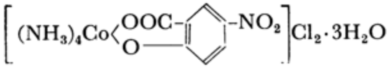
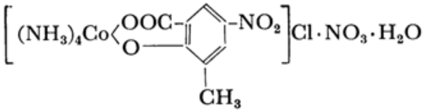
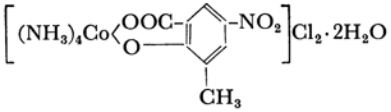
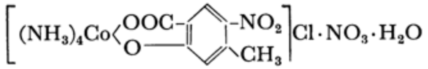
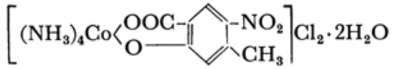
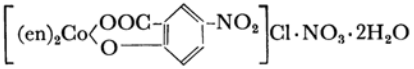
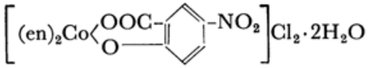
16) J. Turkevich and P. Selwood, *J. Am. Chem. Soc.*, **63**, 1077 (1941).

17) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

TABLE 2. THE ESR AND MAGNETIC PROPERTIES OF COBALT(IV) AMMINECOMPLEXES WITH 5-NITROSALICYLATO OR SIMILAR LIGANDS

Substance	Form	g-Value	Line-width (Gauss)	Curie-Weiss const. (θ) (°K)	Bohr magneton number (B. M.)
	P., sl. sym., r.t.,	2.0046	24.7		1.9
	P., asym., r.t.,	2.0046		0	1.7
	P., asym., r.t.,	2.0036			1.7
	P., asym., r.t.,	2.0036		−20	1.7
	P., sl. sym., r.t.,	2.0070		−18	1.7
	P., asym., r.t.,	2.0070	26.7	−14	1.7
	P., sym., r.t., W., sl. sym., r.t., W., sl. sym., liq. N_2	2.0038 2.0030 2.0031	23.6 22.0 25.6	−22	1.6
	P., sl. sym., r.t., MeOH, asym., r.t., 35% HCl, asym., r.t.,	2.0038 — —	30.6 — —	−26	1.6

sym.: symmetric, sl. sym.: very slightly asymmetric, asym.: asymmetric, P.: powder, W.: in water, r.t.: room temperature

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