Magnetic Properties of Bi- and Uni-Nuclear Chromium(III) Complex Compounds at Low Temperatures

By Hanako KOBAYASHI,* Taiichiro HASEDA and Masayasu MORI

(Received November 30, 1964)

There are various theories on the mechanism of the superexchange interaction between magnetic ions in crystals. Kanamori,[1] for instance, studied the superexchange interaction, taking into consideration the symmetry of the electron orbitals of magnetic ions. It was shown that the sign** of the superexchange interaction is closely connected with the symmetry of the orbitals of the magnetic ions and non-magnetic ions which are in the path of the superexchange interaction. The cases in which each cation is subject to an octahedral cubic field and in which the lines connecting cations to the intervening anion make an angle of either 180° or 90° were discussed as simple and typical examples. His study suggested that the 180° superexchange interaction is antiferromagnetic and the 90° one, ferromagnetic in the case of $Cr^{3+}\cdots Cr^{3+}$ interaction. In the real crystals, there are usually both paths, 180° and 90°, of the superexchange interaction. The sign of the superexchange interaction in a magnetic substance depends on all the contributions from relevant paths. There is, in general, no simple and direct way to examine the above-cited theory by experimentation. Moreover, there have been few papers[2] which make clear any mechanism of the superexchange interaction actually occurring in the observed crystal.

It seems that the investigation of some sort of bi-nuclear complex salts, in which the superexchange interaction between two magnetic ions passes through only one path, either 180° or 90° would make possible a direct examination of the relation between the bond angle and the sign of the superexchange interaction.

The first part of the present paper will concern the study of the magnetic properties of bi-nuclear complex compounds. The experimental results of magnetic and optical measurements of the following four bi-nuclear complex salts will be discussed; μ-hydroxo-bis-{pentamminechromium(III)} 3/2-chloride 7/2-perchlorate 1/2-hydrate,[3] μ-hydroxo-{hydroxotetramminechromium(III)-pentamminechromium(III)}tetrachloride 1-hydrate, μ-oxo-bis{pentamminechromium(III)}perchlorate, and

---

* Present address: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto.

** Through this paper, a negative sign is used for the antiferromagnetic exchange interaction.

[1] J. Kanamori, *J. Phys. Chem. Solids*, **10**, 87 (1959).

[2] J. Kondo, *Prog. Theor. Phys.*, **22**, 41 (1959).

[3] H. Kobayashi, T. Haseda, E. Kanda and M. Mori, *J. Phys. Soc. Japan*, **15**, 1646 (1960).

μ-dihydroxo-bis{tetramminechromium(III)}dithionate 4-hydrate.

In the cases of μ-hydroxo-bis{pentamminechromium(III)}3/2-chloride 7/2-perchlorate 1/2-hydrate, μ-hydroxo{hydroxotetramminechromium(III)-pentamminechromium(III)}tetrachloride 1-hydrate and μ-oxo-bis{pentamminechromium(III)}perchlorate, the linkage of the superexchange interaction is considered to pass through a path of about 180°, connecting two chromic ions via one oxygen atom. In the case of μ-dihydroxo-bis{tetramminechromium(III)}dithionate 4-hydrate, the linkage of the superexchange interaction is considered to turn at oxygen atoms, making angles of about 90°. We have already measured[3] the susceptibilities of some of these salts and have suggested some interpretations. We now add the salt which has a nearly 90° angle linkage. We shall discuss all of these experimental data from the above-mentioned point of view.

The second problem of the present paper is the comparison of the superexchange interaction among Cr^{3+} ions which are octahedrally co-ordinated by various ligands. The interaction between two magnetic ions depends on the distance between the two ions and on the linkage from one magnetic ion to the other magnetic ion. If some ligands in a complex ion are replaced by other atoms or by atomic groups, leaving the distances almost the same as before substitution, the experimental results of the substituted compounds will contribute to an understanding of the interactions among magnetic ions through various linkages.

The following co-ordination compounds of Cr^{3+} ions with various kinds of ligands were investigated: hexamminechromium(III) chloride, chloropentamminechromium(III) chloride, dibromo-diaquo-diamminechromium(III) bromide, and dihydroxo-diaquo-diamminechromium(III) bromide.

Preparation

μ-Hydroxo-bis{pentamminechromium(III)}3/2-chloride 7/2-perchlorate 1/2-Hydrate[4] was prepared by Mori, Ueshiba and Yamatera's procedure (Ref. 5).

μ-Hydroxo-{hydroxotetramminechromium(III)-pentamminechromium(III)}tetrachloride 1-Hydrate was prepared by Jörgensen's procedure (Ref. 4).

μ-Oxo-bis{pentamminechromium(III)}perchlorate.—Two hundred milliliters of 30% perchloric acid (guaranteed grade) were carefully neutralized with sodium carbonate (guaranteed grade) until the mixture was only slightly acidic to methyl red. Twenty milliliters of concentrated aqueous ammonia was then added, and the mixture was filtered. To the filtrate was added 5 g. of μ-hydroxo-bis{pentamminechromium(III)}3/2-chloride 7/2-perchlorate 1/2-hydrate, and the mixture was cooled in an ice bath for 30 min. with occasional stirring. The deep blue precipitate was collected on a glass filter and washed with alcohol and ether. After it had been dried for several minutes under strong suction, the compound was kept in a desiccator with soda lime and dry ammonia gas under protection from light.

μ-Dihydroxo-bis{tetramminechromium(III)}-dithionate 4-Hydrate.—The procedure of preparation was that given by Dubsky in Ref. 6.

Hexamminechromium(III) Chloride.[7]—A green solution containing chromium(III) salt was prepared in a 1000 ml. beaker by mixing 30 g. of potassium dichromate, 40 ml. of ethanol and 80 ml. of concentrated hydrochloric acid. This solution was then transferred into a smaller beaker and covered with a 3-cm. layer of liquid paraffine. Sixty grams of pure zinc grains were added, and the mixture was heated to 80—90°C on a steam bath. When the solution had become perfectly blue, the container was cooled in running water, then the solution was removed, together with the mineral oil, into an Erlenmeyer flask containing a mixture of 200 ml. of concentrated aqueous ammonia, 50 g. of ammonia chloride and 50 g. of ammonium sulfate. The whole mixture was gently stirred and cooled in an ice bath for several minutes. To this was added 10 g. of powdered iron(II) ammonium sulfate. Finally the vessel was loosely stoppered and allowed to stand in an ice bath over night or longer. The yellow crystals thus formed were washed on a Buchner funnel with 50% ethanol, and dissolved in 400 ml. of water. After the addition of 2 ml. of concentrated aqueous ammonia and 2 ml. of 30% hydrogen peroxide, the solution was filtered, treated with 400 ml. of 12 N hydrochloric acid and 800 ml. of ethanol, and cooled in an ice bath. The yellow precipitate of hexamminechromium(III) chloride 1-hydrate thus obtained was dissolved in water, recrystallized by the addition of hydrochloric acid and ethanol, and dehydrated at 80°C until a constancy in weight was attained. The anhydrous salt was preserved in a desiccator under protection from light.

Chloro-pentamminechromium(III) Chloride was prepared by the procedure described in Ref. 8.

Dibromo-diaquo-diamminechromium(III) Bromide: Ref. 9.

Dihydroxo-diaquo-diamminechromium(III) Bromide: Ref. 9.

Experimental Results

The Magnetic Susceptibility of Bi-nuclear Complex Salts.—The magnetic susceptibilities

---

[4] S. M. Jörgensen, *J. prakt. Chem.*, **25**, 321 (1882).

[5] M. Mori, S. Ueshiba and H. Yamatera, This Bulletin, **32**, 89 (1959).

[6] J. B. Dubsky, *J. prakt. Chem.*, **90**, 60 (1914).

[7] S. M. Jörgensen, ibid., **30**, 6 (1884); M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 253 (1953).

[8] H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry" (Translated by W. T. Hall and A. A. Blanchard), 2nd Ed., John Wiley & Sons, New York, N. Y. (1928) p. 185.

[9] A. Werner and J. L. Klein, *Ber.*, **35**, 285 (1902).

were measured by an a.c. bridge method in the temperature range between 1.5°K and room temperature. The a.c. bridge was constructed so as to enable to measure magnetic susceptibilities of the order of 10×10^{-6} c.g.s.e.m.u. with an accuracy of ±1%, when the amount of the sample was about 1 g. The cryostat and the procedure for measurment have been described in the literature.[10] The susceptibility is given in molar units for each compound. The calibration for diamagnetism was made by using the values listed in Table I.

TABLE I. CALIBRATION FOR DIAMAGNETISM

Atomic or atomic group	χ, c.g.s.e.m.u.
Br^-	−0.000031
Cl^-	−0.000025
ClO_4^-	−0.000033
Cr^{3+}	−0.000015
H_2O	−0.000013
NH_3	−0.000001
-O-	−0.000005
-OH-	−0.000009

The molar magnetic susceptibility of μ-dihydroxo-bis{tetramminechromium(III)}dithionate 4-hydrate is shown as a function of the temperature for a couple of Cr^{3+} ions in Figs. 1 and 2, together with the results for the other bi-nuclear complexes which were studied before.[3] The susceptibility of this salt decreased with a decrease in the temperature in the liquid hydrogen and helium regions.

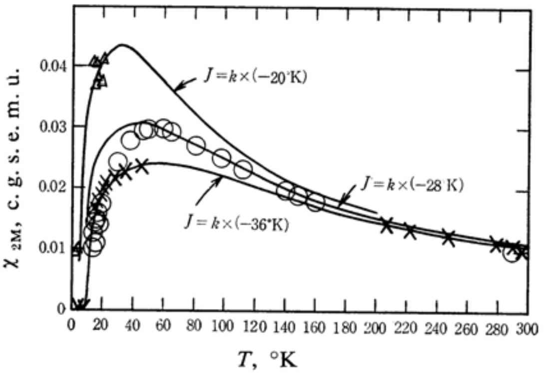

Fig. 1. Molar magnetic susceptibilities as a function of temperature.
○ : μ-Hydroxo-bis{pentamminechromium-(III)}3/2-chloride 7/2perchlorate 1-hydrate
× : μ-Hydroxo-{hydroxotetramminechromium(III)-pentamminechromium(III)}tetrachloride 1-hydrate
◬ : μ-Dihydroxo-bis{tetramminechromium-(III)}dithionate 4-hydrate

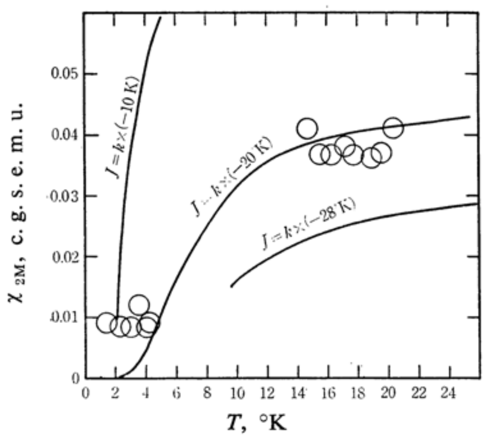

Fig. 2. Molar magnetic susceptibility of μ-dihydroxo-bis{tetramminechromium(III)} dithionate 4-hydrate as a function of temperature.

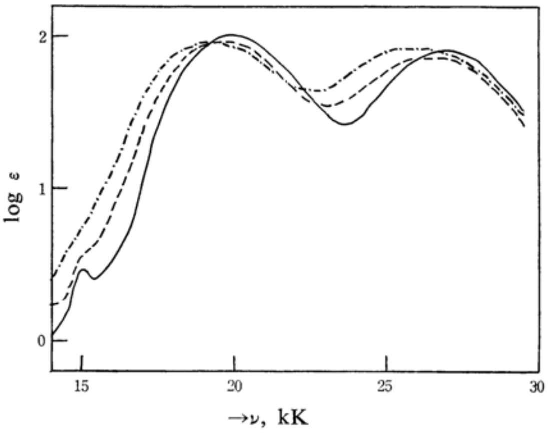

Fig. 3. Absorption Spectra of Binulear Chromammines.
——— $[Cr(NH_3)_5OHCr(NH_3)_5]Br_5\ H_2O$
– – – $[Cr(NH_3)_5OHCr(NH_3)_4OH_2]Br_5\ H_2O$
·—·—· $[Cr(NH_3)_5OHCr(NH_3)_4OH]Br_4\ H_2O$

Figure 3 gives the absorption spectra of aqueous μ-hydroxo-bis{pentamminechromium-(III)}bromide 1-hydrate, μ-hydroxo-{hydroxotetramminechromium(III)-pentamminechromium(III)}bromide 1-hydrate and μ-hydroxo-{aquotetramminechromium(III)-pentamminechromium(III)}bromide 1-hydrate. These spectra resemble each other. The former two salts have the cations in common with the salts studied magnetically, though their anions are not the same.

The Magnetic Susceptibility of Uni-nuclear Co-ordination Compounds of Cr^{3+} Ions.—The reciprocals of the molar magnetic susceptibilities of hexamminechromium(III) chloride are shown as a function of the temperature in Fig. 4 and Table II. These salts have magnetic

---

[10] H. Kobayashi, thesis, Tohoku University, Sendai, 1962.

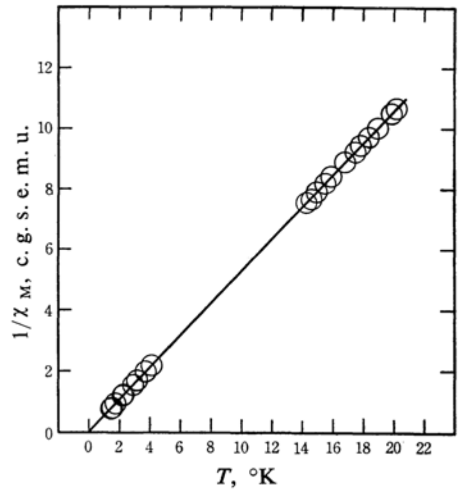

Fig 4. Reciprocal of molar magnetic susceptibility of hexamminechromium(III) chloride as a function of temperature.

TABLE II. MOLAR MAGNETIC SUSCEPTIBILITY OF HEXAMMINECHROMIUM(III) CHLORIDE

T, °K	χ_M c.g.s.e.m.u.	P	T, °K	χ_M c.g.s.e.m.u.	P
20.27	0.0939	3.9	3.43	0.551	3.9
19.46	0.0981	3.9	3.29	0.565	3.9
18.97	0.0993	3.9	3.02	0.615	3.9
18.46	0.1026	3.9	3.00	0.629	3.9
17.92	0.1065	3.9	2.78	0.672	3.9
17.50	0.1093	3.9	2.54	0.741	3.9
16.89	0.1126	3.9	2.49	0.745	3.9
15.93	0.1189	3.9	2.29	0.806	3.8
15.57	0.1203	3.9	2.03	0.920	3.9
15.02	0.1250	3.9	1.84	1.044	3.9
14.61	0.1295	3.9	1.76	1.057	3.9
14.33	0.1316	3.9	1.74	1.107	3.9
4.22	0.445	3.9	1.57	1.232	3.9
3.80	0.491	3.9	1.45	1.264	3.8

susceptibilities which follow the Curie-Weiss law.

The molar magnetic susceptibility of dibromo-diaquo-diamminechromium(III) bromide is shown in Fig. 6 as a function of the temperature, while that of dihydroxo-diaquo-diamminechromium(III) bromide is shown in Fig. 7. The susceptibilities of both salts follow the Curie-Weiss law down to the temperature region of liquid hydrogen and have maxima at about 3°K and about 3.5°K respectively. The shape of the maximum is broad in the former and steep in the latter.

Discussion

Bi-nuclear Complex Salts.—The magnetic susceptibilities of μ-hydroxo-bis{pentamminechromium(III)}3/2-chloride 7/2-perchlorate 1/2-hydrate and μ-hydroxo{hydroxo-tetramminechromium(III)-pentamminechromium(III)}-tetrachloride 1-hydrate are similar, as is shown in Fig. 1. They have broad maxima near 50°K and become very small in the temperature region of liquid helium. The magnetic behavior of these salts indicates that their electronic structures and the mechanisms of their magnetic interaction are similar. The resemblance of the absorption spectra of these complex cations, as may be seen in Fig. 3, also seems to support this.[11] In this case, the difference in anions is probably of little importance since it is complex cations that are mainly responsible for both the absorption spectra and the magnetic susceptibilities of these compounds.

The energy levels of Cr^{3+} spins ($S=3/2$) in the bi-nuclear salts can easily be calculated under the following simplified conditions. If the orbital angular momentum of the Cr^{3+} ion in the bi-nuclear complex salts is assumed to be completely quenched, the spins of Cr^{3+} ions in the same cation are expressed as S_1 and S_2, with the expectation value of $S=3/2$. In this case, the Hamiltonian of the two spins under a magnetic field, H, can then be written as:

$$\mathscr{H} = JS_1S_2 + g\mu_B\ (S_1+S_2)H$$

where J is a coefficient of the exchange interaction between the two Cr^{3+} ions and is negative in the case of these two salts. The magnetic susceptibility can be calculated by a standard method. The calculated curves of χ_{2M} with a parameter of J are shown in Fig. 1 as a function of the temperature, where g is assumed to be 2.00. The experimental values of μ-hydroxo-bis{pentamminechromium(III)}-3/2-chloride 7/2-perchlorate 1/2-hydrate fit well the calculated curve with $J=k\times(-28°K)$, and the values of μ-hydroxo-{hydroxotetramminechromium(III)-pentamminechromium(III)}tetrachloride 1-hydrate agree with the calculated curve with $J=k\times(-36°K)$. Judging from the chemical or photo-chemical inspections,[12] angle made by the lines connecting the two Cr^{3+} ions to the intervening oxygen atom of the hydroxide group seems to be nearly 180°. The agreement of the experimental results with the above-mentioned calculations indicates that the superexchange interaction between two Cr^{3+} ions through the oxygen of the hydroxide in these bi-nuclear complex cations has a constant of the superexchange interaction of about $k\times(-28°K)$—$k\times(-36°K)$.

---

[11] Y. Inamura and Y. Kondo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 627 (1953).

[12] W. K. Wilmarth, H. Graff and S. T. Gustin, *J. Am. Chem. Soc.*, **78**, 2683 (1956).

The magnetic property of μ-oxo-bis{pentamminechromium(III)}perchlorate was expected to show the typical character of the 180° superexchange interaction of $3d^3$ electrons through a linear linkage. The minute details of the temperature dependence of the susceptibility could not be determined because of its change is too small. If the same calculation is applied as with the former two salts, J is negative and is quite large ($>|k\times 200°\mathrm{K}|$), as was expected. This means the antiferromagnetic interaction between Cr^{3+} ions by the hydroxide group in the former two complex salts is much weaker than that of the perfect 180° bridge because of their deviation from linear linkage. μ-Dihydroxo-bis{tetramminechromium(III)}dithionate 4-hydrate is a sample which is considered to have two nearly-90° bridges between two Cr^{3+} ions. In the case of the 90° path between two Cr^{3+} ions, the sign of the superexchange interaction may be expected to be plus.[1] The results of the measurements of magnetic susceptibility are shown in Figs. 1 and 2. In the region of the liquid hydrogen temperature, the experimental curve roughly agrees with the calculated curve, with negative $J\simeq k\times(-20°\mathrm{K})$.

From these results, we may conclude that μ-oxo-bis{pentamminechromium(III)}perchlorate has 180° superexchange interaction and that the paths of the superexchange interaction of μ-hydroxo-bis{pentamminechromium(III)}-3/2-chloride 7/2-perchlorate 1/2-hydrate and μ-hydroxo-{hydroxotetramminechromium(III)-pentamminechromium(III)}tetrachloride 1-hydrate deviate from linear linkage. The path of μ-dihydroxo-bis{tetramminechromium(III)}-dithionate 4-hydrate shows the smallest value of J, but it does not yet show a positive sign.

Uni-nuclear Complex Salts.—The crystalline structure of hexamminechromium(III) chloride is of the bismuth fluoride type. Each Cr^{3+} ion is octahedrally co-ordinated by six ammonia molecules in the salt. The exchange interaction among the magnetic ions in this salt is through the following path:

$Cr_3{}^+$……NH_3……Cl^-……H_3N……Cr^{3+}
ligand anion ligand

The experimental magnetic susceptibility curve as a function of the temperature follows the Curie-Weiss law quite well, with the absolute value of the Curie-Weiss constant, Θ, smaller than 0.01°K, as is shown in Fig. 4. The sign of the Θ could not be determined from the experiment with the above-mentioned accuracy. The spectroscopic splitting factor, g, can be calculated from the next equation when the absolute value of Θ is smaller than 0.01°K:

$$\chi_{\mathrm{M}} = \frac{N\mu_{\mathrm{B}}^2}{3k}\,\frac{g^2S(S+1)}{(T-\Theta)}$$

The mean g-value at the temperatures of liquid helium and liquid hydrogen is 2.00 ± 0.02. The very small absolute value of the Curie-Weiss constant implies quite a weak interaction among Cr^{3+} ions in this salt.

The co-ordination of the ligands of chloropentamminechromium(III) chloride is not of the pentamminerhodium(I) chloride type, but of the chloropentamminerhodium(III) chloride type: that is, a ligand ammonia of the hexamminechromium(III) ion is replaced by a chlorine ion. The crystalline structure of this salt is of the calcium fluoride type,[13] so the paths of the interactions among Cr^{3+} ions may be considered to pass through any of the following:

Cr^{3+}……Cl^-……Cl^-……H_3N……Cr^{3+}
ligand anion ligand
Cr^{3+}……Cl^-……Cl^-……Cl^-……Cr^{3-}
ligand anion ligand
Cr^{3+}……NH_3……Cl^-……H_3N……Cr^{3+}
ligand anion ligand
Cr^{3+}……Cl^-……H_3N……Cr^{3+}
ligand ligand
Cr^{3+}……Cl^-……Cl^-……Cr^{3+}
ligand ligand
Cr^{3+}……NH_3……H_3N……Cr^{3+}
ligand ligand

From the magnetic susceptibility curve as a function of the temperature, a Curie-Weiss constant, Θ, of about $-0.8°\mathrm{K}$ was obtained, as is shown in Fig. 5. This shows that the superexchange interaction between Cr^{3+} ions

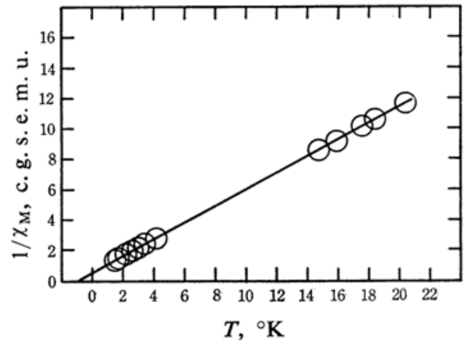

Fig. 5. Reciprocal of molar magnetic susceptibility of chloropentamminechromium(III) chloride as a function of temperature

---

[13] Y. Nakao, S. Oi, Y. Komiyama and H. Kuroya, The 13th Symposium on Co-ordination Chemistry, Nagoya, 1963.

is considerably large than that of hexamminechromium(III) chloride, which may reasonably be attributed to the presence of the paths of the latter three types. The latter three paths, which do not pass through anions, are shorter than the former, and the presence of a large ion in the path strengthens the superexchange interaction. The mean value of g is 1.95±0.09 in the temperature region of liquid helium and liquid hydrogen, when 3/2 is given as the spin quantum number, S.

The crystal structure of dibromo-diaquo-diamminechromium(III) bromide has not yet been analyzed. However, some paths of the superexchange interaction can be considered to be the shortest, as in the case of chloropentamminechromium(III) chloride. The Curie-Weiss constant, Θ, is estimated to have a larger absolute value than that of chloropentamminechromium(III) chloride, because the number of large Br^- ligands is two in this salt, one more than in the case of chloropentamminechromium(III) salt. The Θ obtained was about -3°K. The curve of the molar magnetic susceptibility as a function of the temperature has a broad maximum at 2.5°K, showing a transition to an antiferromagnetic state (Fig. 6).

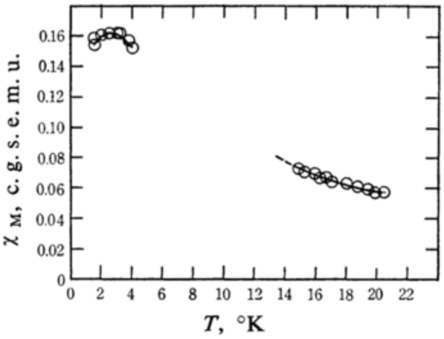

Fig. 6. Molar magnetic susceptibility of dibromo-diaquo-diamminechromium(III) bromide as a function of temperature

Dihydroxo - diaquo - diamminechromium(III) bromide has two hydroxyl groups in place of two bromine ligands of dibromo-diaquo-diamminechromium(III) bromide. The crystalline structure is not yet known. The experiment of the magnetic susceptibility gave a Curie-Weiss constant of about -9°K and a mean g-value of about 2.00±0.01, when S was taken as 3/2. This Curie-Weiss consant is larger than that of dibromo-diaquo-diamminechromium(III) bromide. The magnetic susceptibility-versus-temperature curve shows a steep peak at about 3.5°K±0.2°K, as is shown in Fig. 7. Perhaps this is a transition to an antiferromagnetic state, though its shape is different from the typical antiferromagnetic transition.

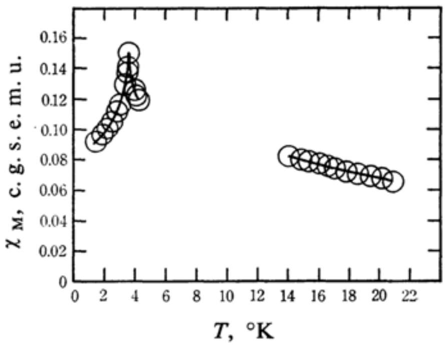

Fig. 7. Molar magnetic susceptibility of dihydroxo-diaquo-diamminechromium(III) bromide as a function of temperature

It may be noted that dihydroxo-diaquo-diamminechromium(III) salts are almost insoluble in water, although all chromammines with similar chemical formulae are known to be freely soluble. This peculiar insolubility and the comparatively large superexchange interaction of dihydroxo-diaquo-diamminechromium(III) bromide may be an indication that this compound is a co-ordination polymer, with each hydroxyl group ligated to different chromium ions. If this is the case, the above nomenclature must be revised somewhat, although names correctly expressing their true status will be hard to devise.

Summary

The experimental study of the magnetic properties of bi- and uni-nuclear chromium(III) complex compounds in the low temperature

TABLE III.

Multi-nuclear Cr(III) complex ion	Estimated angle of Cr-O-Cr linkages	Coefficient of the superexchange interactions
$(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5$	180°	$k\times(-200°K)$
$(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5$	~180°	$k\times(-28°K)$
$(NH_3)_5Cr\text{-}OH\text{-}Cr(OH)\text{-}(NH_3)_4$	~180°	$k\times(-36°K)$
$(NH_3)_4Cr\langle{}^{OH}_{OH}\rangle Cr(NH_3)_5$	90°	$k\times(-20°K)$

TABLE IV.

Uni-nuclear Cr(III) complex salt	Transition point	Curie-Weiss constants	*g*-Values
$[Cr(NH_3)_6]Cl_3$		$\|\Theta\|<$ 0.01°K	2.00± 0.02
$[CrCl(NH_3)_5]Cl_2$		-0.8°K	1.95± 0.09
$[CrBr_2(OH_2)_2(NH_3)_2]\text{-}Br$	ca. 2.5°K	-3°K	1.69± 0.04
$[Cr(OH)_2(OH_2)_2\text{-}(NH_3)_2]Br$	ca. 3.5°K	-9°K	2.00± 0.01

region has given the results summarized in Tables III and IV. As has been mentioned above, the results listed in Table III show the tendency expected from the superexchange interaction theories.

The authors would like to thank Professor Eizo Kanda for his continuous interest in this problem.

Research Institute for Iron,
Steel and Other Metals
Tohoku University
Katahira-cho, Sendai (H.K. & T.H.)

Faculty of Science
Osaka City University
Sumiyoshi-ku, Osaka (M.M.)