The Magnetic Susceptibilities of Mononuclear and Binuclear Chromium(III) Complexes*

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A chromium(III) ion under the ligand field in an octahedral environment has three unpaired electrons in the three-fold degenerated t_{2g} orbitals, irrespective of whether the field is strong or weak. Since the degree of the covalency of the bonding in a chromium(III) complex cannot, in general, be estimated by measuring only the magnetic susceptibility, the measurement has so far been of little interest to investigators of chromium(III) complexes.

In spite of this, however, there have been found almost diamagnetic binuclear complexes, such as $[Cr_2(NH_3)_{10}O](ClO_4)_4$,[1] and nitrosyl complexes of abnormal valency, such as $K_4\cdot[Cr(CN)_5NO]\cdot H_2O$,[2] whose magnetic moment, 0.7 B. M., is smaller than the spin-only value for three unpaired electrons.

In addition, there have been several reports[3-5] with respect to the magnetic susceptibility of mono- and bi-nuclear chromium(III) complexes, but most of them have not described the magnetic moment and have not even mentioned the relation between the presence of the exchange interaction between two chromium atoms and the color of the binuclear complexes. In order to establish the relation in detail, the magnetic susceptibility of several mono- and bi-nuclear chromium(III) complexes and of the salts consisting of complex cations and anions was measured.

Experimental

The samples used for the measurement of the magnetic susceptibility are those listed in Table I. The methods of preparing several of them will be described below; otherwise they were prepared as in the foot notes in the table.

***cis*-Potassium Hydroxobis(oxalato)aquochromate(III) Hydrate, $K_2[Cr(OH)ox_2(H_2O)]\cdot H_2O$.**—This was prepared by adding pyridine to the *cis*-potassium bis(oxalato)diaquochromate(III) (6) in Table I.

Found: Cr, 14.78. Calcd.: 15.24%.

Hydroxooxalatoaquoethylenediaminechromium(III), $[Cr(OH)ox(H_2O)en]$.—This was prepared by adding pyridine to the oxalatodiaquoethylenediaminechromium(III) bromide (8) in Table I.

Found: Cr, 22.43; N, 11.95. Calcd.: Cr, 22.11; N, 11.91%.

Di-μ-hydroxobis(bisethylenediaminechromium(III)) Bromide Dihydrate, $[en_2Cr(OH)_2Cr\,en_2]Br_4\cdot 2H_2O$.—This was prepared by the reaction of ammonium bromide with the binuclear complex (9) in Table I.

Found: Cr, 13.95; N, 13.18. Calcd.: Cr, 13.99; N, 15.26%.

The molecular conductivity, Λ_{10000}, was 480.9 mho·cm²/mol. at the concentration of 10^{-4} mol./l. at 25°C.

Sodium Di-μ-hydroxobis(bisoxalatochromate(III)) Tetrahydrate, $Na_4[ox_2Cr(OH)_2Crox_2]\cdot 4H_2O$.—This was prepared by the reaction of sodium

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* Read at the 13th Symposium on Coordination Compounds of the Chemical Society of Japan, Nagoya, October, 1963.

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[2] W. P. Griffith, *J. Chem. Soc.*, 1963, 3286.

[3] E. Rosenbohm, *Z. phys. Chem.*, 93, 693 (1919).

[4] D. M. Bose, *Phil. Mag.*, 5, 1048 (1928).

[5] D. M. Bose, *Z. Physik.*, 65, 677 (1930).

bromide with ammonium di-μ-hydroxobis(bisoxalatochromate(III)).

Found: Cr, 14.94. Calcd.: Cr, 15.07%.

$\Lambda_{10000}=504.3$.

Di-μ-hydroxobis(bis-α-alaninatochromium (III)), $[\alpha\text{-ala}_2Cr(OH)_2Cr\ \alpha\text{-ala}_2]\cdot H_2O$.—This was prepared from a mixed solution of chromic chloride hexahydrate and α-alanine in a way similar to that used for the binuclear glycinato complex (16) in Table I.

Found: Cr, 20.72; N, 11.92. Calcd.: Cr, 21.65; N, 11.66%.

Samples 18, 19 and 20 in Table I were precipitated by mixing the saturated solutions of the two complex salts containing a corresponding cation or anion.

The magnetic susceptibility was measured by a Gouy balance at room temperature. The effective magnetic moment per chromium atom was evaluated from the value of the magnetic susceptibility on the assumption that the magnetic susceptibility is inversely proportionate to the absolute temperature, as $\chi=C/T$, where χ, C and T are the magnetic susceptibility, a Curie constant, and the absolute temperature respectively.

Results

The values of the magnetic susceptibility and of the calculated magnetic moment of mono- and bi-nuclear complexes and salts consisting of the complex cation and anion are listed in Table I. The table shows that the magnetic moment of the mononuclear complexes, except for sample 9, is close to the spin-only value for three unpaired electrons.

The values of the magnetic moment of binuclear complexes are remarkably lower than the value of the magnetic moment for the spin-only value except for sample 11. This fact makes us expect the exchange interaction between two chromium atoms in the binuclear complexes.

However, when we compare the values in detail, it is found that even if the binuclear complex ions contained are the same, the magnetic moment of sample 11 is larger than that of sample 12, and that that of 13 is larger than that of 14, where the former two samples have the same binuclear cation and the latter two have the same binuclear anion. Since the ionic radius of the anti-ion of the binuclear complex cation in 11, the dithionate ion, is larger than that of the bromide ion in 12, and since that of the potassium ion in 13 is larger than that of the sodium ion in 14, we may

TABLE I. THE MAGNETIC SUSCEPTIBILITY PER GRAM χ_g AND THE EFFECTIVE MAGNETIC MOMENT, μ_{eff} PER A CHROMIUM OF ATOM MONONUCLEAR AND BINUCLEAR COMPLEXES AND SALTS CONSISTING OF THE COMPLEX CATION AND ANION

		Temp., °K	$\chi_g\times10^6$	μ_{eff}(B. M.)
(1)	$KCr(SO_4)_2\cdot 12H_2O$	291.2	12.6	3.95
(2)	$[Cren_3]Cl_3\cdot 3\cdot 5H_2O$ 6)	298.2	14.9	3.89
(3)	$[Croxen_2]Br$ 6)	297.5	17.2	3.81
(4)	$K[Crox_2en]\cdot H_2O$ 6)	286.5	17.1	3.75
(5)	$K_3[Crox_3]\cdot 3H_2O$ 7)	294.2	12.3	3.85
(6)	*cis*-$K[Crox_2(H_2O)_2]\cdot 2H_2O$ 8)	289.2	18.3	3.87
(7)	$K_2[Cr(OH)ox_2(H_2O)]\cdot H_2O$	288.3	17.3	3.95
(8)	$[Crox(H_2O)_2en]Br$ 6)	289.6	18.9	3.80
(9)	$[Cr(OH)ox(H_2O)en]$	287.2	23.6	3.65
(10)	$[Crgly_3]\cdot H_2O$ 9)	289.2	21.5	3.89
(11)	$[en_2Cr(OH)_2Cren_2](S_2O_6)_2$ 10)	296.2	16.5	3.81
(12)	$[en_2Cr(OH)_2Cren_2]Br_4\cdot 2H_2O$	289.2	14.0	3.55
(13)	$K_4[ox_2Cr(OH)_2Crox_2]\cdot 6H_2O$ 10)	301.2	13.7	3.63
(14)	$Na_4[ox_2Cr(OH)_2Crox_2]\cdot 4H_2O$	298.7	14.4	3.43
(15)	$[oxenCr(OH)_2Croxen]$ 10)	289.2	23.8	3.53
(16)	$[gly_2Cr(OH)_2Crgly_2]\cdot H_2O$ 9)	298.2	20.3	3.37
(17)	$[\alpha\text{-ala}_2Cr(OH)_2Cr\alpha\text{-ala}_2]\cdot H_2O$	290.2	20.3	3.43
(18)	$[Cren_3][Crox_3]$	298.2	18.4	3.55
(19)	$[Croxen_2][Crox_2en]$	297.7	21.0	3.74
(20)	$[Cr(OH)(H_2O)en_2][Cr(OH)ox_2(H_2O)]$	300.7	25.4	3.88

6) E. Kyuno, N. Tanaka and M. Kamada, Read at the 12th Symposium on Coordination Compounds of the Chemical Society of Japan, Tokyo, November, 1962.

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8) A. Werner, W. J. Bowis, A. Hoblik, H. Schwarz and H. Surber, *Ann.*, **406**, 261 (1914).

9) H. Ley, *Ber.*, **45** 380 (1912).

10) E. Kyuno, R. Honjo and R. Tsuchiya, Read at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

suppose that, as the radius of the anti-ion becomes smaller, the exchange interaction between the chromium atoms through the hydroxy group becomes stronger.

The magnetic moments of samples, 15, 16 and 17 are especially small. This fact can be understood by considering that the exchange interaction between two chromium atoms in a binuclear complex is very large, though the reason for this can not be exactly determined. In addition, there may be some exchange interaction between chromium atoms in the neighboring complex molecules in these cases, since they do not contain the anti-ions.

The values of the magnetic moments of 18 and 19 are obviously lower than the spin-only value, which suggests the presence of an exchange interaction between chromium atoms in the neighboring complex cation and anion.

The magnetic moments of mono- and bi-nuclear complexes in relation to their color and the position in their synthetic course are summarized in Fig. 1. The qualitative information is deduced from Fig. 1 that the complexes which have a normal magnetic moment (close to 3.87 B. M.) exhibit a reddish color in general, except for a few fundamental complexes used as starting materials, whereas the complexes

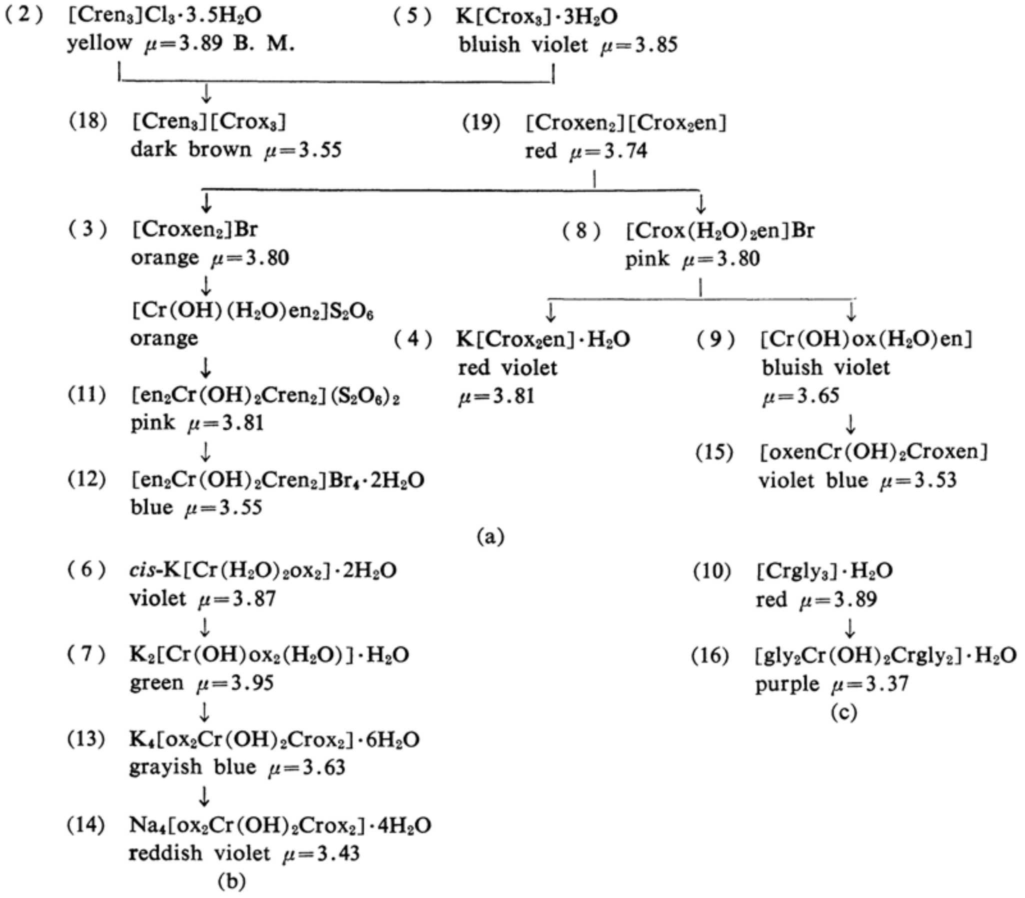

Fig. 1. The magnetic moment and the color of the complexes in the diagrams of the synthesis course of (a) ethylenediaminechromium(III) series, (b) oxalatochromium(III) series and (c) glycinatochromium(III) series.

TABLE II. THE WAVELENGTH AT A PEAK IN THE FIRST ABSORPTION BAND, λ_{max}, OF THE BINUCLEAR COMPLEXES AND THE MONONUCLEAR ONES WHICH ARE THE MOTHER MATERIALS FOR THE SYNTHESES OF THE FORMERS

Mother material	λ_{max}, mμ	Binuclear complex	λ_{max}, mμ
$[\mathrm{Cr(H_2O)_2en_2}]^{3+}$	515[6]	$[\mathrm{en_2Cr(OH)_2Cren_2}]^{4+}$	530[10]
$[\mathrm{Crox_2(H_2O)_2}]^-$	570[6]	$[\mathrm{ox_2Cr(OH)_2Crox_2}]^{4-}$	580[10]
$[\mathrm{Crox(H_2O)_2en}]^+$	524[6]	$[\mathrm{oxenCr(OH)_2Croxen}]$	550[10]

which have a subnormal magnetic moment (lower than the spin-only value) show a bluish color such as samples 9, 12, 13, 14 and 15 or, at least, show purple, as does 16.

The wavelengths at the maximum absorption peak in the first absorption band of the binuclear chromium(III) complexes, λ_{max}, are compared with those of the mononuclear complexes which are the mother materials for the syntheses of the former in Table II. It may be concluded from Fig. 1 and Table II that, as the exchange interaction between the chromium atoms appears, the first absorption band is shifted to red and that, as a result, the color of the compounds changes from reddish to bluish.

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