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Magnetic Studies on the Nitrate and Bromide Salts of the Cation Di-μ-Hydroxobis[di(1,10-phenanthroline)chromium(III)]$^{4+}$

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The magnetic susceptibilities of powdered samples of di-μ-hydroxobis[di(1,10-phenanthroline)chromium(III)]$(NO_3)_2 \cdot 7H_2O$, and the analogous bromide octahydrate salt have been determined in the temperature range 5 to 283 °K. The dimers exhibit antiferromagnetic exchange interactions with the best fits to the Van Vleck expression for exchange coupled $S = 3/2$ ions including biquadratic exchange yielding, for the nitrate salt, $g = 1.98 \pm 0.03$, $2J = -42.2 \pm 0.5$ cm^{-1}, and $j = 0$ cm^{-1} and for the bromide salt, $g = 1.95 \pm 0.03$, $2J = -29.2 \pm 0.6$ cm^{-1}, and $j = 0.5 \pm 0.1$ cm^{-1}.

Introduction

The nitrate salt of the cation di-μ-hydroxobis[di-(1,10-phenanthroline)chromium(III)]$^{4+}$ was first reported in 1961 by Inskeep and Benson [1], who determined the complex to be a dimer by means of a potentionetric titration. In the same year, Ernshaw and Lewis reported [2] the magnetic properties of the iodide salt of the same cation, but preparative details were not reported. The first structure determination of the cation, as the chloride salt, was reported recently by Veal, Hatfield, and Hodgson [3]. Preliminary investigations [4] indicate that the structure of the nitrate salt is similar in structure to that reported for the chloride salt; the bridge bond angles and the bond lengths about the approximately octahedrally-coordinated chromium atoms in the chloride salt are shown in Figure 1.

Because of the greatly differing values reported for the singlet–triplet splitting factor in di-μ-hydroxochromium(III) complexes whose magnetic properties have been studied [5], an investigation of the magnetic properties of the nitrate and bromide salts of the cation di-μ-hydroxobis[di(1,10-phenanthroline)chromium(III)]$^{4+}$ was undertaken in order to determine the extent of interaction between chromium atoms in these two salts.

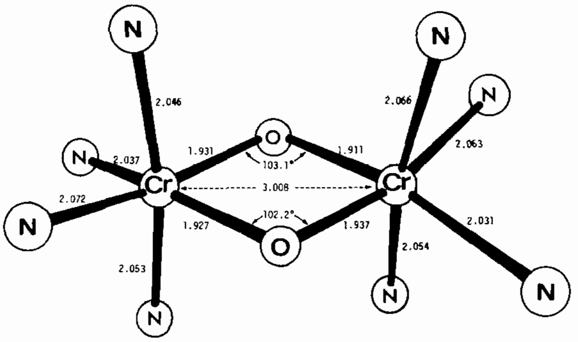

Figure 1. Structural parameters of the hydroxo bridging unit in di-μ-hydroxobis[di(1,10-phenanthroline)chromium(III)]-n hydrate (adapted from reference 3).

Experimental

The nitrate and bromide salts of the cation di-μ-hydroxobis[di(1,10-phenanthroline)chromium-(III)]$^{4+}$ were prepared as reported in the literature; the nitrate by a method of similar to that of Inskeep and Benson [1] and the bromide by methathesis from the nitrate salt [6]. The elemental analyses were consistent with seven and eight waters of hydration, respectively, although Inskeep and Benson reported the nitrate salt to be a monohydrate [1].

ANALYSIS for $[(C_{12}H_8N_2)_2(OH)Cr]_2(NO_3)_4 \cdot nH_2O$

	calculated, $6H_2O$ (M.W. = 1214.95)	calculated, $7H_2O$ (M.W. = 1232.96)	found
%C	47.45	46.76	46.74
%H	3.82	3.92	3.59
%N	13.83	13.63	13.60

for $[(C_{12}H_8N_2)_2(OH)Cr]_2Br_4 \cdot nH_2O$

	calculated, $6H_2O$ (M.W. = 1286.57)	calculated, $8H_2O$ M.W. = 1322.60)	found
%C	44.81	43.59	43.50
%H	3.60	3.81	3.51
%N	8.71	8.47	8.23
%Br	24.84	24.17	25.13

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The magnetic susceptibility measurements on powdered samples of the nitrate and bromide salts were made over the temperature ranges 5.35 to 268.3 °K and 4.98 to 282.8 °K, respectively, using a Foner-type [7] vibrating sample magnetometer [8] with the magnet calibrated at the operating field of 10,000 gauss by magnetic resonance techniques. The temperature of the samples was measured using a calibrated precision gallium arsenide diode sensor [9] located on the sample drive rod near the sample. Absolute temperature accuracy is at least ±0.02 °K below 77.3 °K and better than ±0.1 °K above 77.3 °K. The magnetic susceptibility standard $HgCo(NCS)_4$ was used to calibrate the magnetometer [10]. The data were calculated per monomer gram molecular weight, and were corrected for the diamagnetism of constituent atoms using Pascal's constants [11], and for temperature independent paramagnetism (T.I.P.) by assuming that T.I.P./Cr^{3+} equals 60×10^{-6} c.g.s.u. [12].

Results and Discussion

The magnetic susceptibility data for the nitrate and bromide salts were fitted to the expression for the susceptibility of exchange coupled $S = 3/2$ ions, including biquadratic exchange contributions, equation (1), which results from a consideration of the

$$\chi_M = \frac{g^2\beta^2N}{kT}\left\{\frac{2\exp[(2J-6.5j)/kT] + 10\exp[(6J-13.5j)/kT] + 28\exp[(12J-9j/kT]}{1+3\exp[(2J-6.5j)/kT] + 5\exp[(6J-13.5j)/kT] + 7\exp[(12J-9j/kT]}\right\} \quad (1)$$

energy levels obtained by applying the Hamiltonian including a biquadratic exchange term, equation (2), where j is the biquadratic exchange parameter, and

$$H = -2J(S_1 \cdot S_2) - j(S_1 \cdot S_2)^2 \quad (2)$$

substitution of the Zeeman coefficients into the Van Vleck equation. Equation (1) reduces to the expression for exchange-coupled $S = 3/2$ ions if j takes on a value of zero, as is the case when there is no biquadratic exchange.

The best-fit parameters from equation (1) obtained for the nitrate salt are $g = 1.98 \pm 0.03$, $2J = -42.2 \pm 0.5$ cm^{-1}, and $j = 0.0$ cm^{-1} (no biquadratic exchange). Those for the bromide salt are $g = 1.95 \pm 0.03$, $2J = -29.2 \pm 0.5$ cm^{-1}, and $j = 0.5 \pm 0.1$ cm^{-1}. The inclusion of the biquadratic exchange parameter j in the susceptibility expression resulted in a substantially better fit (a 40% reduction in the error parameter) of the data for the bromide salt than when j was set equal to zero, where $g = 1.967$ and $2J = -30.8$ cm^{-1}.

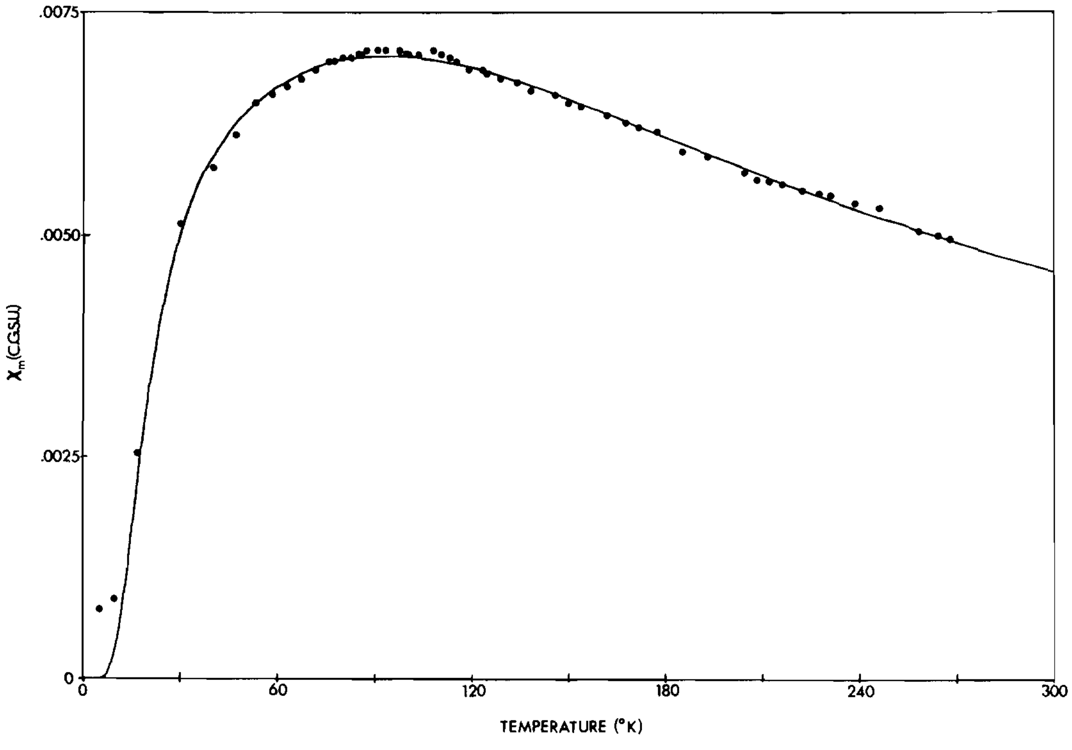

Figure 2. Plot of magnetic susceptibility (c.g.s.u.) *versus* temperature (°K) for the nitrate salt of $[(phen)_2Cr(OH)]_2^{4+}$.

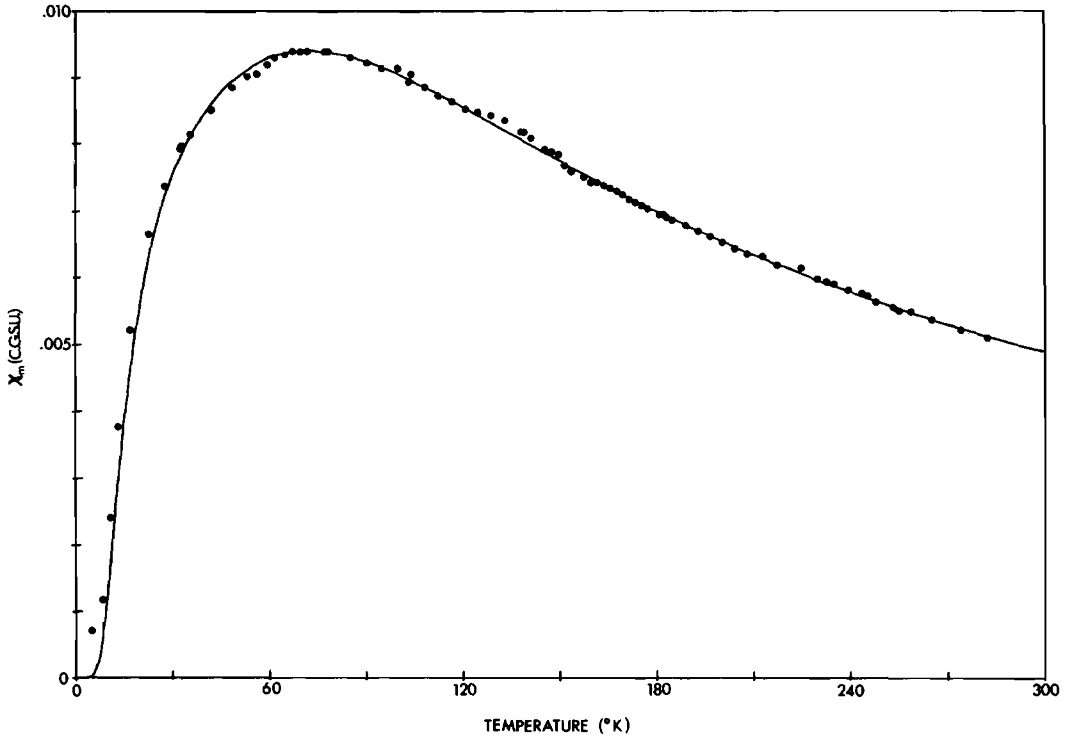

Figure 3. Plot of magnetic susceptibility (c.g.s.u.) *versus* temperature (°K) for the bromide salt of $[(phen)_2Cr(OH)]_2^{4+}$.

TABLE I. A Tabulation of Singlet–Triplet Splitting Parameters, Cr–O–Cr Bond Angles and Cr–O Bridge Bond Distances (where available) for $[Cr(1,10\text{-phenanthroline})_4(OH)_2]^{4+}$ Complexes.

Compound	2J (cm^{-1})	j (cm^{-1})	ΔE cm^{-1}	Cr–O–Cr Bond Angle	Cr–O Bridge Bond Distance, Å	References
$[(phen)_2Cr(OH)]_2(NO_3)_4 \cdot 7H_2O$	–42.2	0.0	–42.2	–	–	This Work
$[(phen)_2Cr(OH)]_2Br_4 \cdot 9H_2O$	–29.2 –30.8	0.5 0.0	–32.4 –30.8	–	–	This Work
$[(phen)_2Cr(OH)]_2Cl_4 \cdot 6H_2O$	–55	–0.8	–50.3	102.7°	1.927(11)	3
$[(phen)_2Cr(OH)]_2I_4 \cdot 4H_2O$	–43.8	1.5	–53.6	102.1°	1.919 (7)	13

A plot of the magnetic susceptibility (c.g.s.u.) *versus* temperature (°K) data for the nitrate salt is shown in Figure 2. The curved line represents the best-fit J- and g-values in the expression for the susceptibility (1) (*vide supra*). The corresponding plot for the bromide salt is shown in Figure 3. The best-fit line includes biquadratic exchange contributions.

The values of 2J and singlet–triplet splitting parameter ΔE, for the $[Cr_2(1,10\text{-phenanthroline})_4(OH)_2]^{4+}$ salts, including those determined in this study, are tabulated in Table I. For ligands other than 1,10-phenanthroline the values of 2J are frequently less than half those values for the 1,10-phenanthroline complexes; the reasons for this behavior are complex [4] and a final explanation must be deferred until additional theoretical advances are made. The signs associated with the tabulated splitting parameter values indicate an antiferromagnetic interaction in all cases. It is convenient to define a singlet–triplet splitting factor ΔE, that being $\Delta E = 2J - 6.5j$. Values for ΔE are tabulated in Table I.

When the structural parameters for chromium(III) dimers are examined, it is tempting to propose a correlation between the Cr–O–Cr bond angle and the magnitude of 2J or ΔE similar to that observed for the Cu–O–Cu bond angles and 2J values in di-μ-hydroxocopper(II) complexes, where the extent of the antiferromagnetic interactions increases with the bridge bond angle [14]. However, no attempt should be made to predict Cr–O–Cr bond angles for the complexes based solely on the magnitude of singlet–triplet splitting parameters since the exchange interaction in chromium dimers are known to be sensitive to changes in bond distances [4]. Structural similarities will have to be documented before a rigorous correlation can be made.

There is no evidence of intermolecular magnetic interactions, but interactions should not be expected in view of the insulation by the bulky ligands, the counter ions, and the waters of hydration. Jasiewicz, Rudolf, and Jezowska-Trzebiatowska [14] have noted that $-J$ decreases in the order $Cl^- > Br^- > I^-$ for the di-μ-hydroxobis[bisethylenediaminechromium(III)]$^{4+}$ salts. Such a trend in $-J$ with the nature of the counter ion is not observed with the 1,10-phenanthroline complexes, and we are led to conclude that the geometry of the Cr_2O_2 unit is strongly influenced by crystal packing forces which include hydrogen bonding between the OH^- bridges, the counter ions, and the waters of hydration.

Acknowledgments

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