Magnetic Properties of the Chromium(III) Dimer Δ(−)₅₄₆-Di-μ-hydroxo(S,S,S,S)-tetrakis(L-prolinato)dichromium(III) Tetrahydrate

SOLVEIG KALLESØE and ERIK PEDERSEN

Chemistry Department I (Inorganic Chemistry), University of Copenhagen, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The magnetic properties of dimeric chromium(III) complexes of the type $[CrL_m(OR)]_2^{n+}$ where L is a mono-, bi-, tri-, or tetradentate ligand and R is a hydrogen atom or an alkyl group have recently been intensely studied.[1−9] A model (the GHP model) has been proposed[1] which quantitatively relates the magnitude of the superexchange coupling with the $Cr-O-Cr$ bridging angle, ϕ, the $Cr-O$ bond length, r, and the dihedral angle between the bridging plane and the OR vector of the bridging group, θ. According to this model the exchange parameter J in the Hamiltonian, eqn. (1), is given as competing antiferro- and ferromagnetic contributions according to eqn. (2), where the values of the constants $a, b,$ and c have been determined from a set of experiments based on magnetic and structural data for fifteen dimers.

$$\mathscr{H} = JS_1 S_2 \tag{1}$$

$$J = J_{af} - J_f = e^{-a(r-1.8)} \tag{2}$$
$$\cdot [b\cos^4\theta / \left\{ 1 - \sin^2\theta / \tan^2\left(\frac{\phi}{2}\right) \right\}$$
$$- c\sin^2\phi / \{1 - \cos\phi\}^2]$$

The structural parameters for one of the isomers of the title complex $[Cr(L\text{-pro})_2OH]_2 \cdot 4\,H_2O$ were recently determined,[2] and we thus have the possibility for another control of the GHP model since all the values of r, θ, and ϕ were determined.

Another set of data may be available for a corresponding bis(ethylenediamine-N,N'-diacetato) complex whose structural[3] and magnetic parameters[4] have recently been determined. The two samples investigated[3,4] were not shown to be identical and, since our repeated preparations inevitably gave an inseparable mixture of several of the many possible isomers, we excluded these data from further consideration.

The title complex was prepared according to the literature method.[2] $[Cr(C_4H_8NCOO)_2OH]_2 \cdot 4H_2O$ was analyzed for Cr, C, H, N. The product was also analyzed by Guinier X-ray technique. Fifteen lines in the range $\sin^2(\theta) \leq 0.034$ (θ is in this case the diffraction angle) for copper radiation were measured, and their positions were found to be in complete agreement with the structural data available for one of the many isomers possible.[2]

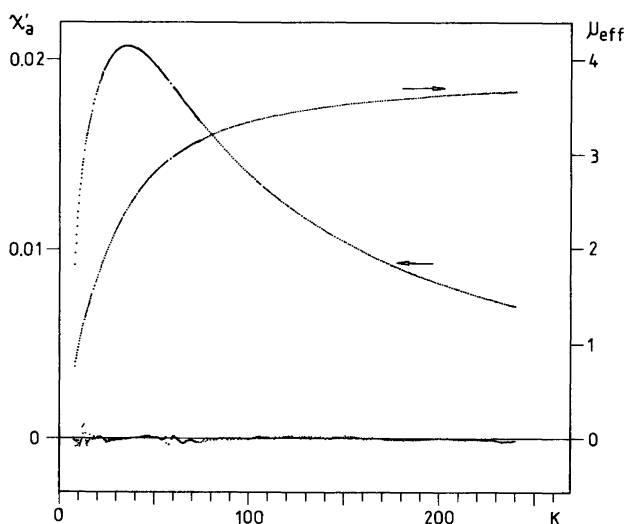The magnetic susceptibility of powdered samples

Fig. 1. Magnetic susceptibility (left scale in c.g.s. units) and effective magnetic moment (right scale in Bohr magnetons) of Δ(−)₅₄₆-di-μ-hydroxo(S,S,S,S)tetrakis(L-prolinato)dichromium(III) tetrahydrate. The lower set of points indicate $(\chi_{obs} - \chi_{calc.}) \times 50$ as obtained from fitting of the results to model 3, *cf.* Table 1.

was measured by the Faraday method at a field of 12.000 Ø in the temperature range 4 – 300 K. A typical result is shown in Fig. 1. The susceptibility data were fitted by a least squares technique to the expression (3), where E_i are the energies of the 16 components of the ground state manifold. Details of the fitting procedure are found elsewhere.[5] The fitting was performed by application of three different models for the exchange Hamiltonian. Model 1 assumed the simple Heisenberg Hamiltonian eqn. (1). Model 2 included a biquadratic exchange term according to eqn. (4). Finally Model 3 assumed independent energies of the triplet, quintet and septet states.

$$\chi'_A = -\frac{N}{H} \frac{\sum_i \left(\frac{\partial E_i}{\partial H}\right) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \qquad (3)$$

$$\mathscr{H} = JS_1S_2 + j(S_1S_2)^2 \qquad (4)$$

Some of the results of the data fittings are displayed in Table 1. It is obvious that the data are not sufficiently well described by model 1. Inclusion of the biquadratic exchange term (model 2) markedly improved the fit, lowering the variance per degree of freedom (var/f) from 17 to 1.6. Moreover inclusion of the additional variable in model 3 led to a further but small improvement; var/f was reduced to 1.2. It is seen from Table 1, however, that the Landé rule for splitting of the ground state manifold as implied by eqn. (1) is followed rather closely, the singlet – triplet separation being 15 cm⁻¹.

The structural parameters for the bridging system were derived from the crystallographic data available.[2] Since the space group is $P2_12_12_1$ and Z

$= 4$ no symmetry requirements are imposed on the molecules, and in the comparison with the theoretical expresseion eqn. (2) average values of r, θ and ϕ were used. This is reasonable because the deviations are small. The values used were $r = $ Cr $- O = 1.948(15)$ Å, $\phi =$ Cr $-$ O $-$ Cr $= 100.0(6)°$, and $\theta = 34°$. The out-of-plane angle, θ, was calculated from the positional parameters via the angles between the O $-$ O vector and the O $-$ H vectors. The estimated standard deviations for r and ϕ are two times those estimated by the crystallographers.[2] The standard deviation for θ was estimated to be $5°$.

These crystallographic results, together with the estimated triplet energy of 15.1(1) cm⁻¹, were used for an expansion of the data set already used in fitting eqn. (2). The calculated values $a = 19(1)$ Å⁻¹, $b = 611(38)$ cm⁻¹ and $c = 172(54)$ cm⁻¹ were found to be identical to their old values.[1] The calculated value of the triplet energy of the title complex was $J = J_{af} - J_f = 26 - 7 = 19$ cm⁻¹ in excellent agreement with the experimental result considering the estimated standard deviation (e.s.d) of 8 cm⁻¹. The main contribution to this rather large e.s.d. is related to the e.s.d.'s of r and θ.

These results reconfirm the validity of the GHP exchange model[1] as expressed in eqn. (2) and illustrate that the exhange parameter in this case is rather small compared to other di-μ-hydroxo complexes, with similar r values as expected when the hydrogen atoms of the μ-hydroxo groups are displaced so much out of the bridging plane.

1. Glerup, J., Hodgson, D. J. and Pedersen, E. *Acta Chem. Scand. A* **37** (1983). *Submitted*, and references therein.
2. Oki, H. and Yoneda, H. *Inorg. Chem.* **20** (1981) 3875.
3. Srdanov, G., Herak, R., Radanović, D. J. and Veselinović, D. S. *Inorg. Chim. Acta* **38** (1980) 37.
4. Hatfield, W. E., MacDougall, J. J. and Shepherd, R. E. *Inorg. Chem.* **20** (1981) 4216.
5. Michelsen, K. and Pedersen, E. *Acta Chem. Scand. A* **32** (1978) 847.
6. Decurtins, S., Güdel, H. U. and Pfeuti, A. *Inorg. Chem.* **21** (1982) 1101.
7. Scaringe, R. P., Hodgson, D. J. and Hatfield, W. E. *Transition Met. Chem.* **6** (1981) 340.
8. Michelsen, K., Pedersen, E., Wilson, S. R. and Hodgson, D. J. *Inorg. Chim. Acta* **63** (1982). *In press.*
9. Michelsen, K. and Pedersen, E. *Acta Chem. Scand. A* **37** (1983). *In press.*

Table 1. Parameters derived from magnetic susceptibility data for [Cr(L-pro)$_2$OH]$_2$.4H$_2$O.

	Model 1	Model 2	Model 3
J(cm⁻¹)	14.53(5)	13.29(2)	–
j(cm⁻¹)	–	−0.41(1)	–
$E(1)^a$(cm⁻¹)	14.53(5)^b	15.96(3)^b	15.06(11)
$E(2)$(cm⁻¹)	43.5(2)^b	45.4(1)^b	45.01(9)
$E(3)$(cm⁻¹)	87.2(4)^b	83.4(2)^b	81.6(2)
g	2.023(3)	1.977(1)	1.970(1)
var/f^c	17.3	1.60	1.27
f	425	424	423

^{a} $E(1-3)$ refer to triplet, quintet and septet energies.
^{b} Values calculated from J and j for comparison with model 3. ^{c} Variance per degree of freedom.