A Novel Correlation between Magnetism and Structural Parameters in Superexchange Coupled Chromium(III) Dimers

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There has been intense recent research activity in the magnetochemistry of dimeric transition metal complexes. While for the electronically simple copper(II) $[d^9,d^9]$ complexes of the type $[CuL_m(OH)]_2^{n+}$ an empirical relationship between structural and magnetic properties has been demonstrated,[1,2] for the electronically more complex chromium(III) $[d^3,d^3]$ systems this is not the case. For dimers of the type $[CrL_m(OR)]_2^{n+}$ where L is mono- or bidentate, and R is a hydrogen atom or an alkyl group,[3-16] the magnetic interaction has been shown to vary with the Cr–O–Cr bridging angle, ϕ,[6,16,20-22] the Cr–O bond length, r,[20,22] and recently particular emphasis has been placed on the dihedral angle between the bridging plane and the OR vector of the bridging group, θ.[11,16,20,23,24] Apart from our own preliminary reports[25,26] quantification of these dependencies has not been given.

In this paper we propose a model which correlates the magnitude of the magnetic interaction with r, ϕ and θ. The model is consistent with widely varying magnetic and structural data for all fifteen dimeric chromium(III) complexes of the aforementioned type being well characterized at present. The model is an extension of our own calculations,[27] based on Anderson's superexchange model,[28,29] allowing the concepts of the angular overlap model to account for the influences of ϕ and θ on competing ferro- and antiferromagnetic contributions. Further theoretical details are the subject of a forthcoming publication.[30]

Theory. The ground state manifold in chromium(III) dimers with $S=0$, 1, 2 and 3 consists of two coupled $^4A_2$ states derived from the $|t_2^3(a), t_2^3(b)\rangle$ configuration where $^4A_2$ and t_2^3 refer to their octahedral parentage functions and a and b to the two centers. The lowest energy metal–metal charge transfer states with $S=0$, 1 and 2 belong to the configuration $1/\sqrt{2}\ \{|t_2^4(a)\ t_2^2(b)\rangle + |t_2^2(a)\ t_2^4(b)\rangle\}$. It has been shown for a linear μ-oxo complex[27] that these symmetry adapted configurations interact *via* a one-electron ligand field matrix element. This can be generalized,[30] and in the present cases this matrix element is mainly of the type $\langle d_{zx}(a)|V_L|d_{yz}(b)\rangle$ with the coordinate systems defined in Fig. 1. In the angular overlap model these matrix elements are proportional to the product of the corresponding overlap integrals of the types $\langle d_{zx}(a)|p_z\rangle$ *and* $\langle d_{yz}(b)|p_z\rangle$ involving a p_z-orbital on the bridging oxygen atom. This configuration interaction gives rise to an antiferromagnetic coupling in the ground states of the chromium dimers according to the Heisenberg Hamiltonian $\mathcal{H}=JS_a \cdot S_b$ with

$$J_{af} \propto \frac{|\langle d_{zx}(a)|V_L|d_{yz}(b)\rangle|^2}{E_{C.T.}} \qquad (1)$$

where $E_{C.T.}$ is the energy of the charge transfer configuration. The energy of this configuration and the radial part of the overlap integrals have been estimated earlier.[27]

As part of our model, we assume that the orbitals on the bridging oxygen atoms are $2s$–$2p$ hybrids pointing towards the two metal atoms and the R group. They participate in three σ-bonds. This leaves a lone pair in an orthogonal sp-hybrid orbital. If the OR-vector is in the bridging plane this lone pair is in a pure p_z-orbital which gives maximum values of the π-overlap integrals.

For other geometries of the bridging system it can be shown[30] that

$$\langle d_{zx}(a)|V_L|d_{yz}(b)\rangle \propto \cos^2\theta/\{1-\sin^2\theta/\tan^2(\phi/2)\} \qquad (2)$$

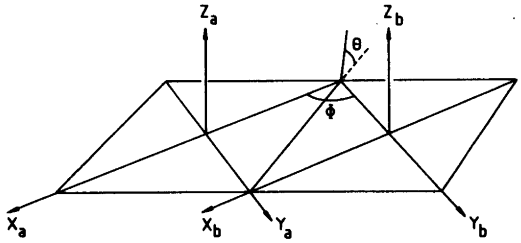

Fig. 1. Choice of coordinate systems for di-μ-hydroxochromium(III) complexes.

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0302-4377/83 $2.50

Through the application of eqn. 1 this leads to an angular dependence of the antiferromagnetic contribution according to

$$J_{af} \propto \cos^4\theta/\{1-\sin^2\theta/\tan^2(\phi/2)\}^2 \quad (3)$$

The next nearest charge transfer configuration is $1/\sqrt{2}\ \{|t_2^3e(a)t_2^2(b)\rangle + |t_2^2(a)\ t_2^3e(b)\rangle\}$ with energy $E_{C.T.}+\Delta+E_{rep}$ where $\Delta=10$ Dq, and E_{rep} is an interelectronic repulsion term. It interacts with the ground state configuration mainly *via* a matrix element of the type $\langle d_{z^2}(a)|V_L|d_{xy}(b)\rangle$ which is non-vanishing because there is a hybrid orbital having a σ-overlap with Cr(a) and a π-overlap with Cr(b) and *vice versa*. The angular dependence of these matrix elements can be shown to be

$$\langle d_{z^2}(a)|V_L|d_{xy}(b)\rangle \propto \sin\phi/\{1-\cos\phi\} \quad (4)$$

Transfer of an electron to the $e(a)$ orbital leads to $S=2$ or 1 on Cr(a) and similarly for Cr(b). This gives rise to two sets of charge transfer configurations. One set having states with $S=S_s+S_b=1$, 2 and 3 is derived from $S_a=2$ and $S_b=1$ and *vice versa*. The states with $S=3$ are
$1/\sqrt{2}\ \{|t_2^3e(a)(S_a=2)t_2^2(b)(S_b=1)\rangle +$
$|t_2^2(a)(S_a=1)t_2^3e(b)(S_b=2)\rangle\}$.
The other set having states with $S=0$, 1 and 2 is derived from $S_a=S_b=1$. The states with $S=2$ are
$1/\sqrt{2}\ \{|t_2^2e(a)(S_a=1)t_2^2(b)(S_b=1)\rangle -$
$|t_2^2(a)(S_a=1)t_2^3e(b)(S_b=1)\rangle\}$.

These sets give competing ferro- and antiferromagnetic contributions, respectively, to the magnetic interactions of the ground states, both according to the Heisenberg Hamiltonian. The states derived from the first configuration are lower in energy due to interelectronic repulsions. The ferromagnetic term will, therefore, be dominating. The net result is a ferro-magnetic term according to

$$J_f \propto \sin^2\phi/\{1-\cos\phi\}^2 \quad (5)$$

Hence, the observable exchange parameter is $J=J_{af}-J_f$.

Since the π-overlap integrals involved are expected to be small, J_{af} and J_f are expected to show an exponential decay with increasing Cr–O distances. Hence the total expression for J in the Heisenberg Hamiltonian is

$$J=J_{af}-J_f=e^{-a(r-1.8)}[b\cos^4\theta/ \{1-\sin^2\theta/\tan^2(\phi/2)\}^2-c\sin^2\phi/\{1-\cos\phi\}^2] \quad (6)$$

Here $r=1.8$ Å was arbitrarily chosen as zero-point for distance to reduce the correlation coefficients between the parameter sets a,b and a,c. b and c are, of course, dependent on $E_{C.T.}$, Δ and the interelectronic repulsion parameters; but the available dimers contain only oxygen and nitrogen ligators and the variations are, therefore, expected to be small.

Table 1. Observed and calculated coupling constants.

Compound	r/Å [a]	ϕ/deg [a]	θ/deg [a]	J_{exp}/cm^{-1} [b]	J_{calc}/cm^{-1} [c]
$[Cr(NH_3)_4OH]_2Cl_4\cdot aq$ [3]	1.975(2)	99.9(1)	41(3)	5.23(1)	9(3)
$[Cr(NH_3)_4OH]_2(S_2O_6)_2\cdot aq$ [3]	1.965(2)	101.5(1)	24(3)	9.12(1)	17(4)
$[Cr\,en_2\,OH]_2(S_2O_6)_2$ [4]	1.979(10)	100.0(4)	57(3)	3.40(10)	3(2)
$[Cr\,en_2\,OH]_2Cl_2(ClO_4)_2$ [5]	1.949(4)	103.4(2)	2(3)	26.8(5)	27(3)
$[Cr\,en_2\,OH]_2Cl_4\cdot aq$ [6]	1.944(6)	102.4(1)	5(3)	29.4(5)	30(7)
$[Cr\,acac_2\,OMe]_2$ [7]	1.962(10)	101.0(5)	29.8(5)	9.6(4)	16(5)
$[Cr(Cl\text{-}acac)_2OMe]_2$ [8]	1.959(4)	101.1(2)	24.4(10)	9.82(10)	18(5)
$[Cr(Br\text{-}acac)_2OMe]_2$ [9]	1.962(8)	101.5(4)	25.7(10)	8.53(50)	16(5)
$[Cr(Br\text{-}acac)_2OEt]_2$ [9]	1.951(12)	101.8(6)	18.3(10)	17.90(20)	23(7)
$[Cr(2\text{-}picetam)_2OH]_2(S_2O_6)_2$ [10,11]	1.945(8)	101.8(2)	0(5)	32.9(1)	29(9)
$[Cr(2\text{-}picetam)_2O]_2Cl_2\cdot aq$ [12]	1.890(10)	95.5(5)	–	83(2)	80(21)
$[Cr\,phen_2\,OH]_2Cl_4$ [13]	1.927(14)	103.1(6)	0(10)	43.0(5)	42(13)
$[Cr\,mal_2\,OH]_2Na_4\cdot aq$ [15]	1.988(4)	99.3(2)	54(6)	–2.16(4)	3(2)
$[Cr(Cl\text{-}dipic)aq\,OH]_2$ [16]	1.947(10)	100.7(4)	41(8)	10.24(6)	15(5)
$[Cr(NH_3)_5O_{1/2}]_2Cl_4\cdot aq$ [d]	1.815(10)	180(0)	–	450(2)	456(91)

[a] r,θ and ϕ are the structural parameters of the bridging system (see text). [b] Coupling constants obtained from magnetic susceptibility data. [c] Coupling constant calculated from eqn. (6). [d] The value of r was calculated from the atomic coordinates in Ref. 17 using unit cell constants determined by us (Ref. 18). The result is close to the average of the values reported in Refs. 17 and 19.

Discussion. The results of fitting the available data to eqn. (6) by a least squares technique are shown in Table 1. As standard deviations of r, ϕ and θ we have used the crystallographer's values multiplied by two. According to the resulting value of variance per degree of freedom *var*/f=0.09 the model describes all the data within the experimental standard deviations. The following parameters were obtained: a=19(1) Å^{-1}, b=611(39) cm^{-1}, c=172(56) cm^{-1}. The complex cation $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ is included in the data set since, although structurally different, it also has two Cr–O π-overlaps. The data for the di-μ-oxo complex has a large influence on the parameter c. A later publication[30] will include data for a μ-hydroxo-μ-oxo complex[12] and a better estimate of the ferromagnetic term is thus expected.

An analysis of the standard deviations of J_{calc} showed that the main contributions came from the standard deviations of the crystallographic parameters r and θ. The need for more sophisticated models for isotropic exchange interactions in chromium(III) dimers of the present type seems to be limited, therefore, by the accuracy of the X-ray methods.

Earlier work[27] showed that within certain approximations J_{af} can be expressed as

$$J_{af}=\tfrac{8}{9}\{\Delta(t_2)\}^2/E_{C.T.} \qquad (7)$$

where $\Delta(t_2)$ is the one-electron splitting of the t_2 level caused by the tetragonal distorsion. (The holohedrized symmetry of each center in the dimers is approximately tetragonal.) In cases where the angular part of eqn. (6) corresponds to maximum overlap, θ=0° and ϕ=90°, for example, a very simple correlation emerges from eqn. (7).

$$\tfrac{8}{9}\{\Delta(t_2)\}^2/E_{C.T.}=439\,e^{-19(r-1.8)} \qquad (8)$$

This does indeed make sense because $\Delta(t_2)$ is expected to decrease and $E_{C.T.}$ to increase with increasing bonding distance. The earlier estimate of $E_{C.T.}$ of 36.000 cm^{-1} in the μ-oxo complex[27] is, therefore, considered to be the lowest possible in the present series of dimers with two π-overlaps. In dimers with weak exchange and r-values near 2 Å, $E_{C.T.}$ is estimated to be in the range 60–100 kK in agreement with earlier estimates.[28]

Acknowledgements. We are very grateful to Mrs. Solveig Kallesøe whose preparations and measurements have contributed much to the data available. This research was supported by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO) through grant No. 1318, by the Petroleum Research Fund, administered by the American Chemical Society, through grant No. 12128-AC 3.6 (to D.J.H.) and by the Danish Natural Science Research Council through grants (to E.P.) Nos. 511–742, 511–3993 and 511–10516.

1. Hodgson, D. J. *Prog. Inorg. Chem. 19* (1974) 173.
2. Crawford, V. H., Richardson, H. W., Wasson, J. R., Hodgson, D. J. and Hatfield, W. E. *Inorg. Chem. 15* (1976) 2107.
3. Cline, S. J., Hodgson, D. J., Kallesøe, S., Larsen, S. and Pedersen, E. *Inorg. Chem. 22* (1983). *In press.*
4. Cline, S. J., Scaringe, R. P., Hatfield, W. E. and Hodgson, D. J. *J. Chem. Soc. Dalton Trans.* (1977) 1662.
5. Kaas, K. *Acta Crystallogr. B 32* (1976) 2021.
6. Beutler, A., Güdel, H. U. and Snellgrove, T. R. *J. Chem. Soc. Dalton Trans.* (1979) 983.
7. Fischer, H. R., Glerup, J., Hodgson, D. J. and Pedersen, E. *Inorg. Chem. 21* (1982) 3063.
8. Estes, E. D., Scaringe, R. P., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chem. 15* (1976) 1179.
9. Estes, E. D., Scaringe, R. P., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chem. 16* (1977) 1605.
10. Larsen, S. and Hansen, B. *Acta Chem. Scand. A 35* (1981) 105.
11. Michelsen, K. and Pedersen, E. *Acta Chem. Scand. A 32* (1978) 847.
12. Michelsen, K., Pedersen, E., Wilson, S. R. and Hodgson, D. J. *Inorg. Chim. Acta 63* (1982) 141. The X-ray data were kindly provided by Dr. S. Larsen.
13. Veal, J. T., Hatfield, W. E. and Hodgson, D. J. *Acta Crystallogr. B 29* (1973) 12.
14. Scaringe, R. P., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chim. Acta 22* (1977) 175. The oxalato complex was not included in our datafitting since the two hydrogen atoms have widely different θ-values.
15. Scaringe, R. P., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chem. 16* (1977) 1600.
16. Cline, S. J., Kallesøe, S., Pedersen, E. and Hodgson, D. J. *Inorg. Chem. 18* (1979) 796.
17. Urushiyama, A. *Bull. Chem. Soc. Jpn. 45* (1972) 2406.
18. Pedersen, E. *Acta Chem. Scand. A 26* (1972) 333.
19. Yevitz, M. and Stanko, J. A. *J. Am. Chem. Soc. 93* (1971) 1512.

20. Josephsen, J. and Pedersen, E. *Inorg. Chem. 16* (1977) 2534.
21. Hodgson, D. J. and Pedersen, E. *Inorg. Chem. 19* (1980) 3116.
22. Scaringe, R. P., Hodgson, D. J. and Hatfield, W. E. *Transition Met. Chem. 6* (1981) 340.
23. Cline, S. J., Glerup, J., Hodgson, D. J., Jensen, G. S. and Pedersen, E. *Inorg. Chem. 20* (1981) 2229.
24. Güdel, H. U. and Hauser, U. *J. Solid State Chem. 35* (1980) 230.
25. Pedersen, E. *Int. Conf. Coord. Chem. XXI,* Toulouse 1980.
26. Pedersen, E. *Int. Conf. Electron Spin Res.,* Lancaster 1982.
27. Glerup, J. *Acta Chem. Scand. 26* (1972) 3775.
28. Anderson, P. W. *Phys. Rev. 115* (1959) 2.
29. Anderson, P. W. *Theory of Exchange in Isolators.* In *Solid State Phys. 14* (1963) 99.
30. Glerup, J., Hodgson, D. J. and Pedersen, E. *To be published.*

Reveived October 27, 1982.