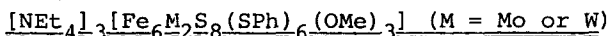


SPIN-EXCHANGE INTERACTIONS IN THE CUBANE-LIKE CLUSTER DIMERS



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ABSTRACT

Average magnetic moments,  $\bar{\mu}_m$ , versus temperature in the range 300-1.8K, and the variation of  $\bar{\mu}_m$  with applied magnetic field, from 0.125 to 2.0T, are reported for  $[\text{NET}_4]_3[\text{Fe}_6\text{M}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$  (M = Mo or W). These data have been interpreted in terms of antiferromagnetic spin coupling between the iron atoms within the separate  $\{\text{Fe}_3\text{MS}_4\}$  cubane-like clusters of the anions.

INTRODUCTION

Recently the isolation and characterisation of several compounds containing  $[\text{Fe}_6\text{M}_2\text{S}_8(\text{SR})_9]^{3-}$  (1-9) or  $[\text{Fe}_6\text{M}_2\text{S}_8(\text{SR})_6(\text{OMe})_3]^{3-}$  (9-12) (M = Mo or W) anions have been described. These complexes consist of two  $\{(\text{RS})\text{Fe}_3\text{MS}_4\}$  units, each with a cubane-like core, linked between their M atoms by three RS- or MeO-  $\mu_2$  ligands. Reports of the magnetic behaviour of these systems are sparse, with the most detailed report to date being a footnote by Wolff *et al* (8), which gave  $\bar{\mu}_m$  at three temperatures for the compounds  $[\text{NET}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_9(\text{SET})_8]$ ,  $[\text{Et}_3\text{NCH}_2\text{Ph}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SET})_9]$ , and  $[\text{Me}_3\text{NCH}_2\text{Ph}]_3[\text{Fe}_7\text{Mo}_2\text{S}_8(\text{SET})_{12}]$ . In addition these authors commented that the complexities of these systems have not yet allowed a satisfactory interpretation of the behaviour of  $\bar{\mu}_m$  as a function of temperature. Here we report details of the average magnetic moments versus temperature (Figures 1 and 2) and the magnetisation measurements (TABLE) of  $[\text{NET}_4]_3[\text{Fe}_6\text{M}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$  (where M = M or W), and a model which provides a satisfactory interpretation of these data.

RESULTS AND DISCUSSION

The behaviour of  $\bar{\mu}_m$  with temperature of  $[\text{NET}_4]_3[\text{Fe}_6\text{M}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$  (M = Mo or W) suggests that the electronic spins in the anions are coupled, almost certainly in an antiferromagnetic sense. The proposed model involves treating the cubane-like cluster dimers as two isolated  $\{\text{MFe}_3\text{S}_4\}$  sub-units, in each of which the metal ions have a total of eleven positive charges. We favour the representation of these charges as the formal oxidation states  $2\text{Fe}(\text{III}) + \text{Fe}(\text{II}) + \text{M}(\text{III})$ , the oxidation states for the iron atoms being consistent with the  $^{57}\text{Fe}$  Mossbauer isomer shifts for these compounds (10,12). We have attempted to use

the possible alternative formulation  $\text{Fe(III)} + 2\text{Fe(II)} + \text{M(IV)}$ , but this has failed to give a satisfactory account of the magnetic data. In addition to the above assignment of formal oxidation states to the metal atoms we have assumed that all of the observed paramagnetism is associated with the iron atoms. Any unpaired electrons formally associated with molybdenum or tungsten atoms are assumed to be paired through a combination of the distorted octahedral geometry about these atoms and exchange across the bridging region. This view is consistent with the  $^1\text{H}$  n.m.r. shifts of these complexes, where the shifts attributed to the terminal ligands from their diamagnetic positions are much greater than those of the bridging ligands (9).

Within the above framework we have calculated  $\chi_{\parallel}$  and  $\chi_{\perp}$  for each cubane-like sub-unit using the perturbing spin-Hamiltonian (1).

$$H = -2\alpha J \hat{S}_1 \cdot \hat{S}_2 - 2J \hat{S}^* \cdot \hat{S}_3 + D[\hat{S}_z'^2 - \frac{1}{3}S'(S'+1)] \\ + \beta[g_{\parallel} H_z \hat{S}_z' + g_{\perp}(H_x \hat{S}_x' + H_y \hat{S}_y')] \quad \text{----- (1)}$$

The centres 1 and 2 in equation (1) are the Fe(III) atoms, which are initially coupled to give a set of resultant spins,  $S^*$ , (13). The  $S^*$  are then coupled with the electronic spin,  $S = 2$ , of the Fe(II) atom to give a set of final resultant spins,  $S'$ , for the cubane sub-unit. The principal magnetic susceptibilities were calculated by applying the zero-field splitting and Zeeman effects as simultaneous perturbations to each of the  $S'$  states and using equation (2)

$$\chi_j = \frac{N}{H} \frac{\sum_i (-dw_i/dH) \exp(-w_i/kT)}{\sum_i \exp(-w_i/kT)} \quad \text{----- (2)}$$

where  $j = z$  or  $x$ . Average values were obtained from  $\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$ ,  $\chi_{\text{m}} = 2\bar{\chi}$ , and  $\bar{\mu}_{\text{m}} = 2.828 (\chi_{\text{m}} \times T)^{\frac{1}{2}}$  B.M. was used for both the calculated and experimental data. The calculations involved the assumption that the same numerical values of the parameters  $D$ ,  $g_{\parallel}$  and  $g_{\perp}$  are applicable to each  $S'$  state.

In applying the model we placed no restrictions on the parameters  $\alpha$ ,  $J$ ,  $D$ ,  $g_{\parallel}$ , and  $g_{\perp}$ . Whilst the effects of individual parameters are not entirely independent, some generalisations are apparent. For  $\bar{g}$  values close to 2, the variation of  $\bar{\mu}_{\text{m}}$  with temperature and its general order of magnitude is largely controlled by  $J$  and  $\alpha$ . The variation of  $\bar{\mu}_{\text{m}}$  with applied magnetic field,  $H$ , at low temperature is mainly dependent on the magnitude and sign of  $D$  for a given set of  $J$  and  $\alpha$ . Satisfactory fits to the variation of  $\bar{\mu}_{\text{m}}$  with temperature, and with  $H$  at low temperature, have been achieved, see Figures 1 and 2 and TABLE. The parameters required do not appear to be in anyway unusual for these types of systems. The  $g$  values are a little lower than, but comparable with, those reported from solution measurements on  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$  ( $g_{\parallel} = 2.05$ ,  $g_{\perp} \sim 1.93$ ,  $\bar{g} \sim 1.97$ ) (14). The value of  $\alpha J$ , the exchange coupling between the Fe(III) atoms is ca  $-180 \text{ cm}^{-1}$ , which is similar to the values of  $-158$  and  $-148 \text{ cm}^{-1}$  reported for the compounds  $[\text{NET}_4]_2[\text{Fe}_2\text{S}_2\text{Cl}_4]$

(15) and  $[\text{AsPh}_4]_2[\text{Fe}_2\text{S}_2(\text{S}_2\sigma\text{-xy1})_2]$  (16). Similarly the values of  $J$ , the exchange integral between the resultants of the coupling of the Fe(III) spins and the spin of Fe(II), is close to the range of values reported for  $2\text{FeFd}_{\text{red}}$  ( $-70$  to  $-110 \text{ cm}^{-1}$ ) (17) and to the  $X_\alpha$ -VB calculations on the model compound  $[\text{Fe}_2\text{S}_2(\text{SH})_4]^{3-}$  ( $-76$  to  $-82 \text{ cm}^{-1}$ ) (18).

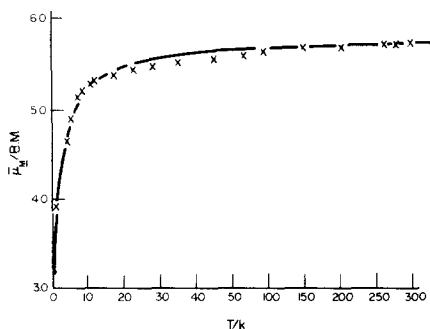


Fig. 1

Comparison of experimental (x) and calculated (—)  $\bar{\mu}_m$  for  $[\text{NET}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$ . Parameters used,  $J = -60 \text{ cm}^{-1}$ ,  $\alpha = 2.956$ ,  $g_{\parallel} = 1.93$ ,  $g_{\perp} = 1.90$ ,  $D = +1.70 \text{ cm}^{-1}$ .

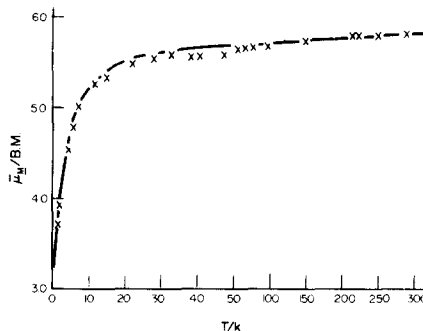


Fig. 2

Comparison of experimental (x) and calculated (—)  $\bar{\mu}_m$  for  $[\text{NET}_4]_3[\text{Fe}_6\text{W}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$ . Parameters used,  $J = -60 \text{ cm}^{-1}$ ,  $\alpha = 2.950$ ,  $g_{\parallel} = 1.95$ ,  $g_{\perp} = 1.92$ ,  $D = +1.75 \text{ cm}^{-1}$ .

TABLE. Comparison of Observed and Calculated  $\bar{\mu}_m$  versus Applied Magnetic Field, H. The Parameters used are those in Figures 1 and 2.

Temp/K	$[\text{NET}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$				$[\text{NET}_4]_3[\text{Fe}_6\text{W}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$			
	4.18		1.96		4.18		2.20	
H/T	$\bar{\mu}_m$ (obs)	$\bar{\mu}_m$ (calc)	$\bar{\mu}_m$ (obs)	$\bar{\mu}_m$ (calc)	$\bar{\mu}_m$ (obs)	$\bar{\mu}_m$ (calc)	$\mu_m$ (obs)	$\mu_m$ (calc)
0.125	4.66	4.66	3.93	3.94	4.53	4.57	3.91	3.96
0.25	4.66	4.66	3.92	3.94	4.55	4.57	3.92	3.96
0.50	4.65	4.66	3.92	3.92	4.51	4.56	3.89	3.94
0.75	4.64	4.64	3.87	3.88	4.50	4.55	3.91	3.91
1.00	4.63	4.63	3.85	3.84	4.49	4.54	3.84	3.87
1.50	4.63	4.59	3.80	3.72	4.48	4.50	3.78	3.78
2.00	4.57	4.54	3.72	3.60	4.42	4.45	3.68	3.67

The magnetic calculations result in the lowest spin-state being  $S' = 1$  for both the molybdenum- and tungsten- containing compounds. The only other spin-state to be significantly thermally populated below 60K is  $S' = 2$  in both cases. For the molybdenum compound the  $S' = 2$  state is  $5.28 \text{ cm}^{-1}$  above  $S' = 1$ , whilst for the tungsten compound  $S' = 2$  is  $6.00 \text{ cm}^{-1}$  above  $S' = 1$ .

The approach to the interpretation of the magnetic properties of cubane-like cluster dimers outlined in this communication seems to be extremely useful and we are currently extending it to other double-cubane clusters. It would also seem worthwhile applying the technique to the  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-,3-}$  clusters for which there appears to be no entirely satisfactory interpretations of the magnetic data (14,19).

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#### REFERENCES

1. G. Christou, C.D. Garner, F.E. Mabbs and T.J. King, J.C.S. Chem. Comm., 740, (1978).
2. G. Christou, C.D. Garner, F.E. Mabbs and M.G.B. Drew, J.C.S. Chem. Comm., 91, (1979).
3. S.R. Acott, G. Christou, C.D. Garner, F.E. Mabbs, T.J. King, and R.M. Miller, Inorg. Chim. Acta., 35, L337, (1979).
4. G. Christou, C.D. Garner, R.M. Miller, and T.J. King, J. Inorg. Biochem., 11, 349, (1979).
5. T.E. Wolff, J.M. Berg, K.O. Hodgson, R.B. Frankel, and R.H. Holm, J. Amer. Chem. Soc., 101, 4140, (1979).
6. T.E. Wolff, J.M. Berg, P.P. Power, K.O. Hodgson, R.H. Holm and R.B. Frankel, J. Amer. Chem. Soc., 101, 5454, (1979).
7. T.E. Wolff, J.M. Berg, P.P. Power, K.O. Hodgson and R.H. Holm, Inorg. Chem., 19, 430, (1980).
8. T.E. Wolff, P.P. Power, R.B. Frankel and R.H. Holm, J. Amer. Chem. Soc., 102, 4694 (1980).
9. G. Christou and C.D. Garner, J.C.S. Dalton Trans., in press.
10. G. Christou, C.D. Garner, T.J. King, C.E. Johnson and J.D. Rush, J.C.S. Chem. Comm., 503, (1979).
11. G. Christou, C.D. Garner and T.J. King, unpublished results.
12. G. Christou, C.D. Garner, R.M. Miller, C.E. Johnson, and J.D. Rush, J.C.S. Dalton Trans., in press.
13. F.E. Mabbs and D.J. Machin, "Magnetism and Transition Metal Complexes", Chapman and Hall, London, 1973, Chapter 7.
14. E.J. Laskowski, J.G. Reynolds, R.B. Frankel, S. Foner, G.C. Papaefthymiou and R.H. Holm, J. Amer. Chem. Soc., 101, 6562, (1979).
15. G.B. Wong, M.A. Bobrik and R.H. Holm, Inorg. Chem., 17, 578, (1978).
16. W.O. Gillum, R.B. Frankel, S. Foner and R.H. Holm, Inorg. Chem., 15, 1095, (1976).
17. H. Blum, F. Adar, J.C. Salerno and J.S. Leigh Jr. Biochem. Biophys. Res. Commun. 77, 650, (1977).
18. J.G. Norman Jr., P.B. Ryan, L. Noodleman, J. Amer. Chem. Soc., 102, 4279, (1980).
19. E.J. Laskowski, R.B. Frankel, W.O. Gillum, G.C. Papaefthymiou, J. Renaud, J.A. Ibers, and R.H. Holm, J. Amer. Chem. Soc., 100, 5322, (1978).