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Spin–spin exchange interactions in a binuclear tetra-pivalate bridged manganese(II) complex

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The magnetic properties of a Mn^{II} dimer $L_2Mn_2(\mu\text{-OOCCMe}_3)_4$ (L = 2,6-diaminopyridine) can be correctly described with allowance for isotropic bilinear ($-2J_1$ = 16.5 cm^{-1}) and biquadratic ($-2J_2$ = 0.49 cm^{-1}) exchange, the latter crucially influencing the magnetic susceptibility in the whole temperature range.

Exchange interactions in polynuclear and supramolecular systems containing transition metal atoms are of considerable interest because the exchange parameters depend on the electronic structure of complexes[1] and play a determining role in the formation of high-spin ground states of a new class of magnetic materials, molecular magnets.[2] From the standpoint of simplicity and reliability of interpretation of experimental data on the magnetic properties, it is most appropriate to study binuclear complexes. Among them are 3*d* metal carboxylates $LM(\mu\text{-OOCR})_4ML$ with the famous four-bridged structure. It is the class of compounds whose investigation led to a model of exchange channels,[1–3] which predicts changes in the exchange parameters within a series of isostructural complexes. However, the magnetic properties of binuclear Mn^{II} tetracarboxylates can be poorly interpreted in terms of the Heisenberg model, the exchange parameters obtained being strongly different from those predicted by the model of exchange channels.[4,5]

Here, we report on high-precision studies of the magnetic properties of the binuclear complex $L_2Mn_2(\mu\text{-OOCCMe}_3)_4$ (L = = 2,6-diaminopyridine), which was obtained as a solvate containing four acetonitrile molecules (Figure 1) and structurally characterised earlier.[5]

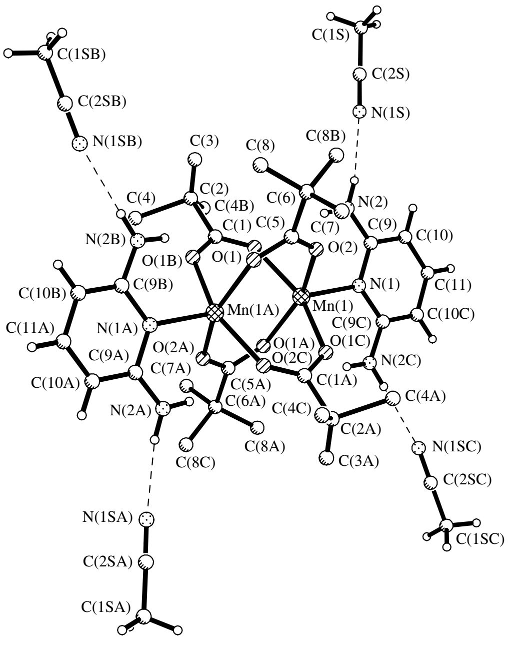

Figure 1 Structure of the $L_2Mn_2(\mu\text{-OOCCMe}_3)_4\cdot 4MeCN$ solvate (L = = 2,6-diaminopyridine).

To improve the reliability of experimental data interpretation, the static magnetic susceptibility χ was measured at 2–300 K using powders prepared from specially grown single crystals (MPMS-5S Quantum Design SQUID magnetometer, H = 5 kOe).

The experimental values of the effective magnetic moment, $\mu_{\text{eff}} = (8\chi T)^{1/2}$, per mole of binuclear molecules are plotted *vs.* temperature in Figure 2. At T ~ 300 K, $\mu_{\text{eff}} > 7\mu_B$ (Bohr magneton, $\mu_B = 4.668\cdot 10^{-5}$ cm^{-1} Gs^{-1}).[1] This means that Mn^{II} atoms in the binuclear molecules are in the high-spin state with $S_a = S_b = 5/2$. As the temperature decreases, μ_{eff} rapidly decreases owing to strong antiferromagnetic interactions.

The magnetic properties of this system can be described by the spin Hamiltonian

$$\hat{H} = -2J_1(\hat{S}_a\hat{S}_b) - 2J_2(\hat{S}_a\hat{S}_b)^2 + g\mu_B(\hat{S}_{za} + \hat{S}_{zb})H_z, \qquad (1)$$

where $\hat{S}_a$, $\hat{S}_b$ are the spin operators of the centres *a* and *b*, respectively; $-2J_1$ and $-2J_2$ are the parameters of bilinear and biquadratic exchange, respectively; *g* is the isotropic *g*-factor ($g = 2$) because the metal ions are in the high-spin state $^6A_1$[1] and H_z is the external magnetic field strength. Accurate to an insignificant shift of the energy origin, the solution to the exchange part of this spin Hamiltonian has the form[1]

$$E(S) = [-J_1 + 2S_a(S_a + 1)J_2]S(S + 1) - 1/2J_2S^2(S + 1)^2, \qquad (2)$$

where $S = S_a + S_b, S_a + S_b - 1, \ldots, |S_a - S_b|$ (=0).

This allows us to calculate the magnetic susceptibility using the relationship[1]

$$\chi(\mathrm{T,S}) = \frac{N_\mathrm{A}g^2\mu_\mathrm{B}^2}{3kT}\,\frac{\sum_S S(S+1)(2S+1)\exp[-E(S)/kT]}{\sum_S(2S+1)\exp[-E(S)/kT]}, \qquad (3)$$

$$\mu_\mathrm{ee} = (3kT/N\beta^2)^{1/2},$$

where N_A is Avogadro's number and k is the Boltzmann constant.

Relationship (3) is valid for an ideal binuclear molecule. The expression for the susceptibility χ^t of a real molecule also allows for the influence of intermolecular exchange interactions[1] and includes a correction for the monomer impurity. The parameters of the model were determined by numerical minimization of an error functional

$$\sigma = \sqrt{1/N\textstyle\sum_i[(\chi_i^t - \chi_i^e)/\chi_i^e]^2}, \qquad (4)$$

where summation is performed over all temperature points at which the magnetic susceptibility χ_i^e was measured, and N is the number of points.

According to calculations, ignoring biquadratic exchange leads to $\sigma > 0.2$, which exceeds the experimental error by an order of magnitude. At the same time, taking into account bilinear ($-2J_1 = 16.5$ cm^{-1}) and biquadratic ($-2J_2 = 0.49$ cm^{-1}) exchange only allows good agreement between theory and experiment ($\sigma = 0.045$) to be achieved (see Figure 2).

The fact that $-2J_2 > 0$ ($-2J_2 \sim 0.05|-2J_1|$) indicates that the predominant contribution to this parameter is made by the exchange striction mechanism[6,7] rather than Coulomb interactions. This conclusion was first reported[8] based on the analysis of a great body of high-precision experimental data obtained for various high-spin systems. From relationship (2), it follows that this type of biquadratic exchange strongly renormalises the bilinear exchange parameter $-2J_1$ toward a weakening of antiferromagnetism. At the same time, the term $-1/2J_2S^2(\mathrm{S}+1)^2$ strongly shifts the high-spin states upward along the energy scale. Therefore, biquadratic exchange generally precludes the stabilization of high-spin ground states.

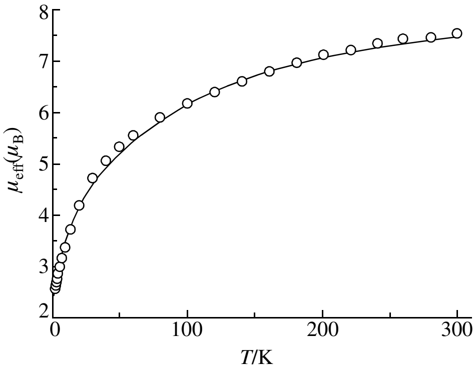

Figure 2 Experimental values (open circles) and calculated best fit curve $\chi(T)$ (solid line) for binuclear Mn$^\mathrm{II}$ pivalate obtained with $-2J_1 = 16.5$ cm^{-1} and $-2J_2 = 0.49$ cm^{-1}; $\sigma = 0.045$.

Analysis of the parameter $-2J_1 = 16.5$ cm^{-1} shows that, according to the model of exchange channels,[1–3] we obtain:

$$-2J_\Sigma = -2J_1\times 4S_aS_b = 16.5\ \mathrm{cm}^{-1}\times 25 = 412\ \mathrm{cm}^{-1} = \textstyle\sum_{ij} -2J(i,j), \qquad (5)$$

where summation is performed over all pairs of unpaired electrons of the centres a and b ($i \in a, j \in b$). As can be seen, the experimental antiferromagnetic exchange energy is lower than (even) one of five antiferromagnetic contributions ($i = j$) $-2J(xy,xy) = 1000$ cm^{-1}.[1,3] This means that in Mn$^\mathrm{II}$ carboxylates among the cross-contributions [$-2J(i,j)$ with $i \neq j$] there are also large ferromagnetic contributions. Therefore, we can expect that heteronuclear or heterovalent dinuclear carboxylates characterised by the absence of contributions of the type $-2J(xy,xy)$ can possess strong ferromagnetism.

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References

1 Yu. V. Rakitin and V. T. Kalinnikov, *Sovremennaya magnetokhimiya* (*Modern Magnetochemistry*), Nauka, St. Petersburg, 1994 (in Russian).
2 V. T. Kalinnikov, Yu. V. Rakitin and V. M. Novotortsev, *Usp. Khim.*, 2003, **72**, 1123 (*Russ. Chem. Rev.*, 2003, **72**, 995).
3 Yu. V. Rakitin, V. T. Kalinnikov and M. V. Eremin, *Theor. Chim. Acta*, 1977, **45**, 167.
4 V. M. Novototsev, Yu. V. Rakinin, A. A. Pasynskii and V. T. Kalinnikov, *Dokl. Akad. Nauk SSSR*, 1978, **240**, 355 [*Dokl. Chem.* (*Engl. Transl.*), 1978, **240**, 220].
5 M. A. Kiskin, I. G. Fomina, G. G. Aleksandrov, A. A. Sidorov, V. M. Novotortsev, Yu. V. Rakitin, Zh. V. Dobrokhotova, V. N. Ikorskii, Yu. G. Shvedenkov, I. L. Eremenko and I. I. Moiseev, *Inorg. Chem. Commun.*, 2005, **8**, 89.
6 C. Kittel, *Phys. Rev.*, 1960, **120**, 335.
7 J. C. M. Henning, *Phys. Rev.*, 1971, **B3**, 3852.
8 A. E. Nikiforov, A. N. Men' and V. I. Cherepanov, *Spektroskopiya kristallov* (*Spectroscopy of Crystals*), Nauka, Moscow, 1975, p. 72 (in Russian).

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