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The first unequivocally ferromagnetically coupled squarato complex: origin of the ferromagnetism in an interlocked 3D Fe(II) system

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Received (in Cambridge, UK) 21st February 2003, Accepted 1st May 2003
First published as an Advance Article on the web 16th May 2003

An unprecedented interlocked 3D Fe(II) system, [Fe(squarate)(bpy)(2H_2O)]·3H_2O, 1 (bpy = 4,4′-bipyridine), the first unequivocally ferromagnetically coupled squarato complex to be reported, has been synthesised and magnetically characterized.

The coupling through a squarate bridging ligand is essentially antiferromagnetic.[1] To date, only one μ-squarato bridged copper(II) system showing ferromagnetic coupling has been tentatively reported,[2] but the presence of other bridging ligands makes it impossible to state the unequivocal character of this coupling. With Fe(II) only two complexes have been reported, *i.e.* [$Fe(C_4O_4)(H_2O)_2$][3] and $Fe(C_4O_4)\cdot 4H_2O$,[4] without magnetic interaction *via* squarate bridges. The electronic ground state of Fe(II) complexes is orbitally degenerate ($^4T_1$). The magnetism of their polynuclear complexes is an open problem for which no general solution is available.[5] In the present contribution we report synthesis†, crystal structure determination‡ and the first observation of an unequivocal ferromagnetic interaction in an unprecedented interpenetrated 3D Fe(II)–squarate system along with the origin of ferromagnetism.

The X-ray structural determination evidences a 2D network of Fe(II) ions connected by (μ-O,O′) squarate dianions and 4,4′-bipyridine ligands. The rectangular grid layer (4,4 topology), of dimensions 8.099(2) and 11.610(2) Å along squarate and bpy spacer, respectively, is shown in Fig. 1. The metal ion completes a distorted hexacoordination sphere through two water molecules which form intra-layer hydrogen bonds with O(2) and with a symmetry related one of an interpenetrated layer (O(2″), Fig. 2).

Considering the equatorial O_4 coordination plane, the squarate anion is bent to form a dihedral angle of 22.4(3)°, likely to favour hydrogen bond formation with the coordinated water, while the py rings are essentially perpendicular [85.3(2)°]. The (4,4) nets show inclined interpenetration to form an interlocked 3D structure (Fig. 3).

The lattice water molecules are clathrated between the layers forming H-bonding chains with a rhombohedral motif running along axis *c*, parallel to the -(squarate)-Fe- polymer. In fact, O(2w), located on a crystallographic two-fold axis, is involved in a quadruple hydrogen bonded module (double donor and acceptor hydrogen bonding) connecting molecules O(3w). On the other hand, the latter is anchored to oxygen O(1) of the squarate anion (Fig. 2).

The $\chi_M T$ product measured under a magnetic field of 0.1 T is depicted in Fig. 4. Without considering the decreasing at very low temperature (which can be due to either the *D* parameter of Fe(II) or intermolecular interactions) the shape of the curve from r.t. to 13 K is indicative of ferromagnetic coupling. In order to

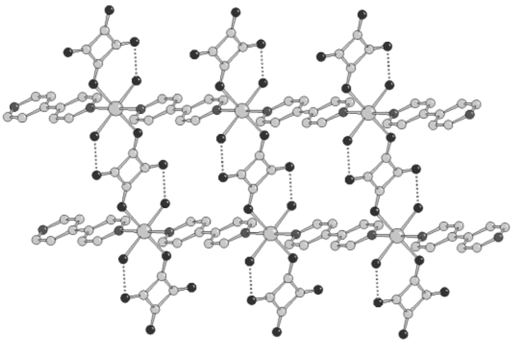

Fig. 1 View of the layered structure with H-bonds indicated by dotted lines.

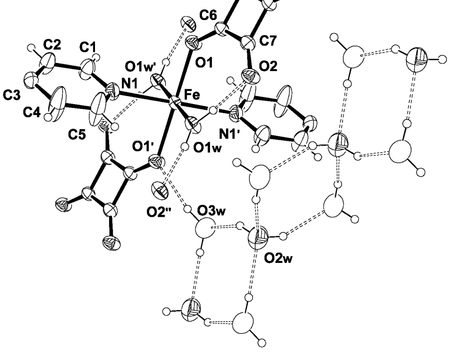

Fig. 2 ORTEP drawing (40% thermal ellipsoids) of the iron coordination sphere and of the H-bond pattern involving uncoordinated water molecules O2w (octant shading) and O3w (boundary ellipsoids). Selected bond lengths (Å) and angles (°): Fe–O(1) 2.145(2); Fe–O(1w) 2.087(2); Fe–N(1) 2.246(3); O(1)–Fe–O(1w) 93.4(1); O(1)–Fe–O(1w′) 86.6(1); O(1)–Fe–N(1) 92.6(1); O(1)–Fe–N(1′) 87.4(1); O(1w)–Fe–N(1) 91.5(1); O(1w)–Fe–N(1′) 88.5(1); O(1w)···O(2) 2.639(3); O(1w)···O(2″) 2.717(4); O(3w)···O(1) 2.869(5); O(2w)–H···O(3w) 2.781(6); O(3w)–H···O(2w) 2.806(5). Fe located on a centre of symmetry.

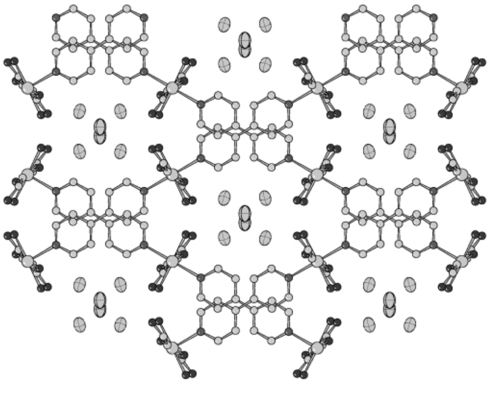

Fig. 3 View of the 3D architecture of the inclined interpenetration of sheets down axis *c*. Lattice water molecules are indicated as ellipsoids.

DOI: 10.1039/b302076b

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evaluate the exchange coupling constant, J, the Fisher formula for a linear chain with $S = 2$ (classical spin) is used from r.t. to 35 K.[6] The best fit parameters are $J = 0.81 \pm 0.3$ cm^{-1} and $g = 2.25 \pm 0.01$. In a second approach a cyclic ring of six Fe(II) has been considered, using the CLUMAG program.[7] The best fit parameters are $J = 0.77 \pm 0.3$ cm^{-1} and $g = 2.25 \pm 0.01$. Finally, by using the approach made by Clemente-Juan *et al.*[8] and a simulation with the MAGPACK program,[9] in the whole range of T, the best results are $J = 0.8$ cm^{-1}, $D = 8$ cm^{-1} and $g = 2.25$. The values of g and D agree with those reported previously for other Fe(II) complexes.[8,10]

Complex **1** is thus the first unequivocally ferromagnetically coupled complex with a squarate bridging ligand but no ferromagnetic long range ordering is observed in it. To understand the origin of this ferromagnetism, we have carried out EHMO calculations of the real structure with the CACAO program[11] assuming a dinuclear system. The magnetic orbitals with unpaired electrons give degenerate molecular orbitals, allowing us to conclude that there is no overlap which can create any antiferromagnetic pathway. To avoid the inconveniences of the real structure, we have calculated EHMO from an ideal molecule moving the C–O–Fe angle from 180° (linear) to 130° (the real angle is close to 131°).

The Walsh diagram of the t_{2g} orbitals is shown in Fig. 5(a) (the e_g orbitals, not shown, are almost exclusively Fe(II) orbitals and degenerate). It is important to underline that in this MO calculation there are not six molecular orbitals ($3t_{2g} \times 2$ iron atoms) but eight due to the contribution of the corresponding orbitals of the squarate bridging ligand. Some interesting conclusions can be drawn:

i) The $1b_g$ and $2a_u$, corresponding to $(d_{xy} \pm d_{xy})$ combinations respectively, are degenerate with the atomic coefficients of the C and O atoms of the squarate equal to zero.

ii) The $1a_u$, $2b_g$ and $3a_u$ MO's are the $(d_{yz} \pm d_{yz})$ combinations. These orbitals, in the case of Fe(II), are filled, thus they do not participate in the magnetic coupling.

iii) The most important orbitals are $1a_g$, $3a_u$, $2a_g$ which participate in the symmetric and antisymmetric combinations of the d_{xz} atomic orbitals $(d_{xz} \pm d_{xz})$ respectively (Fig. 5).

In Fig. 5(b) only the central parts of $1a_g$ and $2a_g$ MO orbitals are drawn: in the $1a_g$, the contribution of the C atoms decreases when the C–O–Fe angles lose their linearity but, in contrast, this contribution increases in the orbital $2a_g$. Thus, in $1a_g$ the global overlap is reduced and the orbital is destabilized, whereas in $2a_g$ the overlap increases and, thus, the orbital is stabilized. In the case of Fe(II) this feature will be favourable for the ferromagnetism. At 130°, the magnetic orbitals ($1a_g$, $2a_g$ and $1b_u$) are, thus, almost degenerate and the participation of the O and C atoms of the squarate bridge is very high. These two factors can create ferromagnetic coupling. According to Fig. 5, assuming unpaired electrons in the d_{yz} orbitals, the coupling would likely be antiferromagnetic: this is the case for the Fe(III) complex (d^5) reported in the literature.[12] In conclusion, new efforts are necessary to synthesize analogous Fe(II) complexes with a squarate bridging ligand for rationalising this possibility of ferromagnetism. Furthermore, the syntheses and magnetic studies of analogous Fe(III), Mn(II), Co(II) and Ni(II) complexes would be very interesting for a general comparison, taking into account the different occupation of the magnetic orbitals.

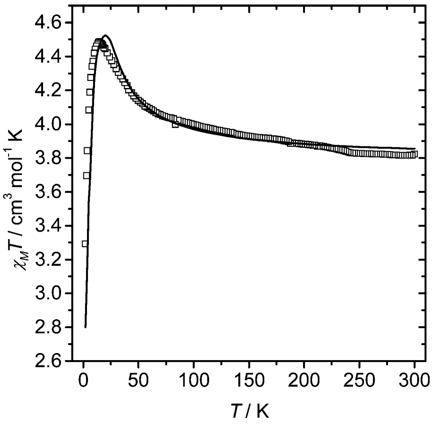

Fig. 4 The temperature dependence of $\chi_M T$ for complex **1**.

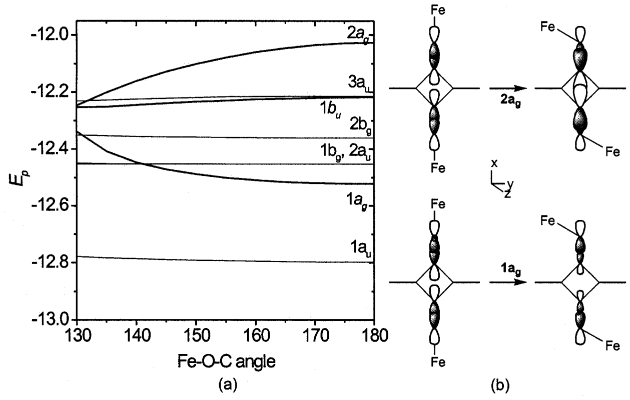

Fig. 5 Walsh diagram for t_{2g} orbitals and schematic drawing of the two most important orbitals.

Notes and references

† A methanolic solution (10 mL) of bpy (1 mmol, 0.156 g) was layered very slowly on an aqueous solution (10 mL) of a mixture of ferrous ammonium sulfate hexahydrate (1 mmol, 0.393 g) and dilithium squarate (1 mmol, 0.128 g). Brown crystals suitable for X-ray analysis were obtained after a few weeks at the junction of the two layers.

‡ Crystal data: $C_{14}H_{18}FeN_2O_9$, $M = 414.15$, monoclinic, space group $C2/c$, $a = 20.198(4)$, $b = 11.456(3)$, $c = 8.099(2)$ Å, $\beta = 109.07(2)°$, $V = 1771.2(7)$ Å^3, $Z = 4$, $D_c = 1.553$ g cm^{-3}, μ(Mo-Kα) = 0.902 mm^{-1}, $F(000) = 856$. θ range for data collection 3.09 to 28.60°. Final $R = 0.0502$, $wR2 = 0.1358$, $S = 1.123$ for 135 parameters and 4065 reflections, 2119 unique [R(int) = 0.0266], of which 1757 with $I > 2\sigma(I)$, max. positive and negative peaks in ΔF map 0.750 and -0.720 e Å^{-3}. CCDC reference number 203690. See http://www.rsc.org/suppdata/cc/b3/b302076b/ for crystallographic files in .cif or other electronic format.

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