β''-(bedt-ttf)$_4$[(H$_2$O)Fe(C$_2$O$_4$)$_3$]·PhCN: The First Molecular Superconductor containing Paramagnetic Metal Ions

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β''-(bedt-ttf)$_4$[(H$_2$O)Fe(C$_2$O$_4$)$_3$]·PhCN [bedt-ttf = bis(ethylenedithio)tetrathiafulvalene] is a superconductor [T_c 8.5(3) K]; from 9–300 K its magnetic susceptibility is dominated by the high-spin Fe^{III} and obeys the Curie–Weiss law (C = 4.375 emu K mol^{-1}, θ = −0.2 K).

Superconductivity and magnetism are intimately bound up with one another.[1] Superconductors whose lattices sustain magnetic moments have therefore been eagerly sought to explore the physics arising from the interplay of these phenomena. In the few cases that have been identified to date,[2] superconductivity is found in the presence of largely noninteracting 4f moments. The latter are examples of continuous lattice compounds but there has been strong interest in superconductors based on molecular units because of the possibility that the mechanism of Cooper pair formation might be different from that in more conventional compounds. We have now synthesised the first organic molecular superconductor containing localised magnetic moments within its structure: β''-(bedt-ttf)$_4$[(H$_2$O)-Fe(C$_2$O$_4$)$_3$]·PhCN [bedt-ttf = bis(ethylenedithio)tetrathiafulvalene] is also the first stoichiometric superconductor of any kind in which such moments arise from 3d rather than 4f electrons.

Numerous superconducting molecular charge transfer salts $D_xA_yS_z$ are known where D is an organo-chalcogen donor molecule, A is an inorganic or organic anion and S (not always present) is a molecule of solvent.[3,4] Within this class the highest T_c currently known is 12.5 K.[5] A significant feature of the structures of these compounds is that the D and A molecular building blocks are segregated into alternate layers. Our strategy for making a magnetic molecular superconductor has therefore been to prepare bedt-ttf salts with transition metal complexes as anions.[6]

Crystals of the title compound were grown electrochemically from bedt-ttf in an H-shaped cell at a current of 1 μA using wet benzonitrile as solvent and (NH$_4$)$_3$Fe(C$_2$O$_4$)$_3$·3H$_2$O as the supporting electrolyte. Crystals adhering to the Pt anode were of two phases, plates and needles. The plate-like phase was identified as (bedt-ttf)$_4$[(NH$_4$)Fe(C$_2$O$_4$)$_3$]·PhCN isostructural with the corresponding K salt whose structure has been determined.[7] It is a semiconductor (σ_{RT} = 10^{-5} S cm^{-1}, E_A = 0.14 eV).

In contrast, four-probe AC (15–33 Hz) resistance measurements on several single crystals of the needle phase indicate metallic behaviour (σ_{RT} = 10^2 S cm^{-1}) from room temperature to 8.5(3) K, where the resistance falls to zero (Fig. 1). The superconducting transition, which has been observed in several crystals is sharp [width 0.2(1) K] and exhibits no hysteresis within the limits of the temperature controller (± 0.1 K). Magnetoresistance measurements were also carried out: applying a magnetic field of 0.7 T parallel to the long axis of the needle, also parallel to the current direction, at 2 K destroys superconductivity (Fig. 1, inset). Normal metallic conductivity is restored with an applied field of 0.1 T perpendicular to the needle.

The quantity of crystals obtained from the electrochemical synthesis was not sufficient to carry out elemental analysis so the formula of the compound was derived from its crystal structure as (bedt-ttf)$_4$[(H$_2$O)Fe(C$_2$O$_4$)$_3$]·PhCN.[8] The salient features of the structure are alternate layers of bedt-ttf cations and layers consisting of Fe(C$_2$O$_4$)$_3$$^{3-}$, PhCN and H$_2$O (Fig. 2). The molecular packing within the bedt-ttf layers resembles that of the metallic β''-phase (bedt-ttf)$_2$X,[9] where X is a linear triatomic anion such as AuBr$_2$$^-$ and ICl$_2$$^-$ and the pressure induced superconductor, (bedt-ttf)$_3$Cl$_2$·2H$_2$O.[10] The tris(oxalato)iron(III) anions are arranged in a triangular two-dimensional array with their trigonal axes perpendicular to the layer. They are separated by H$_2$O linked by hydrogen bonds to the O atoms of the oxalate ions that are not coordinated to the Fe. The

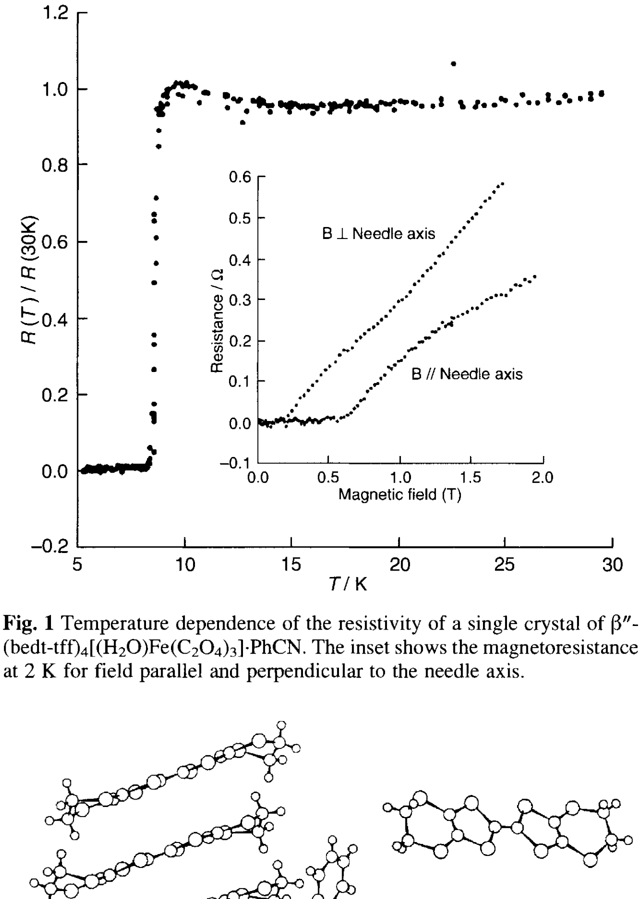

Fig. 1 Temperature dependence of the resistivity of a single crystal of β''-(bedt-ttf)$_4$[(H$_2$O)Fe(C$_2$O$_4$)$_3$]·PhCN. The inset shows the magnetoresistance at 2 K for field parallel and perpendicular to the needle axis.

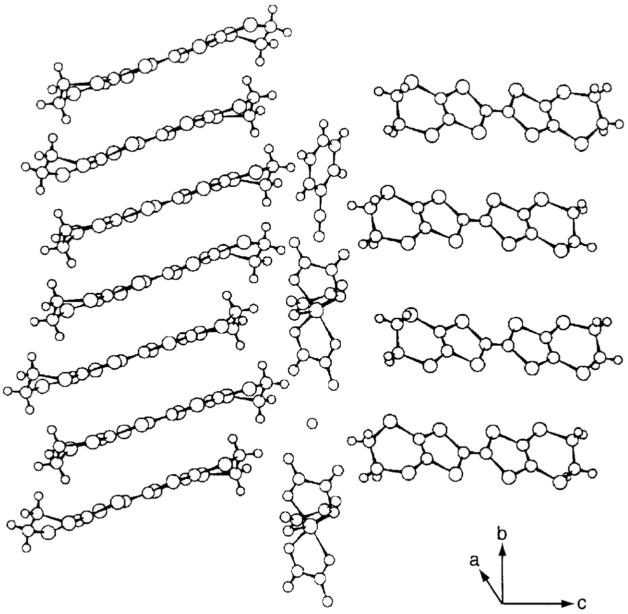

Fig. 2 Molecular arrangement in the crystal, showing the separation of the organic layers by the inorganic ones

whole forms a hexagonal lattice very similar to that found in bimetallic tris(oxalate) salts with organic cations such as $NBu^n_4{}^+$ whose unusual magnetic properties have recently been of great interest.[11] The solvent of crystallisation occupies a hexagonal cavity in the $[Fe(C_2O_4)_3{\cdot}(H_2O)]$ layer.

The magnetic susceptibility of a polycrystalline sample of the superconducting phase was determined as a function of temperature from 2 to 300 K and applied field up to 7 T using a Quantum Design MPMS-7 SQUID magnetometer. After correcting for core diamagnetism, the excess molar susceptibility measured at 10 mT is the sum of two terms, a temperature independent paramagnetic part amounting to 0.002 $cm^3\ mol^{-1}$ and one obeying the Curie–Weiss Law from 300 to 9.4 K with a Weiss constant $\theta = -0.2$ K indicating weak antiferromagnetic interaction between the Fe^{III} moments. The magnitude of the Pauli paramagnetism is comparable to that of other metallic bedt-ttf salts. The Curie constant was $C = 4.375$ emu K mol^{-1} as expected for high-spin Fe^{III} [$3d^5$, ground state ^6A (D_3)]. On cooling a polycrystalline sample in zero applied field and measuring the temperature dependence of the magnetization in fields of 0.5 mT from 2 to 20 K the response is diamagnetic below 8 K, marking the onset of superconductivity (Fig. 3). At higher field the high susceptibility of the Fe centre obscures the transition. The susceptibility measured in applied fields greater than 0.1 T obeys the Curie–Weiss law down to 2 K with a temperature independent paramagnetic term showing that superconductivity has been suppressed.

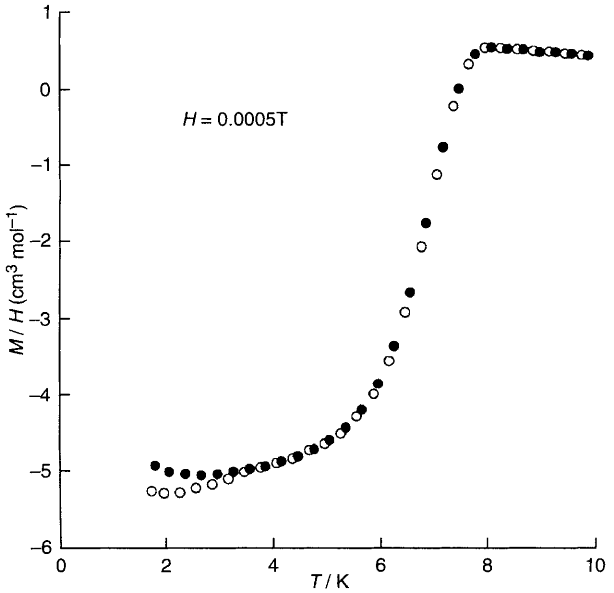

Fig. 3 Temperature dependence of the magnetization. Filled circles are zero-field cooled data and open circles are field cooled data.

Lower temperature studies will be needed to determine what (if any) the effect of long-range magnetic ordering may be. (In a preliminary experiment down to 20 mK the sample remained superconducting[12]). In conclusion, we have prepared the first molecular superconductor with localised magnetic moments embedded in its lattice. Our result points the way, not only to further experiments on the interplay of superconductivity and magnetism, but to a synthetic strategy for obtaining further magnetic molecular superconductors.

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