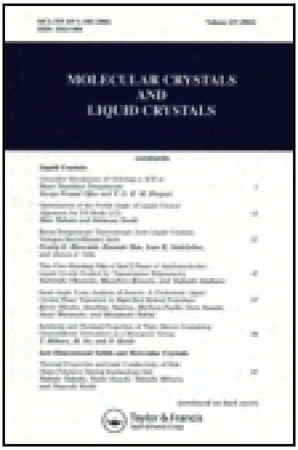

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Unusual Solid State Properties of Transition Metal Complexes of Sulphur-Donor Ligands

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UNUSUAL SOLID STATE PROPERTIES OF TRANSITION METAL COMPLEXES OF SULPHUR-DONOR LIGANDS

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Abstract Metal complexes of 1,2 dithiolene ligands are known to exhibit unusual solid state properties. The properties of the Mercury complexes of the new type of 1,2 dithiolene ligand which includes the TTF molecule framework is described. The structure and magnetic properties of the ferromagnet $NH_4[Ni(mnt)_2].H_2O$ are discussed.

INTRODUCTION

Transition metal complexes of 1,2-dithiolenes have been extensively studied for over thirty years.[1,2] This interest is based on the properties that arise through the delocalised π-MOs on the ligand and the ability of the metal d-orbitals to participate in this bonding. This class of compound is characterised by a number of properties which can be utilised in the development of new materials. They are :

(a) Their ability to exist in several well defined, but interconvertible oxidation states. Interchanged between the so-called neutral, mono- and di-anionic species can be achieved by either chemical or electrochemical methods.

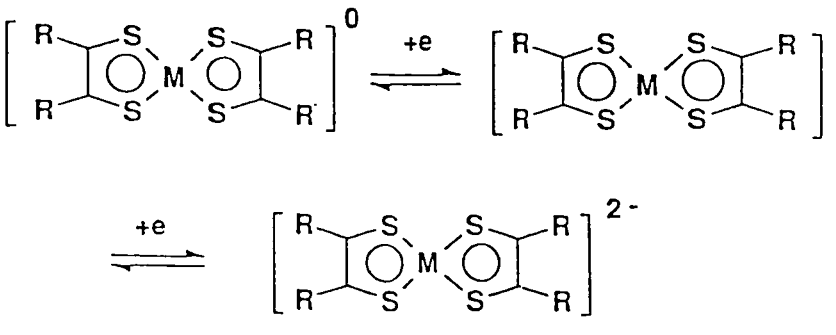


FIGURE 1 The Interconvertible oxidation states of metal dithiolenes

(b) The presence of an intense low energy absorption band corresponding to the HOMO ($2b_{1u}$) to LUMO ($3b_{2g}$) transition.

(c) The presence of an unpaired-electron in the delocalised LUMO in the mono-anion salt.

(d) The ability to tune both the redox behaviour and the position of the low energy HOMO to LUMO transition by substitution on the ligand of electron-withdrawing or electron-donating groups and by changing the central metal.[2]

In the solid state the individual metal 1,2-dithiolene molecules or ions can give rise to solid state effects through interactions of the delocalised π-MOs on the molecules facilitated by the large sulphur atoms. Consequently, the S...S inter-molecular interactions are very important in this class of compound. Molecular conductors and superconductors can arise if the metal 1,2-dithiolene molecules are suitably arranged within the crystal lattice in such a way that the π-MOs intend to give rise to a delocalised band structure.[3] Partial application of the band structure can arise through the average charge on the anion being intermediate between 0 and 2. This is brought about by an appropriate stoichiometry arising through the presence of counter cations in the lattice. The size and shape of the counter cations can play a crucial role in determining the intermolecular contacts between the 1,2-dithiolenes and hence can affect the electrical conduction properties.

The presence of unpaired electrons on the anions can result in cooperative magnetic properties for the solids. The mono-anionic salts exhibit a range of magnetic properties including those associated with singlet-triplet behaviour based upon the presence of dimeric species within the lattice and, in one instance, a molecular ferromagnet (see later).

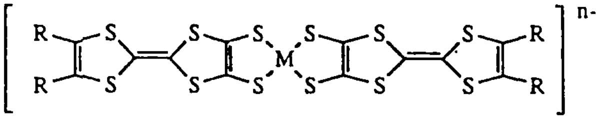
The presence of the intense low-energy absorption band in the molecular species has been targeted for applications in the area of third-order non linear optical materials. The possibility of tuning the edge of the absorption band to optical communication wavelengths was considered to give the opportunity for resonance-enhanced third order effects.[4]

A discussion of some of the these areas of interest follows.

Results and Discussion

1. Metal Complexes of TTF containing Ligands

One of the most extensively studied 1,2-dithiolene ligands is 1,3-dithiole-2-thione-4,5 dithiolate(dmit) and salts of the form $A[M(dmit)_2]_2$ where A is a group 1 metal cation, a closed shell organic cation such as NMe_4^+, or an open shell organic cation such as TTF^+ often exhibit metallic properties.[3] We and other workers in the field have recently developed routes to TTF dithiolates which can be used as ligands for metal complexes which contain the TTF moiety and can be regarded as ligands with an extended dmit system [see (1)].[5,6] Metal complexes of these ligands should therefore have an increased potential for intermolecular orbital overlap which could lead to enhanced conduction properties.



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In addition, the presence of three potential redox-active centres within the same molecule, i.e. the MS_4 core and the two TTF fragments on the ligands, could give rise to multi-state properties in this class of compound. The preparation of the metal anionic complexes of the type $[M(dttfdt)_2]^{2-}$ were made using substituted bis(cyanoethylthio)TTFs using the method of Becher *et al.*[6] The preparation of the metal complexes have been reported.[7]

The mercury complex was isolated as the di-anionic compound with MeN^+ as the counter-cation. Two forms of the ligand were investigated in which the R group was either ethyl or butyl.

Orange plate shaped crystals of $[MeN]_2[Hg(dttfdt)_2]$ (where R = Et) were obtained by the slow diffusion of diethyl ether into an acetone solution of the salt. The X-ray structure of the salt shows a structure to consist of discrete anions and tetramethyl ammonium cations.

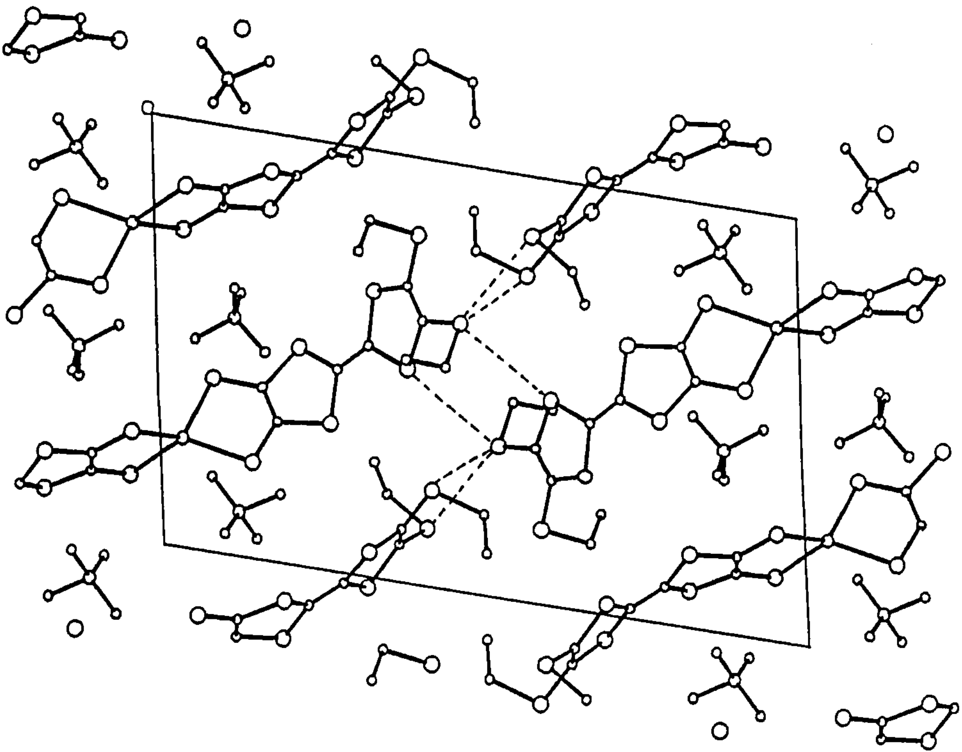

FIGURE 2 Packing diagram for $[Me_4N]_2[Hg(C_{10}H_{10}S_8)_2]$

The mercury atom is approximately tetrahedrally coordination with Hg-distances 2.517(4) - 2.565(4) Å and the S-Hg-S angle within the five membered ring is 88.4° (Av), slightly smaller than the idealised tetrahedral value. The two TTF units in the anion are non-planar with one exhibiting a deviation from planarity of 37.9° and the other 50.7°. These deviations are probably due to packing effects due to adjacent TTF units lying orthogonal to each other and establishing short intermolecular S.....S distances.[7]

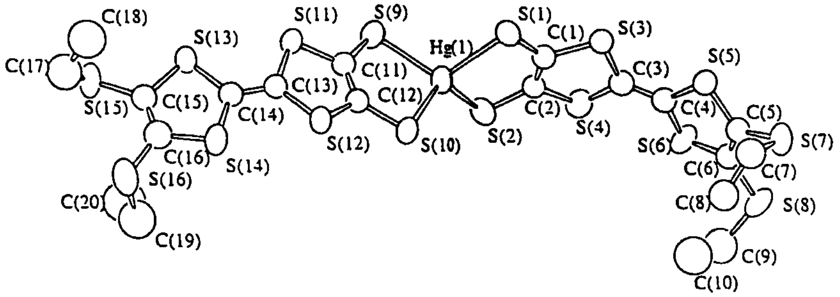

FIGURE 3 Structure of $[Hg(C_{10}H_{10}S_8)_2]^{2-}$

The electrochemical properties of the salt were studied by cyclic voltammetry in dichloromethane and in acetonitrile. In dichloromethane CV reveals four oxidation processes with mid-points at -0.4 V, +0.07 V, +0.76 V and +1.09 V versus SCE and the peak heights are 1:1:2:1 respectively. The peaks at 0.04 V and +0.07 V have been shown to be due to 1-electron oxidations and the third wave has been assigned to the second oxidation of each of the two TTF units within the complex. In acetonitrile solution the first two peaks observed in dichloromethane give rise to a single peak at -0.54 V versus Ag/Ag^+.

The single 2-electron oxidation of the salt in acetonitrile and the very small separation between the first two 1-electron processes in dichloromethane show that the oxidation of the first TTF group does not significantly affect the oxidation of the second TTF group. This indicates the absence of interaction between the two TTF groups. This can be understood in terms of the orthogonal nature of the two ligands about the tetrahedrally coordinated Hg atom.

In acetonitrile solution $[Me_4N]_2[Hg(dttfdt)_2]$ (R = Et) can be oxidised by I_2 to give a brown precipitate of the neutral complex $[Hg(dttfdt)_2]$ (R = Et). The ESR spectrum of this precipitate exhibits a singlet with a g value of 2.0052 consistent with radicals localised on the two TTF units suggesting that the coordination about the Hg atom in the neutral compound is tetrahedral and similar to that observed in the dianion.

Electrical conduction studies on compressed pellets of powdered Hg exhibited an electrical conductivity of 10^{-5} Scm^{-1} at room temperature compared with a conductivity of $<10^{-7}$ Scm^{-1} at room temperature for the dianion salt. It might be expected therefore that high conductivities may be observed for metal complexes in which the coordination about the central metal atom is square coplanar and therefore studies of the corresponding Ni and Pd complexes are in progress.

2. $NH_4[Ni(mnt)_2].H_2O$ - a novel molecular magnet

Complexes of the type $A[Ni(mnt)_2]$ which form segregated stacks of the anion and cation are usually found to be dimerised, anti-ferromagnetic and electrical insulators. These include the group 1 cation salts. However, the ammonium salt was investigated by Isset *et al* and by Underhill and Clemenson and shown to exhibit anti-ferromagnet interactions.[8,9] However, more recently samples of this compound have shown ferromagnet exchange at low temperatures.[10]

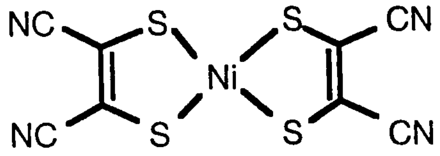

FIGURE 4 Molecular structure $[Ni(mnt)_2]^-$

The structure of this salt shows that the $[Ni(mnt)_2]^-$ anions are arranged in a one-dimensional stack. Unusually, the room temperature structure shows that the separation of the molecules in the stack is equidistant. This is unusual as the monoanions usually show a strongly dimerised structure with either metal over metal or metal over sulphur arrangements.

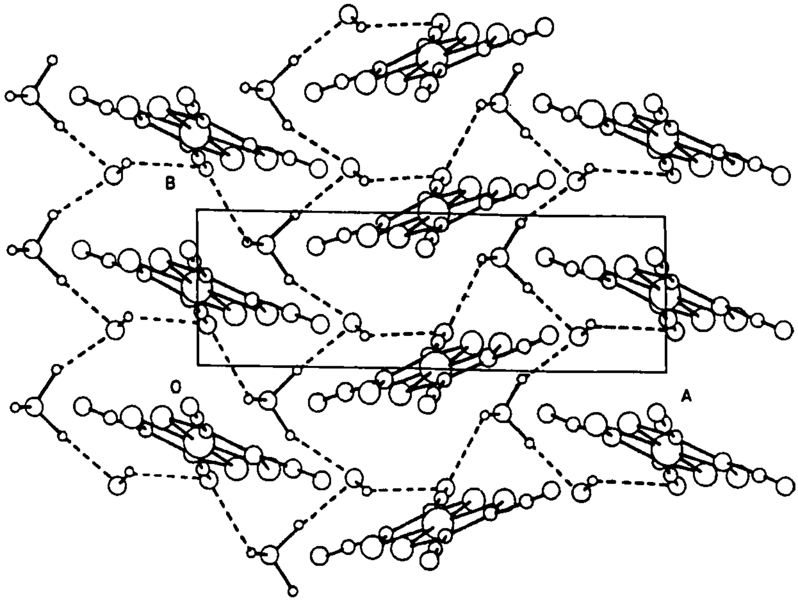

FIGURE 5 A view down the *c* axis of $NH_4[Ni(mnt)_2].H_2O$ showing the arrangement of anion and cation/water sheets with hydrogen-bonding interactions marked by dashed lines

The $NH_4[Ni(mnt)_2].H_2O$ crystals were grown by electro-crystallisation of a solution of urea and the dianion salt in deionised degassed water under a nitrogen atmosphere at a voltage of 1.0 V. The crystals are obtained as elongated platelets.

The susceptibility of polycrystalline samples was measured using a Faraday balance and a paramagnetic susceptibility above 120 K consistent with anti-ferromagnetic exchange was observed. However, below this temperature a cross-over was observed to ferromagnetic behaviour. Fitting a Curie-Weiss Law to the susceptibility data above 100 K gives a negative Weiss constant indicative of anti-ferromagnetic coupling and a Curie constant indicating one g = 2 spin ½ electron per anion formula unit. A fit to the data below 100 K gives a positive intercept with the temperature axis leading to a Weiss constant of 8 K with a Curie constant consistent with only 0.4 - 0.5 g = 2 spin ½ per anion. At low temperatures the susceptibility deviates from the simple Curie-Weiss Law due to long range ferromagnetic ordering.

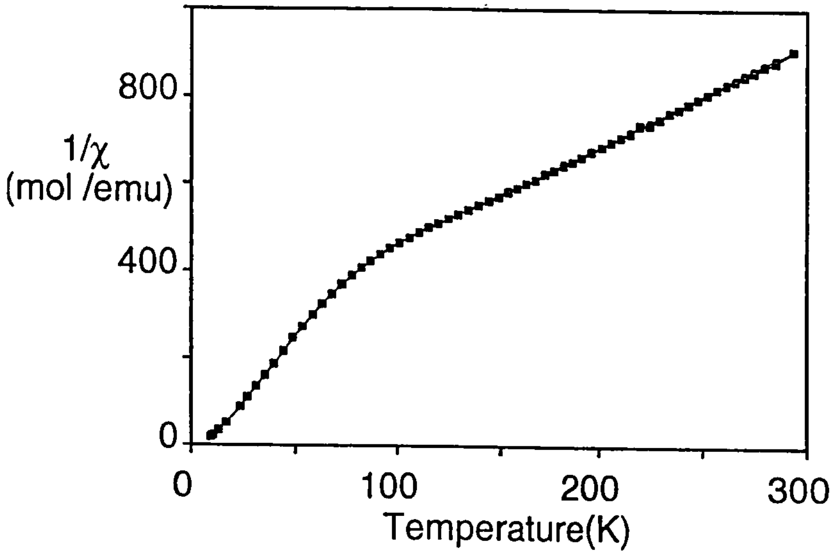

FIGURE 6 Susceptibility of polycrystalline $NH_4[Ni(mnt)_2].H_2O$

The properties of $NH_4[Ni(mnt)_2].H_2O$ below the magnetic ordering temperature (5 K) were investigated using single crystals and a quantum design SQUID magnetometer. Magnetization curves were taken with the long axis of the crystal parallel and perpendicular to the applied field. The long crystal axis of the sample corresponds to the b axis along which the metal complex anions stack. Measurements of the moment parallel to the long axis produced a hard magnetization curve with a steady increase of the magnetic moment with fields. When the stacking axis of the crystal was perpendicular to the field the magnetization was very different showing hysteresis effects with a coersive field of 100 Oersted and a magnetization of 1800 emuG/mol at 2000 Oersted. If g = 2 then the saturation magnetization corresponds to around one-third of a spin ½-electron per metal complex anion.[10]

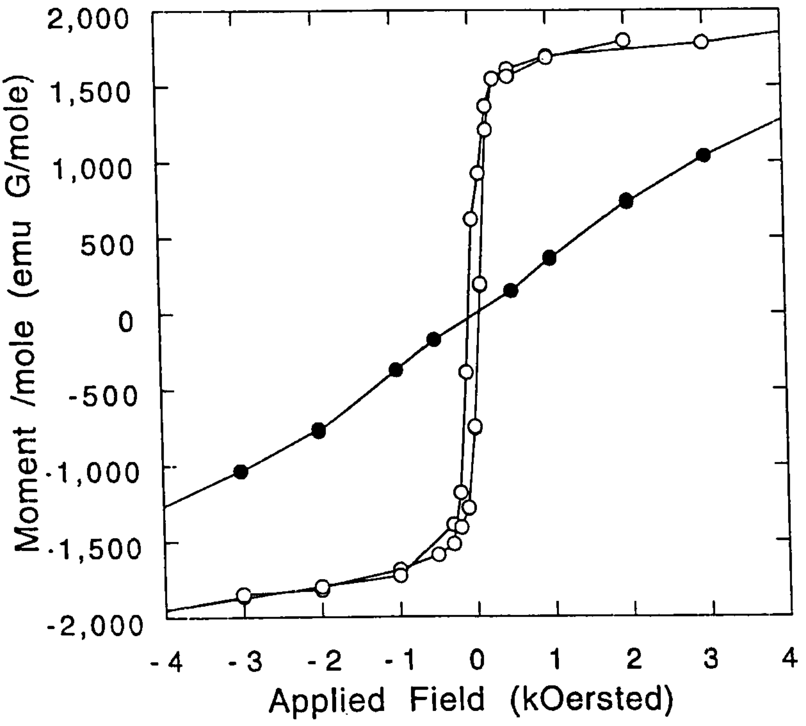

FIGURE 7 Magnetisation curves of a 11μg single crystal of $NH_4[Ni(mnt)_2].H_2O$ taken at 2K. Solid data points are with the applied field parallel to the *b*-axis (stacking axis) and the open circles are for the applied field perpendicular.[10]

Further studies have shown that the Curie temperature increases with hydrostatic pressures up to 6.8 kBar above which the ferromagnetic order abruptly disappears. Further studies of this related compound are in progress.[11]

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