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Abstract - Dianionic and neutral bis TTF dithiolate mercury and nickel complexes have been prepared. X-ray structural studies show the geometry around the mercury to be tetrahedral and CV and esr measurements indicate very little interaction between the two TTF based ligands. Conductivity measurements on the neutral mercury complexes gave $\sigma_{RT} = 10^{-5}$ Scm^{-1} whereas for the neutral nickel complexes values of 10^{-2} - 10^{-1} Scm^{-1} are observed. The salts $[TTF]_x[Fe(tdas)_2]$ x = 2, 3/2 (tdas = 1,2,5-thiadiazole-3,4-dithiol) have been prepared by electrocrystallisation and show conductivities of 10^{-2} Scm^{-1} and 10^{-5} Scm^{-1} respectively. The former salt displays thermally activated magnetic behaviour and the latter shows a Curie-type temperature dependance.

INTRODUCTION

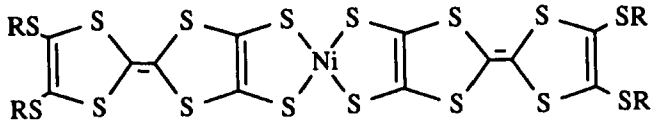
Metal complexes of sulphur donor ligands have aroused great interest in physicists and synthetic chemists since the first observation of metallic behaviour in this class of compound.[1] Much emphasis has been placed on the development of ligands which enhance S...S interactions in the solid state, thus providing the optimum structures for molecular conductors and superconductors.[2] Metal complexes of the ligand dmit (dmit = 2-thioxo-1,3,dithiol-4,5-dithiolate) have been the most extensively studied particularly since the observation of superconductivity in $TTF[Ni(dmit)_2]_2$.[3] Extensive studies involving metals other than nickel and other countercations have led to

compounds exhibiting metallic behaviour down to very low temperatures, such as $Na[Ni(dmit)_2]_2$ and to molecular superconductors containing spectator cations and in which the superconducting properties originate solely from the metal dmit complex.[3,4]

In an effort to extend the range of true molecular metals and to develop compounds in which the superconducting state is stabilised to higher temperatures and at ambient pressures many variations of the sulphur donor ligands have been studied.[5] In this paper we present the results of investigations in which the basic structure of the dmit ligand has been modified by alterations to the secondary ring system and report the solid-state properties of the resulting metal complexes in the neutral state and as salts with open and closed shell organic counter cations.

COMPLEXES OF 4,5-TETRATHIAFULVALENEDITHIOLATES

The development of sulphur donor ligands which incorporate an identifiable TTF moiety is a challenging and intriguing possibility. A bis- complex such as that shown in Figure 1 would potentially possess three redox centres, one localised on the NiS_4 unit and one on each of the TTF molecules. The detailed redox properties would depend upon the extent of interaction between the TTF units and the NiS_4 unit. In addition, the properties would also depend on the cross-talk between the two ligand systems via the central metal atom.



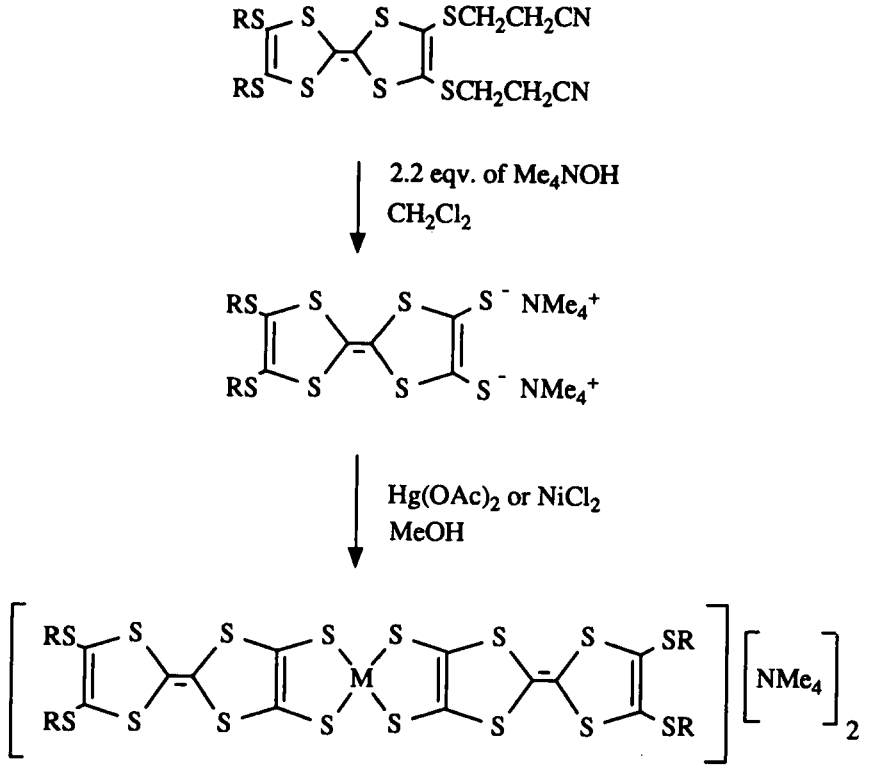
$[Ni(dttfdt)_2]$

FIGURE 1

Routes have recently been developed to TTF dithiolates which can serve as precursors for unsymmetrical TTF derivatives.[6,7] These dithiolates can be used as ligands for metal complexes which contain the TTF moiety. The preparation of the

dianionic metal complexes of the type $[M(dttfdt)_2]^{2-}$ was achieved using bis(cyanoethylthio)TTFs using the method of Becher *et al.*[7]

The potential ligands were deprotected using Me_4NOH in THF to generate the TTF derivatives as shown in Scheme 1. Removal of the THF *in vacuo* followed by dissolution in methanol and addition of the metal salt led to the precipitation of the metal complex.



M = Ni, Hg; R = Et, Bu

SCHEME 1

MERCURY COMPLEX[8]

The mercury complex was obtained as the dianion with Me_4N^+ as the counter cation. Two variations of the ligand were investigated in which the R group was either Et or Bu.

CRYSTAL STRUCTURE

$[Me_4N]_2[Hg(dttfdt)_2]$ (R = Et) was obtained as orange plate shaped crystals by the slow diffusion of diethyl ether into an acetone solution of the salt. The structure consists of discrete anions and cations. The geometry about the mercury atom is approximately tetrahedral with the S-Hg-S angle within the ligand ring system of 88.4° (Av). The two planes formed by the S(1)-Hg(1)-S(2) and S(9)-Hg(1)-S(10) are approximately perpendicular to one another.

The two TTF units within the anion are non planar with deviations from planarity of 37.9 and 50.7°. These are thought to arise from packing effects due to the adjacent TTF units lying orthogonal to each other and resulting in short intermolecular S....S distances.[8]

REDOX PROPERTIES

Cyclic voltammetry of $[Me_4N]_2[Hg(dttfdt)_2]$ (R = Et) reveals four oxidation processes with mid points at -0.04 V, +0.07 V, +0.76 V and +1.09 V *versus* SCE (dichloromethane, nBu_4NBF_4) and peak heights of 1:1:2:1 respectively. Further studies have identified that the peaks at -0.04 V and +0.07 V are due to two one-electron oxidations. The third wave has been assigned to the second oxidation of each of the two TTF units within the complex. Oxidation results in the deposition of a light brown film on the electrode surface as a result of the first oxidation. In acetonitrile solution the first two peaks observed in dichloromethane give rise to a single peak at -0.54 V *versus* Ag/Ag^+ and the other two processes are observed as irreversible oxidations at +0.45 and +0.5 V.

The single 2-electron oxidation of $[Me_4N]_2[Hg(dttfdt)_2]$ (R = Et) in acetonitrile and the very small separation between the first two one-electron processes in dichloromethane shows 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 units.

NEUTRAL COMPLEX [Hg(dttfdt)$_2$] (R = Et)

$[Me_4N]_2[Hg(dttfdt)_2]$ (R = Et) can be oxidised in acetonitrile solution by the addition of I_2 to give a brown precipitate of $[Hg(dttfdt)_2]$ (R = Et). Unfortunately, $Hg(dttfdt)_2$ (R = Et) could not be obtained as single crystals and therefore its structure could not be determined. However, the ESR spectrum exhibits a singlet with a g value of 2.0052 consistent with radicals localised on the two TTF units. This indicates little interaction between the π systems of the two ligands and suggests that the coordination about the Hg atom in $Hg(dttfdt)_2$ (R = Et) is tetrahedral and similar to that observed in the X-ray structure $[Me_4N]_2[Hg(dttfdt)_2]$ (R = Et).

Electrical conduction studies on $Hg(dttfdt)_2$ (R = Et) indicated a value of 10^{-5} Scm^{-1} at room temperature.

NICKEL COMPLEXES[9]

Dianionic nickel complexes of the type $[Me_4N]_2[Ni(dttfdt)_2]$ (where R = Bu, Et or Me) have been prepared. Oxidation of these dianionic salts in solution with iodine yields the corresponding neutral complexes. Preliminary studies on these complexes have been carried out and are described below.

CYCLIC VOLTAMMETRY

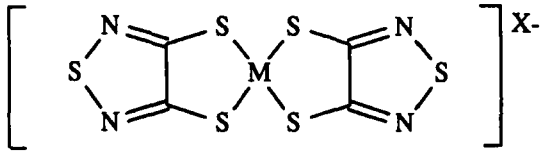
Cylcic Voltammetry on the dianionic salts show two oxidations corresponding to the oxidation from the dianionic complex to the monoanion and from the monoanion to the neutral complex. For R = Et, the first of these occurs at -0.48 V and the second, corresponding to the oxidation to the neutral complex, at -0.07 V (vs SCE, CH_2Cl_2). The corresponding reduction waves are observed at -0.24 and -0.42 V. The oxidation of the dianion to the monoanion is reversible but that from the monoanion to the neutral complex is more complex and is consistent with the deposition of the neutral complex as a film on the electrode. The analgous complex where R = Bu shows similar results.

The electrical conductivity of single crystals of $[Ni(dttfdt)_2]$ (R = Et) has

been determined over the temperature range 290 - 50 K using a four probe method. The room temperature conductivity was 2.7 x 10^{-2} Scm^{-1} and the conductivity decreased with decreasing temperature indicating semi-conducing behaviour. However, studies on a compressed pellet of $[Ni(dttfdt)_2]$ (R = Me) indicated a room temperature conductivity of 10^{-1} Scm^{-1} with a metallic type of temperature dependence from 300 - 275 K followed by semi-conductor behaviour below 275 K. The room temperature conductivities of these neutral nickel complexes are significantly higher than values normally observed for neutral complexes of dithiolenes ($Ni(dmit)_2$ is unusually conductive with σ_{RT} = 3.5 x 10^{-3} Scm^{-1}, many others have reported values of around 10^{-6} Scm^{-1})[2,3]. Further studies on this class of compound are in progress.

PREPARATION, ELECTRICAL CONDUCTIVITY AND MAGNETIC PROPERTIES OF [TTF][$Fe(tdas)_2$]; x = 2 OR 3/2

In recent years, a series of complexes has been synthesised involving the ligand 1,2,5-thiadiazole-3,4-dithiol (tdas) (fig. 2) which have shown themselves to be capable of displaying cooperative solid state behaviour via intermolecular metal-sulphur interactions.[10]



M = Ni; X = 2,1. M = Cu, Pd, Pt; X = 2. M = Fe, Au; X = 1

FIGURE 2

These studies have led to the discovery of the unusual magnetic behaviour of $[TBA][Fe(tdas)_2]$ which shows an antiferromagnetic interaction between dimerised metal complexes and two magnetic transitions at 182 K and 232 K.[11] The magnetic parameters above 232 K and below 182 K were identical, while an intermediate temperature phase with a different structure exists between these two temperatures

suggesting reentrant behaviour which is unusual in solid-to-solid phase transitions. In addition to this, high electrical conductivity in tdas salts has been demonstrated in $[TTF]_2[Ni(tdas)_2]$.[10]

We have investigated therefore, the preparation and properties of salts containing $[Fe(tdas)_2]^-$ anions and TTF cations as this could potentially lead to materials combining the properties of high conductivity and long range magnetic ordering. Recent studies elsewhere have led to the first molecular supercondctor containing paramagnetic ions[12] and in $[BETS]_2[FeCl_4]$ the interaction of magnetic ions with delocalised electrons.[13]

RESULTS AND DISCUSSION

Salts of the type $[TTF]_x[Fe(tdas)_2]$ (x = 2 or 3/2) were prepared by electrocrystallisation of acetonitrile solutions of TTF and $[TBA][Fe(tdas)_2]$. Depending on the value of the constant current either $[TTF]_2[Fe(tdas)_2]$ (1-2 μA) or $[TTF]_{3/2}[Fe(tdas)_2]$ (5 - 10 μA) was formed. Both materials were obtained as metallic black crystals. The conductivities of crystals of both products were measured using a four probe method and results are summarised in Table 1. Variable temperature magnetic susceptibility measurements were also carried out on 1 and 2 and the results are included in Table 1.

TABLE 1

Compound	σ_{RT}/ Scm^{-1}	Temperature dependance	Magnetic behaviour
$[TTF]_2[Fe(tdas)_2]$	3×10^{-2}	Semiconductor, BG=0.18eV	thermally activated
$[TTF]_{3/2}[Fe(tdas)_2]$	3×10^{-5}	Semiconductor, 110-160K, BG=0.14eV	Curie

For the salt $[TTF]_2[Fe(tdas)_2]$, χ_p increases with increasing temperature which

suggests that the $[Fe(tdas)_2]$ units form an antiferromagnetic dimer. In addition, there is a temperature independent paramagnetic susceptibility presumably arising from the TTF cations. If a ground state of 3/2 is assumed, which was observed for the $TBA[Fe(tdas)_2]$ salt, then the data can be described by an equivalent equation to this salt[11] but with an additional temperature independent parameter $\chi_p' = 1.1 \times 10^{-3}$ emu mol^{-1} attributed to electrons associated with TTF.

From this fit, values of the coupling constant $J/k_B = 154K$, $g = 2.27$ and the Curie constant $C = 1.0 \times 10^{-3}$ $emuKmol^{-1}$ were derived. Both the coupling constant and g factor are larger than those determined for $TBA[Fe(tdas)_2]$ but a full understanding of these features is not possible in the absence of structural information. Furthermore, a fit assuming the ground state of $Fe(tdas)_2$ to be 5/2 could also be made to the data and confirmation of the spin state of Fe is necessary before further discussion of parameters is possible. The co-existence of indpendent sub-lattices of localised and conducting unpaired electrons seems to be implied by the magnetic data and by the room temperature conductivity of 10^{-2} Scm^{-1}. For the salt $[TTF]_{3/2}[Fe(tdas)_2]$, Curie-type behaviour was observed.

In conclusion, we have demonstrated large changes in the magnetic and conduction properties of TTF salts of $[Fe(tdas)_2]^-$ by changes in the stoichiometry of the salts.

EXPERIMENTAL

Preparation of $[TTF]_2[Fe(tdas)_2]$

TTF (0.014 g, 0.07 mmol) and $[TBA][Fe(tdas)_2]$ (0.026 g, 0.05 mmol) were dissolved in 25 ml of dry acetonitrile and placed in the anode compartment of an H-shaped cell. $[TBA][Fe(tdas)_2]$ (0.026 g, 0.05 mmol) was dissolved in 25 ml of dry acetonitrile and placed in the cathode compartment separated by a porous glass frit. A constant current of 2 μA was passed for 10 days and black crystals of 1 were scraped from the anode (0.010 mg, 0.013 mmol).

$C_{16}H_8N_4S_{14}Fe$	Calc %	N : 7.37	C : 25.26	H : 1.05	S : 58.95
	Found %	N : 7.62	C : 24.92	H : 1.06	S : 65.15

Preparation of $[TTF]_3[Fe(tdas)_2]_2$

A similar procedure was carried out as described above using identical quantities of reagents but using a constant current of 5 μA for 10 days.

$C_{26}H_{12}N_8S_{24}Fe_2$	Calc %	N : 8.51	C : 23.71	H : 0.91	S : 58.36
	Found %	N : 8.71	C : 24.16	H : 0.75	S : 54.43

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