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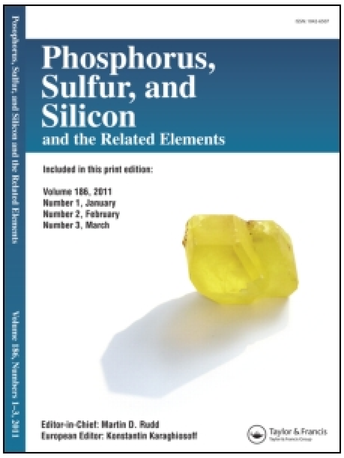

Phosphorus, Sulfur, and Silicon and the Related Elements

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SULPHUR-CONTAINING DONORS AND LIGANDS FOR MOLECULAR CONDUCTORS

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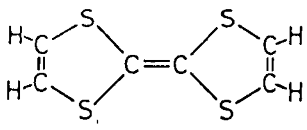
Abstract The structures and properties of molecular conductors based on metal complexes of the sulphur-containing donor ligands mnt and dmit are described.

The first synthetic organic metal, TTF-TCNQ, was reported in 1973 but molecular metals based on transition metal complexes, such as $K_2[Pt(CN)_4]Br_{0.3}\cdot 3.2H_2O$ (KCP), were first prepared in the early 1800's although their metallic properties were not studied until the late 1960's.[1,2] Molecular metals of the KCP type depend for their metallic properties on the close approach of the central metal atoms to allow effective overlap of the metal's d orbitals. Indeed it has been found that this type of molecular metal can only be formed with the third row transition metals which possess the relatively large 5d orbitals. In these compounds metal-metal distances of less than 3 A are necessary to allow sufficient overlap of the orbitals to give metallic properties.[3] This is in contrast to TTF-TCNQ and related organic metals where metallic properties are observed with the closest inter-atomic contact between the sulphur atoms of about 3.7 A.

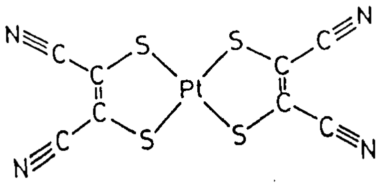
It was realised that the restriction of molecular metals based on metal complexes to those containing third row elements and with intermolecular distances of less than 3 A severly limited the scope for the preparation of new materials. Thus the search for new compounds was widened in two directions. One way was to prepare metal complexes of large macrocyclic ligands such as metallo- porphorins.[4] The other way was to study metal complexes of ligands that had structural similarities to the organic donors that were known to form molecular metals. It is this latter class of compounds that will be discussed.

METAL COMPLEXES OF 1,2-DICYANOETHYLENE-1,2-DITHIOL (mnt)

There is a marked molecular structural similarity between TTF and metal complexes of mnt as shown below:



TTF



$[Pt(mnt)_2]^{x-}$

Transition metal complexes of 1,2-dicyanoethylene-1,2-dithiol (maleonitrile, mnt), have received special study since this ligand can stabilise transition metals in a variety of oxidation states and the high electron affinity of the terminal cyanide groups aids the delocalisation of charge within the complex, thus reducing potential coulombic repulsions.

In an attempt to maximise interactions between the metal dithiolene anions Underhill and Ahmad studied the lithium salt of the $[Pt(S_2C_2(CN)_2)_2]$ cation. Slow aerial oxidation of a 50% aqueous acetone solution of $H_2[Pt(S_2C_2(CN)_2)_2$ and LiCl yielded small shining black needles and black platelets. 4-Probe dc conduction studies on the needle shaped crystals showed the room temperature conductivity along the needle axis to be $\approx 100\ \Omega^{-1}\ cm^{-1}$.[5] The needle shaped crystals were the cation deficient compound $(H_3O)_{0.33}Li_{0.8}[Pt(S_2C_2(CN)_2)_2]\cdot 1.67H_2O$ (LiPt(mnt)). X-Ray studies show that the room temperature structure (Figure 1) of LiPt(mnt) consists of equidistant stacks of nearly eclipsed $[(Pt(mnt)_2]$ anions along the c-axis, with c = 3.639 A.[6] The unit cell is triclinic and the stacks form sheets along b separated along a by Li^+ and H_2O (Figure 1).

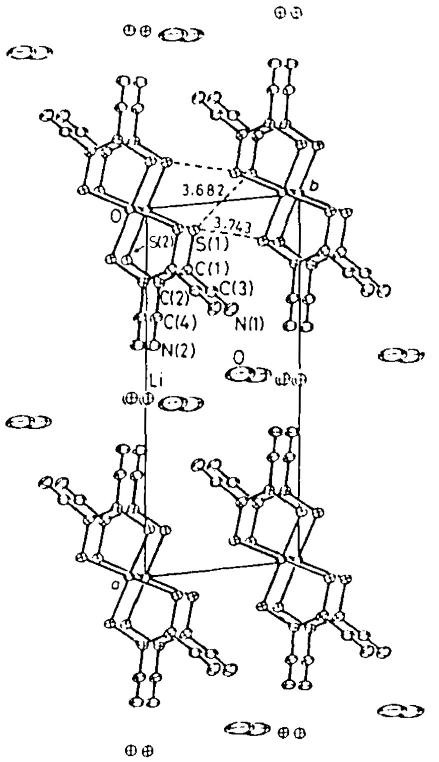


FIGURE 1 The c axis projection of the crystal structure of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$.[6]

There are short sulphur contacts between the chains within the sheets as well as within the chain, suggesting a relatively two dimensional network. Although the compound is cation deficient, the long Pt-Pt interchain separation shows that the bonding within the chain cannot be of the simple metal orbital overlap type found for KCP. The high conductivity must therefore result from interaction of the whole anion in the chain direction. The temperature dependence of $\sigma_{\parallel}$ for freshly prepared crystals slowly increases with decreasing temperature with $\sigma_{\parallel}$ passing through a maximum at about 250 K (Figure 2).

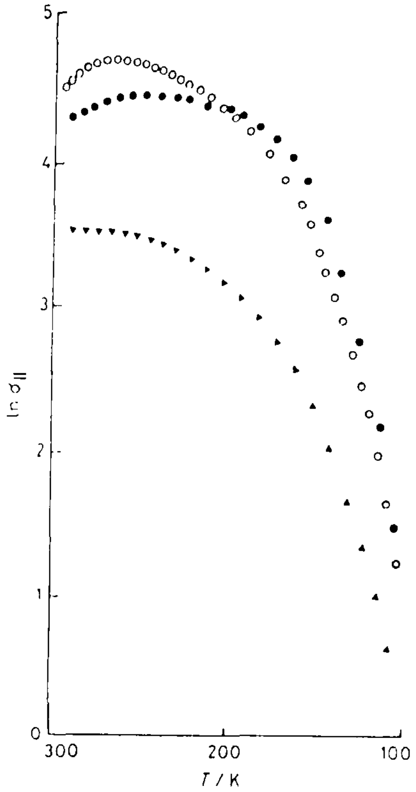


FIGURE 2 Variation of conductivity with temperature for crystals of $Li_{0.75}[Pt(mnt)_2]\cdot 2H_2O$: (O) freshly cropped; (O) crystals stored at 75% relative humidity; (▽) stored at ambient humidity for 14 d.[5]

The conductivity falls to its room temperature value at about 200 K and then falls rapidly with decreasing temperature. Below 100 K the behaviour is that of a semiconductor with activation energy of about 34 meV.

The change over in the conductivity behaviour from that of a metal to that of a semiconductor with decreasing temperature is common in this class of compound. It is a result of the pseudo one-dimensional nature of the interactions which lead to the metallic properties. From the structure of the compound the principal interactions which give rise to intermolecular overlap are the intermolecular sulphur-sulphur contacts in the stack direction. There are also weaker contacts between molecules in adjacent stacks along b. The metal to semiconductor transition is a manifestation of the Peierls instability of a one-dimensional metal.[7] One-dimensional metals are inherently unstable to a periodic lattice distortion which has the effect of splitting the partially filled band of a metal to give filled and empty bands characteristic of a semiconductor. That this occurs in this compound has been confirmed by crystallographic studies which have shown a superstructure below T_C = 215 K which is preceeded by one-dimensional diffuse scattering typical of a Peierls transition. The position of the diffuse line along c indicates that the extent of band filling is 0.41 or 0.59. Studies have shown that the thermopower above T_c is approximately constant and positive implying hole characteristics for the carriers in the metallic region and therefore, the extent of band filling is 0.59. Below T_c the thermopower reflects the intrinsic properties of the charge density wave semiconductor.[8]

The metal to semiconductor described above is due to the one-dimensionality of the material. To suppress the transition it is necessary to increase the interactions between the conducting stacks of metal complex anion. This can be achieved by submitting the material to high pressure. A recent example of this effect is the study on $Cs_{0.82}[Pd(mnt)_2]\cdot 0.5H_2O$. The crystal structure of $Cs_{0.82}[Pd(mnt)_2]\cdot 0.5H_2O$ is shown in Figure 3 and is quite different from any structure previously reported for a $[M(mnt)_2]^-$ monoanion salts.[9] The structure contains $[Pd(mnt)_2]_2{}^{2-}$ dimers in an eclipsed configuration with intra-dimer Pd-Pd distance of 3.329(5) A. The dimers are arranged such that there are short S-S contacts between dimers in both the c and a dirations. This gives rise to a 2D sheet structure in the ac plane, the sheets being separated in the b direction by the caesium ions and water molecules.

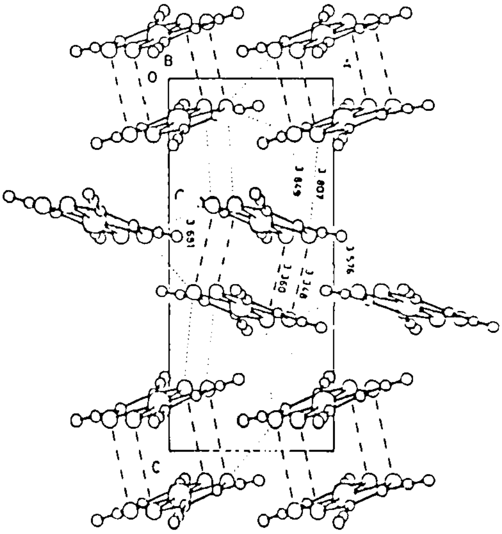


FIGURE 3 The crystal structure of $Cs_{0.82}[Pd(mnt)_2]\cdot 0.5H_2O$.[9]

The electrical conductivity is ≈5 Ω^{-1} cm^{-1} at room temperature and the conductivity is activated below room temperature.[10] Thus the compound does not behave as a true metal even at room temperature. However under increasing pressure (see Figure 4) the value of the room temperature conductivity rises and the temperature dependence of the conductivity becomes that of a metal, ie rising with decreasing temperature.

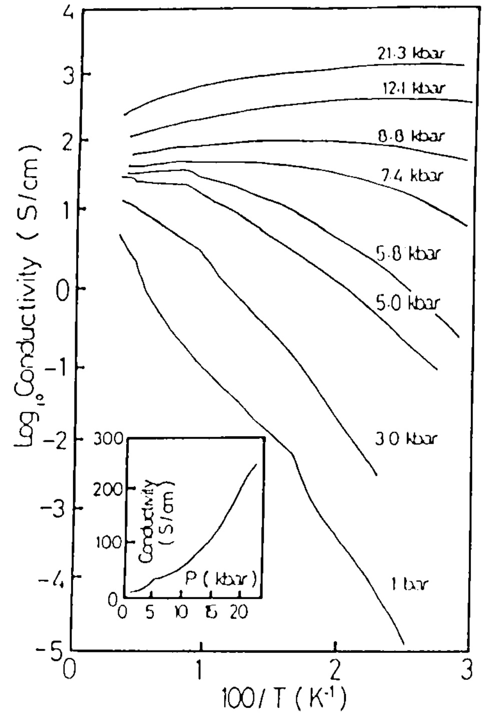


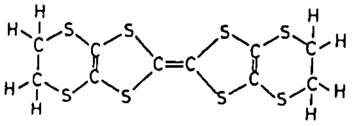
FIGURE 4 Temperature dependence of the conductivity at various pressures of $Cs_{0.82}[Pd(mnt)_2]\cdot0.5H_2O$. Inset shows the pressure dependence of the conductivity at room temperature.[11]

At relatively low pressures there is a metal to semiconductor transition at low temperatures but at the highest pressure studied, 21.3 kbar, the behaviour was that of a metal down to 1.3 K.[11]

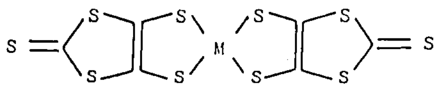
The alternative way to suppress the Peierls instability is to increase the number of sulphur atoms in the molecule and thus increase the possibilities of intermolecular sulphur-sulphur contacts. This is exemplified below with respect to the organic donor BEDT-TTF and the related ligand dmit.

METAL COMPLEXES OF 4,5-DIMERCAPTO-1,3-DITHIOLE-2-THIONE (dmit)

There is considerable structural similarity between the organic donor BEDT-TTF and the metal complexes of dmit.



BEDT-TTF



$[M(dmit)]^{x-}$

Since the discovery that salts of BEDT-TTF with linear triatomic anions such as $(BEDT\text{-}TTF)_2I_3$ were superconductors at low temperatures there has been great interest in studying the effect of structural modification of the donor on the structures and properties of the salts.[12] This has been extended to include the metal complexes of dmit particularly after the discovery by Cassoux and coworkers that $TTF[Ni(dmit)_2]_2$ remained metallic down to very low temperatures and became a superconductor at $T_c = 1.62$ K at 7 kbar.[13]

As was demonstrated with with the salts of $[M(mnt)_2]^{x-}$ with closed shell cations, the size of the cation can be crucial in allowing interanion interactions. Thus we are making a study of the salts of $[M(dmit)_2]^{x-}$ with the Group 1 cations. Of the compounds studied so far $Cs[Pd(dmit)_2]_2$ is the most interesting.[14]

$Cs[Pd(dmit)_2]_2$ is obtained as black plates by electrocrystallisation and exhibits a room temperature conductivity of ≈200 S cm^{-1}. Figure 5 shows the temperature dependence of the conductivity of a single crystal measured along the longest edge of the crystal. It can be seen that the conductivity rises slowly with decreasing temperature to a maximum value at about 70 K. The conductivity then falls slowly until about 40 K when the conductivity falls very rapidly with decreasing temperature.

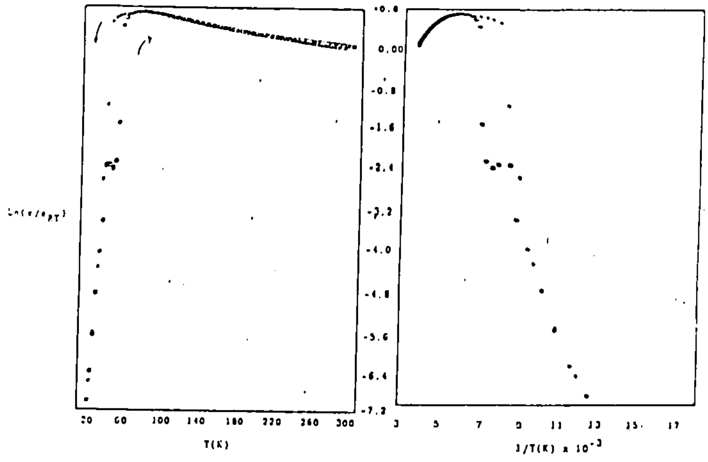


FIGURE 5 The temperature dependence of the conductivity of $Cs[Pd(dmit)_2]_2$; Δ, cooling cycle; □, warming cycle.

The crystal structure of $Cs[Pd(dmit)_2]_2$ at room temperature has been determined and Figure 6 shows the structure viewed along the b axis.[15] It can be seen that the anion dimers form a columnar stack structure along a.

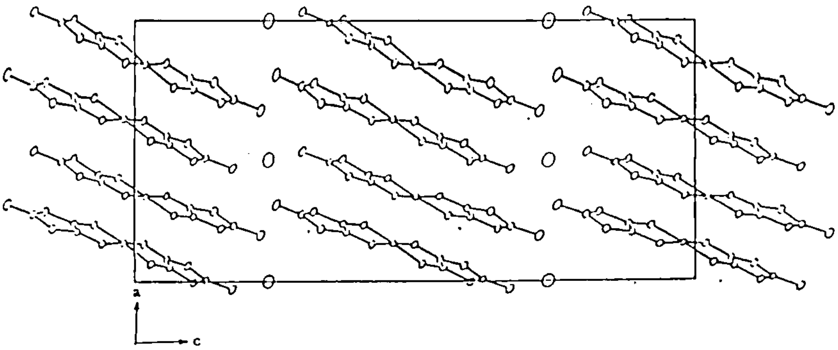


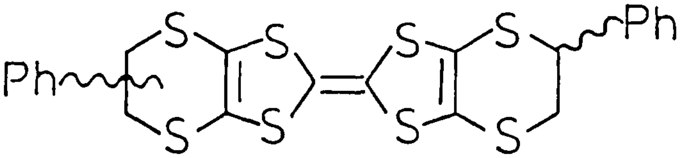
FIGURE 6 The structure of $Cs[Pd(dmit)_2]_2$ viewed along the b axis.[15]

Within the dimers the anions are arranged in an eclipsed configuration with a short intra-dimer separation of 3.210 A. The dimers are arranged in a slipped configuration to form a columnar stacked structure with an inter-dimer separation of 3.850 A.

The columnar stacks of anions form a two-dimensional sheet structure in the ab plane. These sheets of anions are separated along c by the Cs^+ cations. Calculated overlap integrals indicate that the predominant interaction is between the anions within the dimer and with the next largest interaction occurring between dimers within the column. There are also significant interactions between anions in adjacent columns.

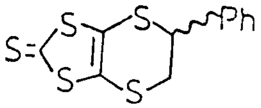
METAL COMPLEXES OF SODIUM 5,6-DIHYDRO-5-PHENYL-2,3-DITHIOLATE (dpdt)

The new organic donor BPhEDT-TTF has recently been synthesised and some of its radical cation salts prepared.[16]

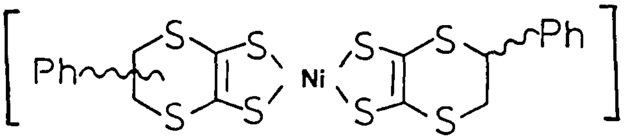


BPhEDT-TTF

Treatment of the thione (1) with NaOEt in EtOH followed by addition of ether yields the new dithiolate ligand as the sodium salt. Treatment with $NiCl_2$ in MeOH followed by addition of TBABr gave the complex (2). Further studies on this series of complexes are in progress.



(1)



$[nBu_4N]$

(2)

GENERAL DISCUSSION

The metal complexes of sulphur donor ligands are a valuable addition to the range of molecules that can be used to form molecular conductors, metals or super- conductors. The structures and properties of the materials can be controlled and are strongly dependent upon three factors.

(a) The size of the cation. Small cations such as those of Group One, allow the close approach of the anions to form extended arrays and thus allow cooperative phenomena to be observed. Large bulky cations, such as Bu_4N^+ prevent these interactions occurring. Indeed subtle changes in cation size can sometimes produce large differences in properties.

(b) The nature of the central metal. Because the HOMO in the metal complex anion possesses considerable metal orbital character the central metal can exert a large influence on the solid state properties of the materials.

This influence is well exemplified by the series $[M(mnt)_2]^-$ (where M is Ni, Pd or Pt). The nickel complexes with the smaller cations possess an equidistant stack structure and the properties of an Heisenberg antiferromagnetic chain. At lower temperature spin- lattice coupling causes dimerisation of the chain and singlet-triplet magnetic properties.[17]

All the platinum compounds would appear to exist with dimerised anions at room temperature and with a large energy separation of the singlet and triplet states leading to a diamagnetic ground state at room temperature.

The $[Pd(S_2C_2(CN)_2)_2]^-$ series of compounds display quite different behaviour. The structure of the Cs^+ salt is unique and reveals strong S....S interactions within sheets of anions separated by the Cs^+ and water molecules. The compound behaves as a semi-metal or small band gap semiconductor at room temperature and atmospheric pressure with a transition to a wide band gap semiconductor at lower temperatures. However, as discussed earlier, under high pressure it is converted to a metal.

(c) The nature of the ligand. As stated earlier the principal inter-anionic contacts are via the sulphur atoms of the ligands. Therefore these interactions are going to be very dependent on the number of sulphur atoms on the ligand. The more extensive-sulphur ring system of dmit compared with mnt will facilitate stronger inter-anion interaction. This is shown in the comparison of the palladium salts of these ligands with Cs^+ as the counter cation. $Cs[Pd(dmit)_2]_2$ behaves as a metal at atmospheric pressure down to 70 K whereas $Cs_{0.82}[Pd(mnt)_2]\cdot 0.5H_2O$ only becomes metallic under pressure.

Complexes containing metal anions of sulphur donor ligands can therefore give rise to new materials with high electrical conductivity. In the future, variation of the cation, central metal, and the nature of the ligand may allow the properties of the material to be varied in a systematic way.

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