

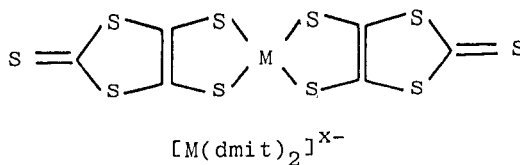
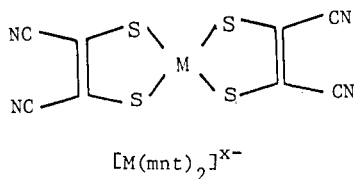
## New materials based on metal complexes of sulphur donor ligands

A.E. Underhill, P.I. Clemenson and R.A. Clark

Department of Chemistry, University College of North Wales, Bangor, Gwynedd, Great Britain, LL57 2UW

**Abstract** - A comparative account is given of the structures and properties of the complexes of the type  $N[M(mnt)_2]$  (where N is a monovalent cation, M is Ni, Pd or Pt and mnt is  $C_4N_2S_2$ ) together with the recently discovered new low-dimensional metal  $Cs[Pd(dmit)_2]_2$  (where dmit is  $C_3S_5$ ).

Metal complexes of sulphur donor ligands have been widely studied, often because their intense colours made them useful in analysis. In the 1960's studies on metal complexes of ligands such as the dithiolenes centred on their unusual redox properties (ref. 1). More recently it has been found that they exhibit a wide range of structures and properties in the solid state dependent upon the nature and extent of the interactions between the metal-complex anions (refs. 2-7). Extensive studies have been made of the complexes formed between the ligands 1,2-dicyanoethylene-1,2-dithiol( $(HS)_2C_2(CN)_2$ ,  $H_2mnt$ ) and 4,5-dimercapto-1,3-dithiole-2-thione (dmit) and nickel(II), palladium(II) and platinum(II) salts. The resulting complex anions are planar and can readily exist either as the mono- or di-anion. The di-anion contains a pair of electrons in the HOMO and therefore inter-anion interactions in the solid state are extremely unlikely. The mono-anion, however, possesses a single electron in the HOMO, and therefore inter-anion interactions due to overlap of the HOMOs on adjacent anions are possible. The occurrence and the nature of these interactions is found to be very dependent on the central metal involved and the size of the cation. Thus the resulting complex can be a diamagnetic semiconductor or insulator, a semiconductor exhibiting a magnetic transition or a low-dimensional metal as discussed below.



### DIAMAGNETIC SEMICONDUCTORS

The salts of  $[Pt(mnt)_2]^-$  with the group one cations  $Na^+$ ,  $K^+$ ,  $Rb^+$  and with  $NH_4^+$  have been obtained by electrocrystallisation of the corresponding dianion salt (ref. 5). All the compounds studied behaved as semiconductors with room temperature conductivities in the range  $10^{-4}$  to  $10^{-6}$  S  $cm^{-1}$ . The crystal structures of the  $Rb^+$  and  $H_3O^+$  salts have been determined and shown to be isostructural (refs. 6,7). The structures consist of columns of anion-dimers, with the anions within the dimers arranged in an eclipsed configuration (see Fig. 1). All the compounds are diamagnetic at room temperature (ref. 5).

### SEMICONDUCTORS EXHIBITING MAGNETIC TRANSITIONS

With large bulky cations, such as  $[N(C_2H_5)_4]^+$ , both  $[Ni(mnt)_2]^-$  and  $[Pt(mnt)_2]^-$  form structures which contain anion dimers (refs. 7,8). However unlike the salts with small Group 1 cations the anions within the dimer adopt a slipped configuration involving a metal over sulphur arrangement as shown in Figure 1(a). These salts have been shown to be the semiconductors with room temperature conductivities of the order of  $10^{-8}$  S  $cm^{-1}$ . They are diamagnetic at low temperatures but become paramagnetic on warming, due to thermal population of a triplet excited state (ref. 9).

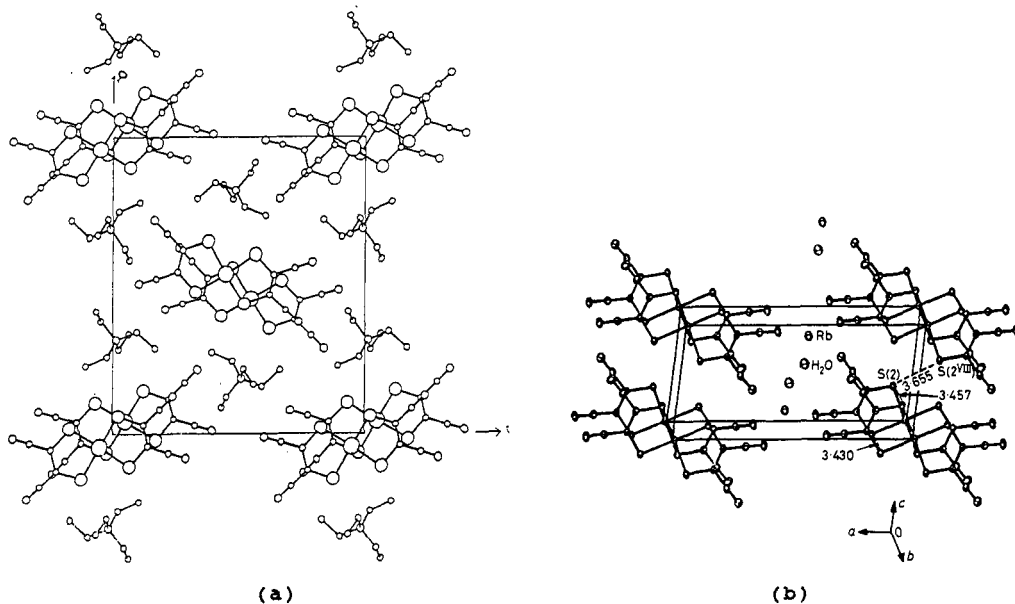


Fig. 1. A comparison of the metal over sulphur arrangement of anions within dimers found in salts of bulky cations e.g.  $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Pt}(\text{mnt})_2]$  ((a), taken from ref. 7) and in small Group 1 cations e.g.  $\text{Rb}[\text{Pt}(\text{mnt})_2] \cdot 2\text{H}_2\text{O}$  ((b), taken from ref. 6).

The salts of  $[\text{Ni}(\text{mnt})_2]^-$  with group one cations Na, K, and Rb and with  $\text{NH}_4^+$  possess an equidistant stack structure. The full crystal structure of the  $\text{NH}_4^+$  salt has been determined and is shown in Figure 2(a). At room temperature the compound behaves as a Heisenberg antiferromagnetic chain with  $J = 300\text{K}$ . At around 180K there is a deviation from the expected magnetic behaviour and the compound becomes diamagnetic (Fig. 3). The low temperature magnetic properties are consistent with that of a singlet ground state with a thermally accessible excited triplet state ( $\Delta = 570\text{K}$ ) (ref. 10). At low temperatures there is a doubling of the c-axis spacing compared with the room-temperature structure consistent with the formation of dimer pairs of anions.

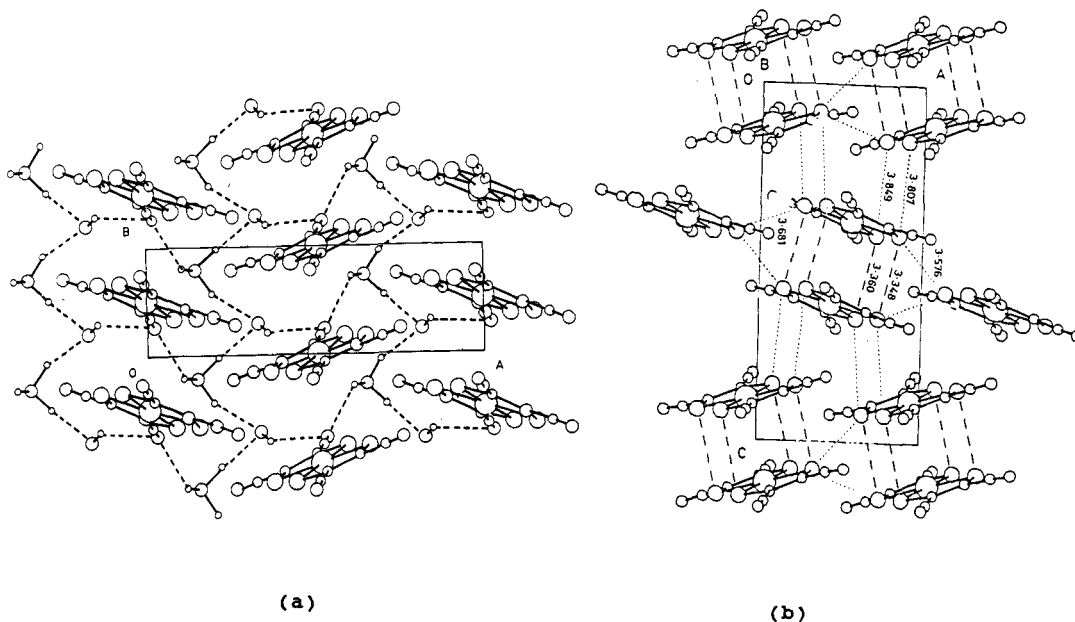


Fig. 2. The crystal structures of (a)  $\text{NH}_4[\text{Ni}(\text{mnt})_2] \cdot \text{H}_2\text{O}$  (taken from ref. 4) and (b)  $\text{Cs}_{0.92}[\text{Pd}(\text{mnt})_2] \cdot 0.5\text{H}_2\text{O}$  (taken from ref. 11).

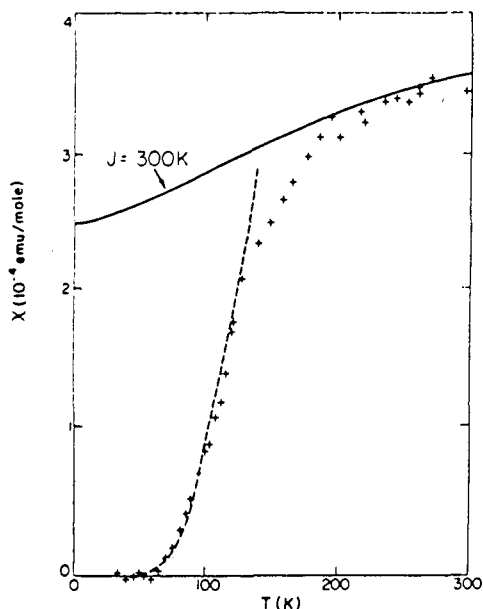


Fig. 3. Temperature dependence of the static magnetic susceptibility of  $\text{NH}_4[\text{Ni}(\text{mnt})_2] \cdot 2\text{H}_2\text{O}$  (taken from ref. 10).

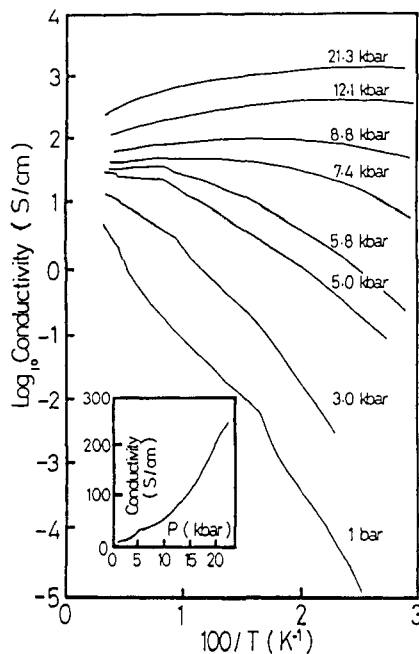


Fig. 4. Temperature dependence of the conductivity at various pressures of  $\text{Cs}_{0.82}[\text{Pd}(\text{mnt})_2] \cdot 0.5\text{H}_2\text{O}$ . Inset shows the pressure dependence of the conductivity at room temperature.

## MOLECULAR METALS

The first molecular metal based on a  $[\text{M}(\text{mnt})_2]^{X-}$  complex anion was  $\text{Li}_{0.8}(\text{H}_2\text{O})_{0.33}[\text{Pt}(\text{mnt})_2] \cdot 1.67\text{H}_2\text{O}$  (ref. 3). This compound behaved as a 1D metal with a Peierls transition to a low temperature semiconductor at 215K.

More recently a detailed study has been made of  $\text{Cs}_{0.82}[\text{Pd}(\text{mnt})_2] \cdot 0.5\text{H}_2\text{O}$ . The crystal structure of  $\text{Cs}_{0.82}[\text{Pd}(\text{mnt})_2] \cdot 0.5\text{H}_2\text{O}$  is shown in Figure 2(b) and is quite different from any structure previously reported for a  $[\text{M}(\text{mnt})_2]^-$  monoanion salt (ref. 11). The structure contains  $[\text{Pd}(\text{mnt})_2]_2^{2-}$  dimers in an eclipsed configuration with intra-dimer Pd-Pd distance of 3.329(5) Å. The dimers are arranged such that there are short S-S contacts between dimers in both the c and a directions. This gives rise to a 2D sheet structure in the ac plane, the sheets being separated in the b direction by the cesium ions and water molecules.

The electrical conductivity is  $\approx 5 \Omega^{-1} \text{cm}^{-1}$  at room temperature and the conductivity is activated below room temperature (ref. 12). There is clear evidence of a smeared out transition at around 240 K. Thermopower studies indicate that the thermopower is about  $+70 \mu\text{V}/\text{K}$  and temperature independent around room temperature. From the thermopower results there is also evidence of a smeared-out transition around 250-230 K and below the transition the thermopower increases rapidly with decreasing temperature. Under pressure the transitions are suppressed and at 21 kbar the conductivity rises with decreasing temperature down to 1.2 K (Fig. 4) (ref. 13).

The ligand dmit has a much more extensive sulphur containing ring system than mnt and therefore metal complexes of this ligand would be expected to exhibit greater inter-anion interactions than the comparable metal complexes of mnt.

$\text{Cs}[\text{Pd}(\text{dmit})_2]$  is obtained as black plates by electrocrystallisation and exhibits a room temperature conductivity of  $\approx 200 \text{ S cm}^{-1}$ . 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.

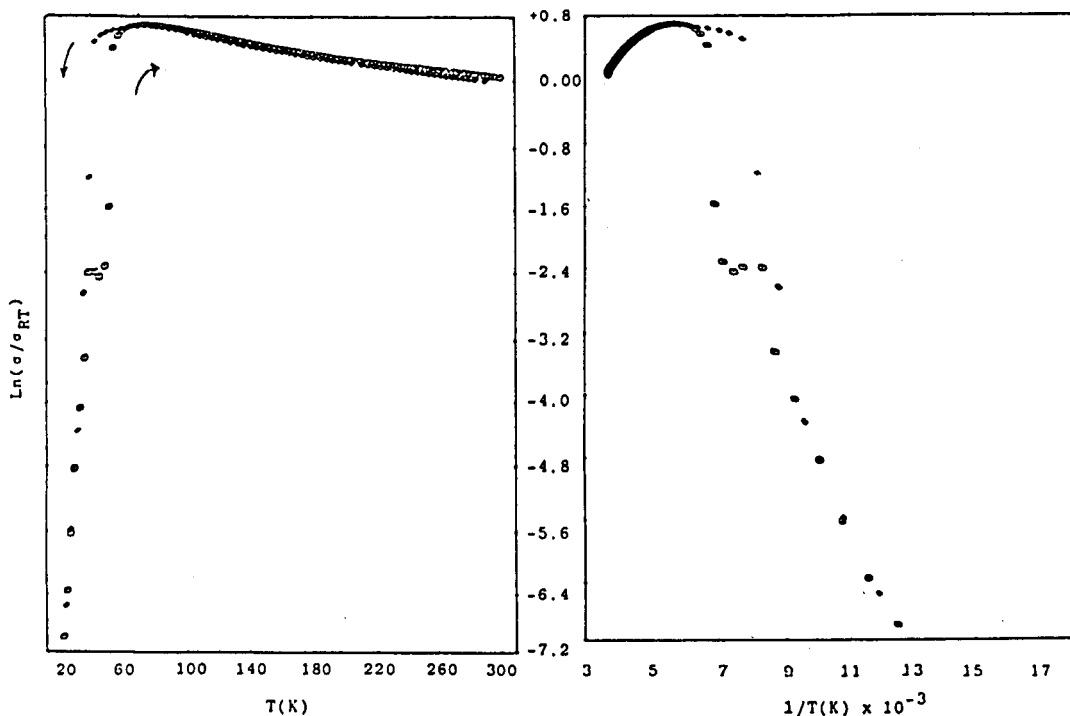


Fig. 5. The temperature dependence of the conductivity of  $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$ :  $\Delta$ , cooling cycle;  $\square$ , warming cycle.

The crystal structure of  $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$  at room temperature has been determined and Fig. 6 shows the structure viewed along the  $b$  axis (ref. 14). It can be seen that the anion dimers form a columnar stack structure along  $a$ .

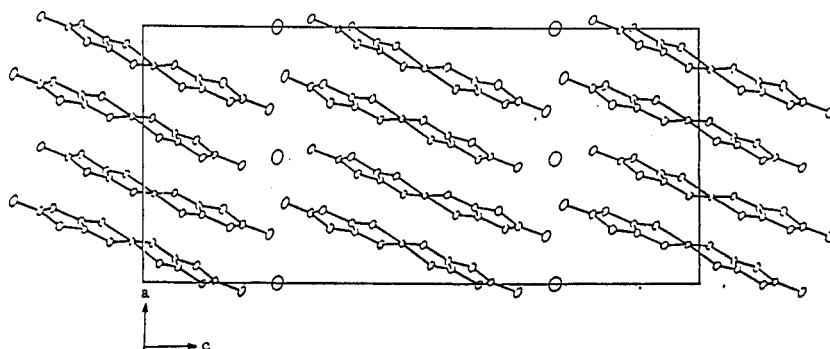


Fig. 6. The structure of  $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$  viewed along the  $b$ -axis.

Within the dimers the anions are arranged in an eclipsed configuration with a short intra-dimer separation of 3.210 Å. The dimers are arranged in a slipped configuration to form a columnar stacked structure with an inter-dimer separation of 3.850 Å (see Fig. 7).

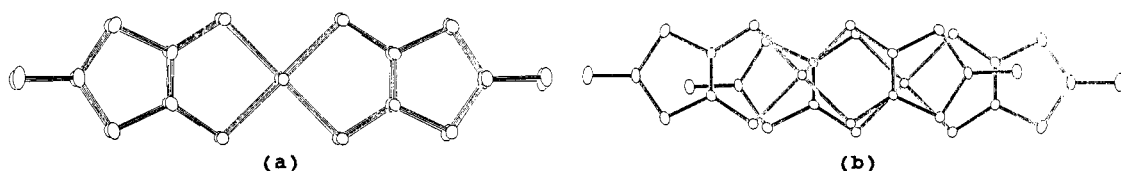


Fig. 7. (a) Intra-dimer, and (b) inter-dimer overlap in  $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$  (ref. 14).

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  $\text{Cs}^+$  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.

## GENERAL DISCUSSION

From the above discussions it can be seen that the structures and properties of metal complexes of sulphur donor ligands are strongly dependent on three factors

(a) The size of the cation: large bulky cations do not allow the anions to form extended arrays with sufficiently short inter-anion contacts to allow cooperative phenomena to be observed.

(b) The nature of the central metal: in the presence of small cations which facilitate extended inter-anion interactions, the nature of the central metal clearly plays an important role. The HOMO of the complex contains a significant metal *d*-orbital contribution. The extent of this contribution and the resulting charge distribution will depend on the size of the *d*-orbitals. This influence is well exemplified by the series  $[\text{M}(\text{mnt})_2]^-$  (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.

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

(c) The nature of 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  $\text{Cs}^+$  as the counter cation.  $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$  behaves as a metal at atmospheric pressure down to 70 K whereas  $\text{Cs}_{0.82}[\text{Pd}(\text{mnt})_2] \cdot 0.5\text{H}_2\text{O}$  only becomes metallic under pressure.

## Acknowledgements

We would like to thank the SERC for studentships (to PIC and RAC) and for support and Johnson Matthey & Co PLC for the loan of precious metal salts.

## REFERENCES

1. J.A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
2. A.E. Underhill and P.I. Clemenson, *Physica*, **143B**, 316 (1986).
3. M.M. Ahmad, D.J. Turner, A.E. Underhill, C.S. Jacobsen, K. Mortensen and K. Carneiro, *Phys. Rev. (B)*, **29**, 4796 (1984).
4. P.I. Clemenson, A.E. Underhill, M.B. Hursthouse and R.L. Short, *J. Chem. Soc., Dalton Trans.* 1689 (1988).
5. P.I. Clemenson, Ph.D. Thesis, University of Wales, 1987.
6. M.M. Ahmad, D.J. Turner, A.E. Underhill, A. Kobayashi, Y. Sasaki and H. Kobayashi, *J. Chem. Soc., Dalton Trans.*, 1759 (1984).
7. P.I. Clemenson, A.E. Underhill, M.B. Hursthouse and R.L. Short, *J. Chem. Soc., Dalton Trans.*, in press.
8. A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **50**, 2650 (1977).
9. J.F. Weiber, L.R. Melby and R.E. Benson, *J. Am. Chem. Soc.*, **86**, 4329 (1964).
10. L.C. Isett, D.M. Rosso and G.L. Bottger, *Phys. Rev. B*, **22**, 4739 (1980).
11. P.I. Clemenson, A.E. Underhill, M.B. Hursthouse and R.L. Short, *J. Chem. Soc., Dalton Trans.*, in press.
12. P.I. Clemenson, A.E. Underhill, M.B. Hursthouse, R.L. Short, G.J. Ashwell, I.M. Sandy, M.T. Jones, C. Jacobsen and K. Carneiro, *Synthetic Metals*, **19**, 579 (1987).
13. I.D. Parker, R.H. Friend and A.E. Underhill, *Synthetic Metals*, in press.
14. A. Kobayashi, H. Kobayashi, A.E. Underhill and R.A. Clark, to be published.