

A New Type of Molecular Conductor

THE STRUCTURE AND PROPERTIES OF $\text{Cs}[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2] \cdot 0.5\text{H}_2\text{O}$

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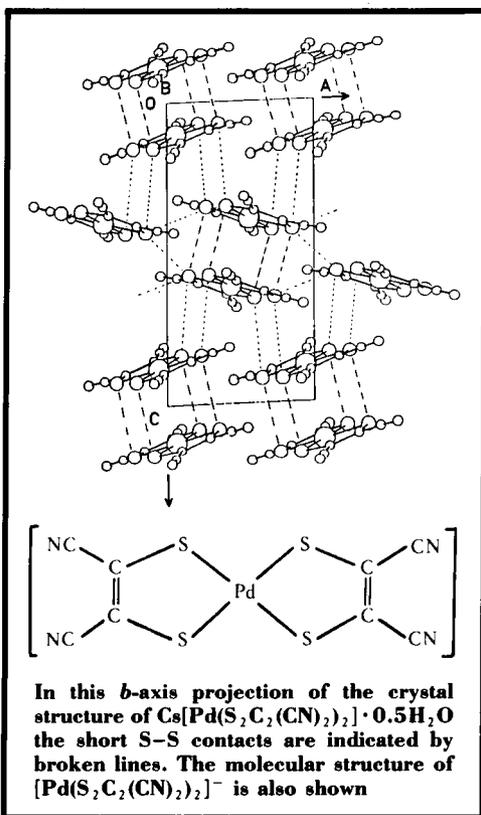
A new type of two-dimensional metallic conductor, based upon a palladium dithiolene complex, has been shown to possess a novel structure involving short S-S contacts in two orthogonal directions, resulting in it having metallic properties down to 40K under high pressure. Studies of compounds of this type may lead to the development of materials for use in a chemical computer and a major programme in this area, to be known as the Molecular Electronics Research Initiative, is to be launched by the British government.

For a number of years we have been investigating the synthesis, structures and properties of novel molecular conductors based on square coplanar anions containing nickel, palladium and platinum. In 1981 we synthesised the first example of a one-dimensional metal based on metal dithiolene anions, $(\text{H}_3\text{O})_{0.33}\text{Li}_{0.8}[\text{Pt}(\text{S}_2\text{C}_2(\text{CN})_2)_2] \cdot 1.67\text{H}_2\text{O}$ (1). Over the past two years Mr. P. I. Clemenson has been investigating the preparation of a series of $[\text{M}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$ (where M is nickel, palladium or platinum) monoanion salts of small cations by electrocrystallisation of solutions containing the dianion salt. This has led to the discovery of compounds exhibiting novel magnetic or electronic properties (2). Using solutions of $\text{Cs}_2[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2]$ he observed the formation of small plate-like black crystals of $\text{Cs}[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2] \cdot 0.5\text{H}_2\text{O}$ growing on the platinum anode. Whereas the monoanion $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$ and $[\text{Pt}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$ salts of Group I cations behave as semiconductors at room temperature with conductivities of $<10^{-2}$ S/cm, the black crystals of the palladium compound exhibited a room temperature conductivity of approximately 5 S/cm. However, the temperature dependence of the conductivity shows the conductivity to be weakly activated between room temperature and

125 K with clear evidence of a smeared out transition at around 240 K. Below about 125 K the crystal behaves as a semiconductor with an activation energy of 41 meV. Thermopower and magnetic susceptibility measurements also indicate that the compound is a small band gap semiconductor or semi-metal at room temperature and all measurements reflect the transition at about 240 K to a low temperature semiconducting state.

The unusually high electrical conductivity is related to the crystal structure of $[\text{Cs}(\text{S}_2\text{C}_2(\text{CN})_2)_2] \cdot 0.5\text{H}_2\text{O}$. This is shown in the figure and is quite different from any structure previously reported for a $[\text{M}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^-$ monoanion salt (3). The structure contains $[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2]^{2-}$ dimers in an eclipsed configuration with intra Pd-Pd distances of 3.329(5) Å. The occurrence of the monoanions as dimer pairs is consistent with the single negative charge on the anion which will result in a single unpaired electron in the highest occupied molecular orbital of the monoanion and hence a strong tendency for the ions to form dimer pairs, a feature which is commonly found for the compounds of platinum dithiolene monoanions.

The dimers are arranged such that there are short S-S contacts between the dimers in both



the *c* and *a* directions. This gives rise to a 2-D sheet structure in the *ac* plane, the sheets being separated in the *b* direction by the caesium ions and water molecules. The large surfaces of the plate shaped crystals correspond to the *ac* plane of the structure and measurements of the anisotropy of conduction show that the most conducting direction is in the *a* direction with an anisotropy of less than 10. Thus the electrical conduction properties and structure show the compound to be a two-dimensional conductor as distinct from the previously prepared one-dimensional metals based on square coplanar complexes.

The pressure dependence of the conductivity of the compound has been studied by Dr. Richard Friend and Mr. Ian Parker at the Cavendish Laboratory at the University of Cambridge (4). They have shown that under pressure the crystals behave as metals, that above 7 kbar pressure the transition observed at

ambient pressure at 240 K is suppressed and at the highest pressure studied (12.1 kbar) the crystals remain metallic down to 40 K. Below 40 K at this pressure, the resistance rise with temperature is relatively small and the conductivity at 1.4 K was found to be above 10 S/cm.

The effect of pressure is to squeeze the dimer monoanion pairs closer together and therefore to increase the extent of the S-S interactions. It has already been shown in organic metals that the effect of pressure is to stabilise the metallic state down to low temperatures and indeed in some instances a superconducting state may be achieved at very low temperatures.

$\text{Cs}[\text{Pd}(\text{S}_2\text{C}_2(\text{CN})_2)_2] \cdot 0.5\text{H}_2\text{O}$ is a new type of molecular metal because it is a stoichiometric metal complex with a two dimensional conducting network as distinct from the previously prepared molecular conductors based on non-integral oxidation state complexes with an essentially one-dimensional conduction pathway.

References

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- 3 M. B. Hursthouse, R. L. Short, P. I. Clemenson and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, submitted for publication
- 4 I. D. Parker, R. H. Friend, P. I. Clemenson and A. E. Underhill, *Nature*, 1986, **324**, (6097), 547

More Organometallic Compounds

The three volume Dictionary of Organometallic Compounds and the first supplementary volume, published by Chapman and Hall, have been reviewed here during the past eighteen months. These have now been followed by the Second Supplement, again edited by Dr. Jane E. Macintyre, running to over 600 pages and priced at £145. A further 315 compounds of the platinum metals are included, all with their molecular formulae, CAS registry number and literature reference. As before, the editor has had the cooperation of a distinguished international advisory board and of a number of specialised editors for individual metals, while sources of further information are given in a substantial list of original publications covering the period up to mid-1985.