An Oxidation–Reduction Reaction, not directly Related to Electrolysis, brought about by the Application of a DC Potential across a Single Crystal of the Partially Oxidised Platinum Atom Chain Compound K$_2$Pt(CN)$_4$Br$_{0.3}$,2·5H$_2$O

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Summary The application of a DC potential ($>$ 150 V cm^{-1}) across single crystals of the partially oxidised platinum atom chain compound K$_2$Pt(CN)$_4$Br$_{0.3}$,2·5H$_2$O induces a oxidation–reduction reaction which commences at the anode and spreads through the crystal to the cathode; the product of the reaction is K$_2$Pt(CN)$_4$,2H$_2$O in a polycrystalline form.

RECENTLY single crystals of transition metal complexes containing linear chains of interacting d^8 metal atoms have been shown to behave as anisotropic ohmic semiconductors with a higher conductivity in the direction of the metal atom chains than in the direction perpendicular to the chains.[1-3] During the course of electrical conductivity measurements on single crystals of the partially oxidised metal chain compound K$_2$Pt(CN)$_4$Br$_{0.3}$,2·5H$_2$O (I), we have observed an oxidation–reduction reaction, on applying DC potentials of greater than 150 V cm^{-1}. The reaction is unusual as it is not directly related to electrolysis and takes place away from the electrodes.

The structure of (I) consists of square-planar [Pt(CN)$_4$]$^{2-}$ units stacked above one another along the c (needle)-axis of the crystal with a Pt–Pt distance of 2·887 Å within the Pt atom chains.[4] All the Pt atoms are crystallographically identical and the crystals do not contain a mixture of Pt^{II} and Pt^{IV} atoms suggesting that the excess charge is delocalised along the metal atom chain. The Br$^-$ ions are in the centres of 64% of the unit cells.

The DC electrical conduction properties of single crystals of (I) (approximate size 1·5 × 0·1 × 0·1 mm) in the direction of the metal atom chains are quite different from those of compounds containing chains of metal atoms with a d^8 (unoxidised) configuration.[1-3] The application of a DC voltage of $<$20 V ($\equiv$150 V cm^{-1}) along the direction of the metal atom chain produces a current which does not remain steady with time but decreases exponentially to a steady value after 5—10 min indicating the presence of space-charge effects.[5] This behaviour is observed for both Ag paste and colloidal graphite electrodes and for crystals with or without a guard-ring. The initial conductivity for crystals without a guard-ring is *ca.* 10^{-4} ohm^{-1} cm^{-1} but this cannot be determined accurately because of the decay characteristics. Similar behaviour is observed for the application of a DC voltage perpendicular to the direction of the metal atom chains, but the initial conductivity is only 10^{-6} ohm^{-1} cm^{-1}. The anisotropy of conduction

(100 : 1) is similar to that previously observed[1-3] for other metal atom chain compounds. Applied voltages of <20 V do not permanently affect the crystals.

At a higher applied voltage, >20 V ($\equiv$ 150 V cm^{-1}) which varies depending on the size of the crystal and the extent of lattice imperfections, the specific conductivity of the crystal increases to approximately double its original value but immediately this occurs there is a change of colour, at the anode end of the crystal, from the metallic copper colour of (I) to a lighter colour with no metallic lustre. The colour change starts at the anode and moves towards the cathode with a sharp boundary between the two colours. The rate of movement of the colour boundary decreases as the reaction proceeds across the crystal and this is accompanied by a rapid decrease in the current. Some crystals are completely changed to the lighter coloured product whilst for others the reaction stops, probably owing to imperfections in the crystal, before reaching the cathode. The speed of the colour boundary moving across the crystal increases with increasing applied voltage. The reaction is irreversible and reversal of the potential before the crystal has completely changed causes the reaction to start at the (new) anode. The application of an AC potential does not produce any reaction, but also indicates a conductivity of 10^{-4} ohm^{-1} cm^{-1}.

If the electrodes are placed perpendicular to the metal atom chains a much higher voltage is needed (3000 V cm^{-1}) before the reaction commences. The colour boundary does not move directly between the electrodes but tends to move out from the anode along the needle axis. Fields in excess of 10,000 V cm^{-1} are needed to convert all the crystal between the electrodes into the lighter coloured product. These results clearly indicate that the reaction proceeds along the metal atom chains.

The reaction product, unlike (I), will not oxidise aqueous KI to iodine and has a C,N, and K content similar to that

expected for $K_2Pt(CN)_4,2H_2O$. Electron probe analysis indicates that the light coloured product has a very much lower Br$^-$ content than (I). X-Ray powder and single-crystal Laue photographs of the product are similar to those observed for $K_2Pt(CN)_4,2H_2O$ and different from those found for (I). The Laue photograph shows the product to be polycrystalline although the overall shape of the original single crystal is retained.

From the nature of the product, and the observation that DC voltages of up to 3500 V cm^{-1} do not produce chemical changes in compounds containing metal atom chains which are not partially oxidised, the reaction observed for (I) appears to be due to the presence of the partially oxidised metal atom chain. Krogmann has suggested that in (I) the top part of the d_{z^2} band is empty and that the excess charge on the metal atom chain, compared[6] with that in $K_2Pt(CN)_4,xH_2O$ is balanced by the presence of the Br$^-$ ions. The mechanism for the reaction is not understood, but it is significant that although (I) is reduced the reaction commences at the anode. It seems likely, therefore, that discharge of the Br$^-$ ions at the anode is an important step and that this is accompanied by the reduction of the Pt atoms in the chain from an oxidation state of +2·3 to +2·0, the electron entering the empty part of the d_{z^2} band.

The AC and DC conductivities were measured as previously described.[2,3]

Added in proof: Minot and Perlstein (*Phys. Rev. Letters,* 1971, **26,** 371) have recently published a value of 4 ohm^{-1} cm^{-1} for the conductivity of $K_2Pt(CN)_4Br_{0.3},2·3H_2O$ using a four-probe method. Our value of 10^{-4} ohm^{-1} cm^{-1} is similar to that (10^{-3} ohm^{-1} cm^{-1}) previously noted by Krogmann and Hausen.[4]

[1] G. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulku, *J. Amer. Chem. Soc.,* 1966, **88,** 4286.

[2] T. W. Thomas and A. E. Underhill, *Chem. Comm.,* 1969, 725.

[3] P. S. Gomm, T. W. Thomas, and A. E. Underhill, *J. Chem. Soc.* (*A*), submitted for publication.

[4] K. Krogmann and H. D. Hausen, *Z. Anorg. Chem.,* 1968, **358,** 67.

[5] F. Gutmann and L. E. Lyons, 'Organic Semiconductors,' Wiley, New York, 1967.

[6] K. Krogmann, *Angew. Chem. Internat. Edn.,* 1969, **8,** 35.