Anisotropic Electrical Conduction in the Halogen-bridged Mixed-valence Compound $Pd^{II}(NH_3)_2Cl_2 \cdot Pd^{IV}(NH_3)_2Cl_4$

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Summary Electrical conductivity in the halogen-bridged mixed-valence compound $Pd^{II}(NH_3)_2Cl_2 \cdot Pd^{IV}(NH_3)_2Cl_4$ is 500 times greater in the direction of the Cl–Pd^{II}–Cl–Pd^{IV}–Cl chains than in the direction perpendicular to these chains.

RECENT studies on single crystals of compounds containing linear chains of metal atoms (*e.g.* bisdimethylglyoximatonickel[1] and Magnus Green Salt[2]) have shown them to possess anisotropic electrical conduction with a relatively high conductivity in the direction of the metal–metal chain. We now report, from studies on single crystals of $Pd^{II}(NH_3)_2Cl_2 \cdot Pd^{IV}(NH_3)_2Cl_4$, (A), the first measurement of similar anisotropic conductance in a mixed-valence compound containing a –X–M^{II}–X–M^{IV}–X– chain.

(A) forms strongly dichroic orthorhombic crystals which do not contain any direct metal–metal interaction but do have chains of –Pd^{II}–Cl–Pd^{IV}–Cl– along the *c* axis which is the needle axis of the crystal.[3,4] We find that single crystals of (A) have the properties of ohmic semiconductors both parallel and perpendicular to the *c* axis. The specific conductivity is, however, very different in these two directions. Parallel to the *c* axis a specific conductivity ($\sigma_{\parallel}$) of $4{\cdot}3 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$ at 20° was observed with an activation energy for conduction (Q) of 0·33 ev, whereas the specific conductivity perpendicular to the *c* axis ($\sigma_{\perp}$) was only about 10^{-12} ohm^{-1} cm.$^{-1}$. The specific conductivities, $\sigma_{\parallel}$ and $\sigma_{\perp}$, are in the ratio 500 : 1, indicating that electron delocalisation is facilitated along the direction of the –Pd^{II}–Cl–Pd^{IV}–Cl– chain. The interaction between

the metal atoms in the different oxidation states probably occurs through the overlap of the d_{z^2} orbitals of the metals with the p_z orbital of the bridging chlorine atom as suggested by Robin and Day for Wolfram's red salt.[5] This type of overlap may lead to the formation of delocalised molecular orbitals along the entire length of the $-Pd^{II}-Cl-Pd^{IV}-Cl-$ chains and thus provide a pathway for conduction.

The ratio $\sigma_{\parallel} : \sigma_{\perp}$ is similar to that found by Collman and his co-workers[6] for crystals of dicarbonylacetylacetonatoiridium for which the higher conductivity was along the direction of direct metal–metal interaction. Although $\sigma_{\parallel}$ for (A) is much less than that observed by Collman for the iridium compound, it is comparable to the value of $3{\cdot}8 \times 10^{-10}$ ohm^{-1} cm.$^{-1}$ at 50° observed by us for bisdimethylglyoximatonickel[1] in which there are direct metal–metal interactions.

The conductivity of compressed-powder discs of (A) followed the non-ohmic relationship $v = I^x$ (where $1{\cdot}0 < x < 2{\cdot}0$) between the current ($I$) and the applied voltage (v) from 0—350 v. This relationship was also observed by Atkinson, Day, and Williams[7] for the conductivity of compressed-powder discs of a range of other platinum and palladium salts. Single crystals of (A) also behaved in this way in the absence of an earthed guard-ring, and, therefore, the observed conduction in compressed-powder discs may be due at least in part to surface conduction along grain boundaries within the discs, as the addition of an earthed guard-ring to the disc did not affect this non-ohmic behaviour. The conductivity of the discs at 50 v applied at 20° was $2{\cdot}1 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$ which is only about one half of that observed along the c axis of the single crystals. Comparison of these results with those observed previously for bisdimethylglyoximatonickel, for which the ratio of single crystal to disc conductivity was $10^5 : 1$, indicates that no simple relationship exists between disc and single crystal measurements. This emphasises the danger of relating measurements made on compressed-powder discs to the structure or electrical properties of single crystals.

Measurements of the d.c. electrical conductivities, $\sigma_{\parallel}$ (0—350 v) and $\sigma_{\perp}$ (0—50 v) were made as previously described,[1] and in all single crystal measurements an earthed guard-ring was present. Compressed-powder discs were made at a pressure of 20,000 p.s.i.

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