Electron Delocalization in Metal Chain Complexes. Evidence for Extrinsic Conductivity in $Pt(NH_3)_4$ $PtCl_4$

By L. V. INTERRANTE

(*General Electric Company, Corporate Research and Development, Schenectady, New York* 12301)

Summary The assumption of intrinsic conductivity behaviour in $Pt(NH_3)_4PtCl_4$ is challenged on the basis of results obtained in single crystal conductivity studies.

THE electrical conductivity of Magnus' green salt (MGS), $[Pt(NH_3)_4PtCl_4]$, and several other "metal chain complexes" has been a topic of considerable recent interest.[1,2] However the possibility that impurities in these complexes may play an important role in determining their unusual solid state behaviour has not been seriously considered. We now report the results of some measurements on MGS which demonstrate the importance of impurity effects in these complexes.

The measurements were carried out on single crystals of MGS prepared using silica gel as a growth medium.[3] The silica gel was formed *in situ* in a U-tube containing a small amount of finely ground MGS powder as seed. The reagents, which consist of 0·2M solutions of K_2PtCl_4 and $Pt(NH_3)_4Cl_2$ obtained from various commercial sources, were then added to either side of the U-tube and allowed to diffuse into the gel for a period of 2 to 8 months. The crystals were removed by sedimentation in water and examined microscopically and by X-ray diffraction methods. Seventeen crystals, ranging up to 0·49 mm^2 in cross section, 2—3 mm long, and free of gross defects were selected and electrical conductivity measurements were carried out *in vacuo* at various temperatures using a four-electrode D.C. conductance method. The conductivity direction in each case was parallel to the needle or metal chain axis in the solid.

Both the conductivity at 25° and the thermal activation energy varied from crystal to crystal, and were dependent on the nature of the preparative reagents. In particular, by using K_2PtCl_4 and $Pt(NH_3)_4Cl_2$ from different commercial sources, batches of MGS crystals of internally consistent but widely varying electrical conductivity and thermal activation energy were prepared. The activation energies ranged from 0·21 eV to 0·40 eV and the conductivity at 25° from $1{\cdot}1 \times 10^{-5}$ to $1{\cdot}2 \times 10^{-2}$ ohm^{-1} cm^{-1}, with a trend toward lower activation energies for the crystals of higher conductivity. The crystals at the high end of this conductivity range are almost two orders of magnitude more conductive than any of the previously reported MGS samples, which range in conductivity from $1{\cdot}6 \times 10^{-6}$ to $4{\cdot}5 \times 10^{-4}$ ohm^{-1} cm^{-1}.[1] Such crystals could be prepared in a consistent and reproducible manner through use of the same reagent combinations.

Analyses of the crystals by wet chemical and electron microprobe methods and examination by X-ray precession and powder methods revealed no significant variations in composition or lattice parameters that could account for these differences. Moreover, repeat determinations carried out on the same crystals after removing the old contacts, gave results which were in quite good agreement with those obtained originally. These observations, as well as the relatively small variance observed within each batch of crystals indicates that the differences do not arise from errors in the measurement procedure.

The variation in electrical properties observed must therefore reflect very small differences in the composition and/or micro-structure of the crystals which presumably arise from differences in the impurity content of the reagents used for the gel growth preparations. The nature of these crystal defects has not yet been definitely established; however, preliminary mass spectral and spectrographic analyses indicate p.p.m. levels of such impurities as Pd, Cu, Fe and possibly Au in the more conductive crystals. These elements, as well as others of the transition series such as Ir, Rh, Os and Ru which could not be accurately determined by the techniques employed, could conceivably substitute for platinum in the MGS structure, leading to quite substantial changes in the electrical properties of the solid. Based upon the results of qualitative thermal e.m.f. measurements on these crystals, which indicate *p*-type conductivity, it appears that these impurities serve as acceptor sites for electrons in the MGS structure releasing holes for electrical conduction.

More information on the solid state properties of this complex is needed before any definite conclusions regarding its electronic structure can be reached; however, it is apparent that impurity effects can be of considerable importance in determining the solid state properties of the complexes of this type and that assumptions of intrinsic semiconductor behaviour in such systems must be greeted with caution in the future.

A more detailed study of impurity effects and of the use of the silica gel crystal growth method for the selective doping of MGS crystals is in progress.

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[1] (a) P. S. Gomm, T. W. Thomas, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1971, 2154; (b) M. J. Minot and J. H. Perlstein, *Phys. Rev. Letters*, 1971, **26**, 371; (*c*) J. P. Collman, L. F. Ballard, L. K. Monteith, C. G. Pitt, and L. M. Slifkin in "International Symposium on Decomposition of Organometallic Compounds to Refractory Ceramics, Metals, and Metal Alloys", ed. K. S. Mazdiyasni, Dayton, Ohio, 1968, pp. 269—283; (d) C. N. R. Rao and S. N. Bhat, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 531.

[2] (a) T. W. Thomas and A. E. Underhill, *Chem. Comm.*, 1969, 725; (b) K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35.

[3] H. K. Henisch, "Crystal Growth in Gels", Pennsylvania State Univ. Press, Univ. Park, 1970.