Application of High-pressure Techniques to the Study of Metal–Metal Interactions in some d^8 Metal Complexes

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Summary New information regarding the intermolecular interactions in Magnus' Green Salt and dicarbonylacetylacetonatoiridium(I) has been obtained from *X*-ray, conductivity, and spectral measurements performed on these materials under high pressure.

IT is known that certain d^8 metal complexes exhibit spectral properties in the solid state indicative of substantial intermolecular interactions between the complex units in the structure. One such complex is Magnus' Green Salt (MGS), $[Pt(NH_3)_4PtCl_4]$, whose absorption spectrum has been much studied.[1] Recently it has been found that MGS and several other d^8 metal complexes, in addition to having unusual spectral properties, also show significant and highly anisotropic electrical conductivity and photoconductivity.[2] The structural feature common to this class of complexes, and presumably responsible for their unusual properties, is the linear chain of metal atoms which results from the parallel stacking of the constituent square planar complex units.

It was suggested several years ago that the overlap of p_z and d_{z^2} orbitals on these metal atoms could give rise to filled and empty bands in the solid leading to intrinsic semiconduction and photoconduction.[1a] The limited experimental information available on the complexes of this type is consistent with this suggestion.[1,2] However, a clear understanding of the intermolecular interactions occurring in the solid state and the dependence of these interactions upon structural parameters such as the metal–metal and metal–ligand distances, requires further experimental work and a more quantitative theoretical treatment.

We have found that high-pressure techniques can be a very useful tool in the study of these systems. By providing a means of reducing the interatomic separations in the solid, it has permitted us to study in much greater detail the dependence of physical properties upon these structural parameters.

Due to the parallel stacking pattern exhibited by these complexes, the metal–metal distance can be obtained directly from *X*-ray powder diffraction measurements, using the positions of the strong 002 reflections as the source of the pertinent "*c*" unit cell parameter.[1a] Such measurements were performed under pressure for MGS and the isoelectronic iridium(I) complex, $[Ir(CO)_2(acac)]$,[2a] [(acac) = acetylacetone] using a diamond anvil press designed by W. Bassett, *et al.*[3]† In both cases the complex was mixed with an equal weight of sodium chloride which was an internal pressure standard.[4] From these measurements it was determined that the crystal structures of the complexes remain unchanged up to at least 60 kbar pressure, but that metal–metal distance decreases by 6—8% over this pressure range. This decrease in metal–metal distance

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appears to be particularly pronounced within the first 10—20 kbar.

Using this same pressure generating apparatus as an absorption cell for a Cary 14 Spectrophotometer, we obtained information regarding the pressure dependence of the absorption spectrum of MGS. Although experimental limitations (diamond absorption and available light energy) permitted observation of only the lowest energy ligand-field band of MGS (at *ca.* 16,500 cm^{-1}) by this technique, this band shifts to lower energies and increases in intensity with pressure in a manner consistent with its previous assignment to a $^1A_{1g} \rightarrow {}^3E_g$ (or $^3B_{1g}$) [$d_{xz,yz}$ (or d_{z^2}) $\rightarrow d_{x^2-y^2}$] transition localized on the $PtCl_4^{2-}$ ions of MGS.[1b]

Using a high compression belt apparatus and conductivity cell as described previously,[5] conductivity measurements were performed on polycrystalline samples of both MGS and [Ir(CO)$_2$(acac)] up to *ca.* 170 kbar pressure. In each case measurements were taken several minutes after an incremental increase in pressure, at which point the resistance was relatively constant with time. Also, the changes in conductivity with pressure were found to be entirely reversible with very little pressure hysteresis.

As is shown in Figures 1A and 2, for both of the complexes studied the initial response to the increase in pressure, and decrease in metal–metal distance, is a substantial increase in conductivity. This result is consistent with both earlier observations on analogues of MGS at ambient pressures[2b] and the supposition that the overlap of valence orbitals on the metal provides the principal pathway for electronic conduction.[2a,b]

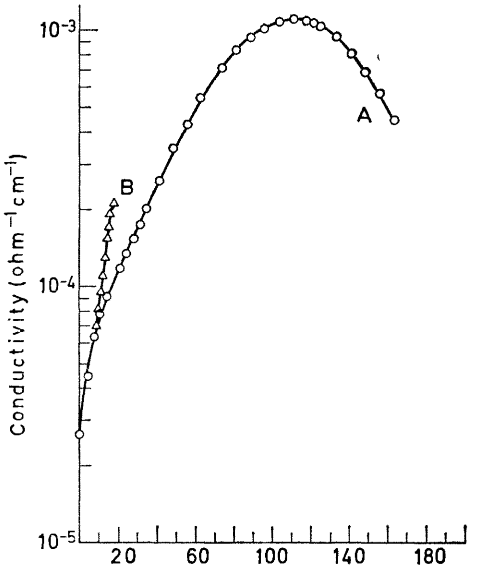

FIGURE 1. *The conductivity of* [Pt(NH$_3$)$_4$PtCl$_4$] *as a function of pressure*; A, *polycrystalline sample*; B, *single crystal, "c" axis direction.*

In the case of MGS, conductivity measurements were also obtained on a single crystal under pressure. This crystal was wired for four-point probe measurements along the metal–metal axis and measurements were taken up to *ca.* 18 kbar using a liquid-filled conductivity cell specially designed for the belt apparatus. In addition to confirming the general increase in conductivity with increasing pressure observed for the polycrystalline sample, the results of this experiment (Figure 1B) indicate that the rate of change in the conductivity along the metal–metal axis in the crystal is significantly greater than that shown by the polycrystalline sample. This suggests that at the maximum in the pressure *vs.* conductivity curves the conductivity along this axis is probably considerably in excess of the already rather large values shown by the polycrystalline samples. Considering the relatively small rate of change in metal–metal distance with pressure indicated by our *X*-ray measurements, our observations show convincingly the importance of this parameter in determining conductivity in this class of compounds.

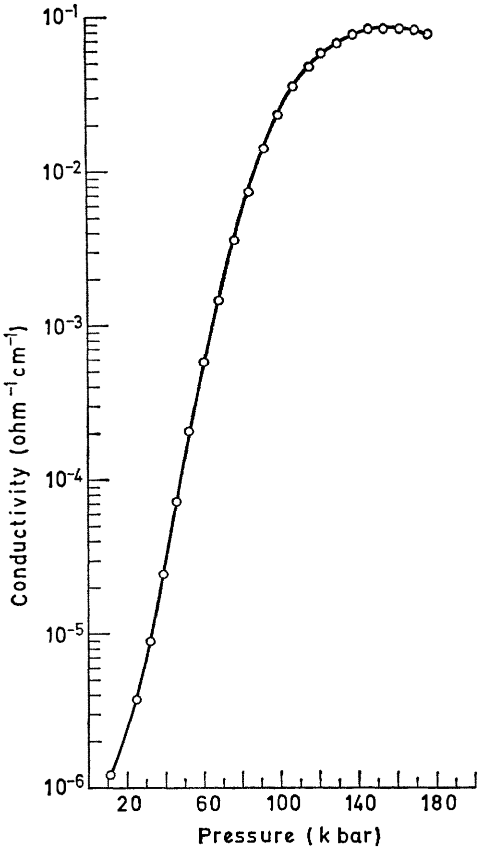

FIGURE 2. *The conductivity of* [Ir(CO)$_2$(acac] *as a function of pressure (polycrystalline sample).*

On the other hand, the decrease in conductivity with pressure observed at higher pressures is difficult to explain by considering only metal–metal distance changes. A similar reversal in the conductivity *vs.* pressure curve has been observed for ferrocene at considerably lower pressures and has been linked to bond distance changes occurring within the molecular units.[6] Preliminary MO calculations carried out on the MGS system, indicate a substantial dependence of the metal–metal interactions upon metal–ligand as well as metal–metal distances.[7] On this basis it appears likely that the explanation for the high pressure conductivity behaviour of the d^8 metal complexes we have studied may also be found in changes occurring within the complex units.

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