−15° gave $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ (0.180 g, 0.26 mmol, 52%) from the first band and $C_5H_5RhP(C_6H_5)_3Br_2$ (0.094 g, 0.16 mmol, 32%) from the second.

Preparation of $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ (7).—Finely powdered zinc dust (2.0 g, 15.3 mg-atoms) was added to a solution of $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ (0.180 g, 0.26 mmol) in *N,N*-dimethylformamide (20 ml). After stirring for 16 hr at 60°, the solvent was removed under reduced pressure. Chromatography of the resulting mixture using Florisil and benzene as eluent first produced a pale yellow band from the column. The solution containing this band was concentrated to 5 ml and hexane (30 ml) was added. Pale yellow crystals of product (0.065 g, 0.12 mmol, 46%) were formed on cooling to −15°.

Preparation of $C_5H_5RhP(C_6H_5)_3(C_2F_4H)I$ (8).—The compound $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ (0.050 g, 0.094 mmol) was dissolved in dichloromethane (10 ml) and 55% aqueous hydriodic acid (0.4 mmol) was added. After stirring for 1 hr and evaporating to dryness, the residue was recrystallized from dichloromethane–hexane. Reddish crystals (0.053 g, 0.081 mmol) were obtained in 86% yield.

Preparation of $C_5H_5RhP(C_6H_5)_3(SnBr_3)Br$.—Stannic bromide (0.22 g, 0.50 mmol) was added to a stirred solution of $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.23 g, 0.50 mmol) in dichloromethane (15 ml). After 1 hr, hexane (30 ml) was added to give red crystals, which were recrystallized twice from dichloromethane–hexane. Thus a sample of pure product (0.21 g, 0.24 mmol, 48%) was isolated.

In an analogous procedure *p*-toluenesulfonyl chloride gave pure $C_5H_5RhP(C_6H_5)_3(SO_2C_6H_4CH_3)Cl \cdot 0.5CH_2Cl_2$ from the first crystallization (82% yield). The infrared spectrum of this compound in a Nujol mull showed typical stretching modes for an SO_2 group[19] at 1224, 1204, 1093, and 1045 cm^{-1}.

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Studies of Intermolecular Interactions in Square-Planar d^8 Metal Complexes. I. The Physical Properties of Magnus' Green Salt and Some Related Complexes at High Pressures[1]

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The intermolecular interactions in Magnus' green salt $[Pt(NH_3)_4PtCl_4]$, dicarbonylacetylacetonatoiridium(I), and some related platinum and palladium complexes are investigated by means of electrical, spectral, and X-ray powder diffraction measurements carried out at pressures up to *ca.* 170,000 atm. The marked changes in spectral and electrical properties observed as a function of pressure are interpreted in terms of the internuclear distance changes occurring in the solid, leading to new information regarding the structure–property relationships in this type of compound.

Introduction

In Magnus' green salt (MGS) $[Pt(NH_3)_4PtCl_4]$, dicarbonylacetylacetonatoiridium(I) $[Ir(CO)_2(acac)]$, and a number of other d^8 metal complexes, the planar complex units stack in columns in the crystal with the metal atoms aligned along the columnar axis, forming continuous chains. The unusual solid-state properties associated with many of these compounds point to the existence of a direct interaction between the metal atoms in these chains. For example, in several cases, highly anisotropic conduction and photoconduction have been observed with room-temperature conductivities as high as 10^{-4} ohm^{-1} cm^{-1} in the direction of highest conductivity, which is coincident with the metal–metal chain direction in the crystal.[2] Moreover, studies of homologous series of complexes such as $M(A)_4MCl_4$ (M = Pd, Pt; A = NH_3, CH_3NH_2, $C_2H_5NH_2$)[3] and $M'(CO)_2(acac)$ (M′ = Ir, Rh)[2a,b] have revealed a dependence of the conductivity upon both the distance between the metal atoms and the principal quantum number of the metal valence orbitals. Similarly, the electronic spectra of the compounds of this type are often markedly different from that of the constituent complex units in solution but tend to approach the solution spectra as the separation between the metal atoms is increased or the principal quantum number of the metal valence orbitals is decreased through structural modifications such as those indicated above.[4]

An intrinsic band model has been proposed which accounts, in a qualitative way, for many of these observations;[2,4] however, further experimental and theoretical studies are clearly needed before any firm conclusions about the electronic structure of these solids can be made. In particular, more detailed information regarding the dependence of the physical properties of such materials upon the structural parameters in the solid would be useful, both for the purpose of testing theoretical hypotheses and as a guide to future synthetic work. The use of high-pressure techniques to obtain structure–property information of this type is well established.[5] With the aid of such techniques, changes in the internuclear distances in solids can be

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(1) Paper presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; a preliminary account has also appeared in L. V. Interrante and F. P. Bundy, *Chem. Commun.*, 584 (1970).

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effected in a controlled and continuous fashion, permitting the detailed study of the relationship between these structural parameters and the physical properties of the material.

The present paper describes the application of such techniques to the study of MGS, $Ir(CO)_2(acac)$, and some analogous platinum and palladium complexes which exhibit columnar stacking in the solid state. In the following paper[6] the results obtained and their implications with regard to the structure–property relationships in this type of compound are discussed in the light of semiempirical molecular orbital calculations carried out on MGS.

Experimental Section

Preparation of Complexes.—The metal complexes tetraammineplatinum(II) tetrachloroplatinate(II) (MGS),[7] tetraamminepalladium(II) tetrachloropalladate(II) $[Pd(NH_3)_4PdCl_4]$,[4] bis(ethylenediamine)platinum(II) tetrachloroplatinate(II) $[Pt(en)_2PtCl_4]$,[8] and dicarbonylacetylacetonatoiridium(I) $[Ir(CO)_2(acac)]$[9] were all prepared as described in the literature cited and their identity verified by means of elemental analyses and X-ray powder patterns. The single crystal of MGS used in the high-pressure conductivity measurements was grown in a silica gel at a pH of *ca.* 3.0 using a 1-in. diameter U tube and 0.2 *M* solutions of K_2PtCl_4 and $Pt(NH_3)_4Cl_2$.[10] This procedure gave clear, green crystals up to 2 mm long and 0.3 × 0.3 mm² in cross section, with the long axis of the crystals coincident with the "*c*" axis of the tetragonal unit cell.[11]

Physical Measurements at High Pressures. X-Ray and Spectral Measurements.—These measurements were performed using a modified Bassett diamond anvil press.[12] The modifications, which have been described previously by Moore and Kasper,[13] include the use of thin metal gaskets between the diamonds to provide more uniform pressure distribution over the sample area. For the X-ray measurements a diamond with a 0.020-in. face was used as the moving anvil and the gaskets were prepared using 0.002-in. thick nickel sheet. The complexes were ground with an equal weight (or, in the case of $Ir(CO)_2(acac)$, half the original weight) of reagent grade sodium chloride in a mortar and then mixed further in a "wig-L-bug" before adding to the press. The pressure was determined from measurements of the (220) and (200) reflections due to the NaCl, using the pressure *vs.* compression values calculated by Decker.[14] The "*c*" unit cell parameters for the metal complexes were obtained from measurements of the (002) reflections.

For the spectral measurements, a diamond with a 0.039-in. face was used as the moving anvil. This permitted, after gasketing, an effective area of sample in the light path of 0.00062 in.² and maximum pressures on the order of 50–70 kbars. The spectral measurements were carried out on finely ground samples of the complex which were pressed into the hole in the metal gasket by repeated pressure cycling up to *ca.* 20 kbars. The press was positioned in the sample compartment of a Cary 14 spectrophotometer equipped with a high-intensity source. The effective spectral range was limited by diamond absorption and available energy to *ca.* 13,333–25,000 cm^{-1}. In the case of MGS the spectrum was calibrated according to the metal–metal distance in the solid by obtaining the X-ray diffraction pattern of the sample at each pressure setting and measuring the position of the (002) reflection of MGS.

Experiments with mixtures of the complex and sodium chloride gave results which were qualitatively the same as those obtained with the complex alone; however, the resultant spectra in these cases were not as well resolved, due to a decrease in the signal to background intensity ratio.

Conductivity Measurements.—These measurements were carried out on polycrystalline samples and, in the case of MGS, also on a single crystal, using the high-compression belt apparatus.[15] The resistance of the polycrystalline samples was measured directly using pressure contacts and a Kiethley 610C electrometer as an ohmmeter. The resistances were then converted to conductivities using sample dimensions obtained after the pressure application. In addition to measurements at room temperature, which were carried out on each of the metal complexes, the conductivity of MGS was also determined as a function of temperature as well as pressure using a "sandwich heater cell" as previously described.[15] The temperature was measured by means of a chromel–alumel thermocouple placed immediately under the sample and was varied from *ca.* 30 to 150° by changing the current through the heater circuit.

The conductivity *vs.* pressure behavior of a single crystal of MGS was determined using a liquid-filled conductivity cell specially constructed for the belt apparatus. This cell consisted of a 0.5-in. diameter by 0.44-in. long cylindrical Teflon box, which contained the crystal, a noninductively wound manganin coil, and isoamyl alcohol which served as the pressure-transmitting medium. The pressure in the cell was measured directly by means of the manganin coil which had been previously pressure seasoned and calibrated using a bismuth sample element in place of the crystal.[16] Both the crystal and the manganin coil were wired for potential probe measurements using 0.002-in platinum wire leads and silver paint contacts. Contact through the cell walls was made using eight self-sealing tapered copper pins which were pushed through undersized holes from the inside of the cell and soldered to the platinum lead wires. The Teflon cell was encased in a close-fitting pyrophyllite cylinder with steel disks placed immediately above and below the cell to provide more uniform pressure distribution. The leads from the copper pins were brought out of the pressurized zone through the pyrophyllite gaskets. The voltage generated across the probes on the manganin coil by a 10-mA dc exciting current was displayed on a 100-mV recorder, permitting continuous monitoring of the manganin resistance and thereby the pressure in the cell. The resistance of the sample was determined using a $\sim 10^{-8}$-A exciting current and a Kiethley 610C electrometer to measure the voltage across the sample voltage probes. The measurements were obtained several minutes after each incremental increase in pressure, at which point the values were relatively constant with time.

In preliminary experiments using Bi sample elements, pressures up to at least 30 kbars were reached using this cell; however, the maximum pressure attained in the measurements on the MGS crystal was *ca.* 18 kbars, at which point the crystal fractured, probably due to strains arising from changes in the cell geometry, transmitted by the platinum lead wires.

Results and Discussion

X-Ray diffraction studies of MGS,[11] $Ir(CO)_2(acac)$,[17] and several related d^8 metal complexes[4] have shown that the metal atoms in these complexes all lie in or near (002) planes in the crystals, leading to strong (002) X-ray reflections. Moreover, the d_{002} spacings determined from these reflections correspond to twice the metal–metal separation in the linear chains of metal atoms of these structures, enabling the direct determination of this important structural parameter from powder diffraction data. Such measurements were carried out as a function of pressure for both MGS and $Ir(CO)_2(acac)$ indicating decreases in metal–metal distance of 8–10% over a 100-kbar pressure change (Figure 1). Aside from a decrease in the unit cell dimensions of the complexes, no phase changes nor reaction with the sodium chloride used as an internal

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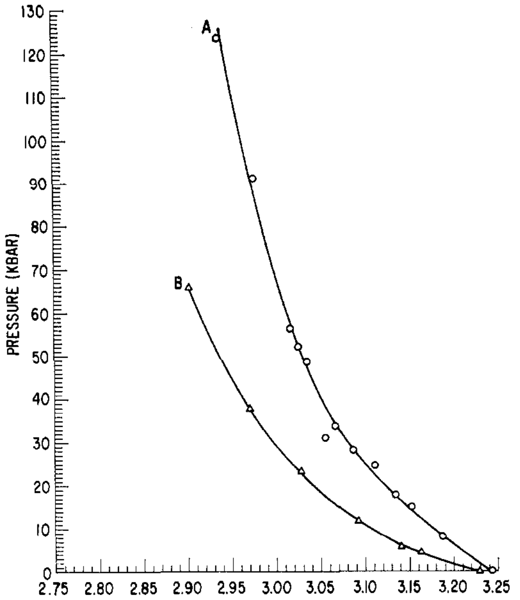

Figure 1.—The metal–metal separation in (A) $Pt(NH_3)_4PtCl_4$ and (B) $Ir(CO)_2(acac)$, as a function of pressure.

pressure standard was evidenced by the X-ray measurements throughout the pressure range studied (up to *ca.* 125 kbars). The consequences of this decrease in internuclear distance upon the interactions between the metal complex units in these solids were investigated using conductivity measurements and, in the case of MGS and the related $Pt(en)_2PtCl_4$ and K_2PtCl_4 complexes, spectral methods.

The electronic absorption spectra of each of these latter complexes in the visible and near-ultraviolet regions appear to be strongly dominated by d–d transitions of the $PtCl_4{}^{2-}$ ion.[4] In K_2PtCl_4, where the metal–metal separations in the chains are 4.13 Å, the absorption bands due to these transitions are comparable in energy and intensity to those observed for the $PtCl_4{}^{2-}$ ion in aqueous solution. However, in $Pt(en)_2PtCl_4$ and MGS, where the separations are 3.40 and 3.25 Å, respectively, all of these bands, except for those involving in-plane $d_{xy} \rightarrow d_{x^2-y^2}$ type transitions, occur at proportionately lower frequencies and with higher intensities. This shift has been ascribed to an "axial perturbation" of the out-of-plane d and p orbitals on the $PtCl_4{}^{2-}$ unit, arising from the adjacent metal atoms in the chain.[4b] One of the absorption bands affected by this axial perturbation is the lowest energy ligand field band of the $PtCl_4{}^{2-}$ ion, which has been assigned to an ${}^1A_{1g}$–${}^3E_g$ ($d_{xz,yz} \rightarrow d_{x^2-y^2}$) transition. Among the $PtCl_4{}^{2-}$ derivatives which exhibit columnar stacking, the position and intensity of this band varies in proportion to the metal–metal distance, ranging from 20.3 kK (ϵ_{max} *ca.* 20) in K_2PtCl_4 to 16.5 kK (ϵ_{max} *ca.* 150) in MGS.

The effect of increased pressure upon this absorption band, in the case of MGS, is illustrated in Figure 2. These results clearly show a continuation of the trend toward lower transition energies with decreasing intermetallic distances indicated by the $PtCl_4{}^{2-}$ derivatives. Indeed, as is demonstrated in Figure 3, where the position of this band is plotted *vs.* the metal–metal distance, this trend is reasonably continuous over a wide range of metal–metal distances and $PtCl_4{}^{2-}$ derivatives. Furthermore, although the quantitative significance of the optical density changes observed as a function of pressure are limited due to the changes in sample dimensions and diffuse scattering occurring under pressure, the results of our measurements (Figure 2) do agree, in general, with the trend toward increasing band intensity with decreasing metal–metal distances established in the earlier studies.[18]

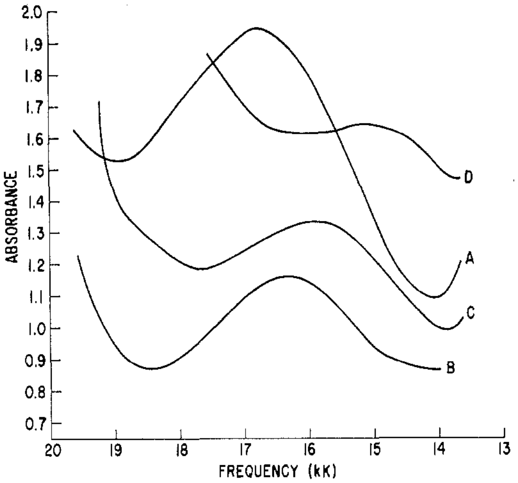

Figure 2.—The effect of pressure upon the absorption spectrum of $Pt(NH_3)_4PtCl_4$: (A) 1 atm, Pt–Pt separation 3.24 Å; (B) *ca.* 2 kbars, 3.23 Å; (C) *ca.* 6 kbars, 3.20 Å; (D) *ca.* 16.5 kbars, 3.14 Å.

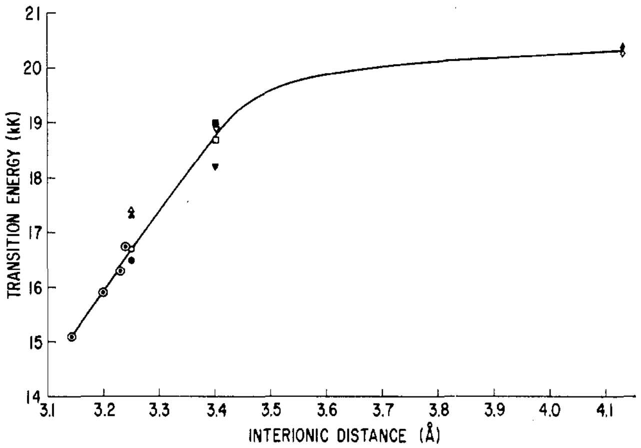

Figure 3.—The ${}^1A_{1g} \rightarrow {}^3E_g$ transition energy as a function of interionic distance in various $PtCl_4{}^{2-}$ derivatives: ◇, ◆, K_2PtCl_4; □, ■, $Pt(en)_2PtCl_4$; ▽, ▼, $Pt(C_2H_5NH_2)_4PtCl_4$; ○, ●; ⊙, $Pt(NH_3)_4PtCl_4$. The symbol ⊙ refers to data obtained on $Pt(NH_3)_4PtCl_4$ in the present study. All other data points were obtained from ref 4a (open symbols) and 4b (closed symbols).

Although experimental limitations have thus far prevented the extension of this study to the remainder of the MGS absorption spectrum, the observations we have made are in good agreement with previous work on the $PtCl_4{}^{2-}$ derivatives and tend to support the conclusion that these complexes do retain their "molecular" identity to a large extent in the solid state. On the other hand, as is clear from the results presented in Figure 3, the influence of metal–metal interactions upon the electronic structure of these solids is becoming increasingly important as the metal–metal distance is

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(18) The analomously high optical density values observed at 1 atm probably arise from diffuse scattering effects as the sample did not remain well compacted upon release of the pressure.

decreased and, particularly below *ca.* 3.4 Å, small changes in this parameter can have a substantial effect upon their physical properties.

This dependence of the MGS absorption spectrum upon the intermetallic distance in the solid is rather similar to that found in earlier studies on the dialkylglyoxime complexes of nickel, palladium, and platinum. These complexes exhibit columnar stacking in the solid much like that in MGS with comparable metal–metal separations. Spectral studies of various alkyl derivatives at both ambient[19] and high pressures[20] have evidenced a red shift and intensity increase for the lowest energy visible absorption band with decreasing metal–metal distance quite analogous to that observed for the $PtCl_4^{2-}$ derivatives.

Spectral measurements on $Pt(en)_2PtCl_4$ and K_2PtCl_4 were carried out under pressure as described for MGS. The lowest energy visible absorption band in these spectra, which also has been assigned to the $PtCl_4^{2-}$ based $^1A_{1g}$–^3E_g transition,[4b] clearly shifts with increasing pressure; however, the degree and direction of this shift are quite unlike that observed for MGS. In the case of $Pt(en)_2PtCl_4$ this band remains practically unchanged in energy up to at least 30 kbars and then gradually shifts to higher energies with a further increase in pressure. For K_2PtCl_4 this shift to higher energies was evident at even lower pressures, although the overall change in energy after a ~30-kbar pressure increase was substantially less than was observed for MGS.

These observations can be understood in terms of opposing effects arising from the inter- and intramolecular distance changes occurring under pressure. The larger metal–metal distances in the latter complexes should result in relatively weaker intermolecular interactions throughout the pressure range studied and, consequently, a decreased tendency of the $^1A_{1g}$–^3E_g transition to shift to lower energies with increasing pressure. Superimposed upon this energy-lowering effect is an energy-increasing contribution due to the distance changes occurring *within* the complex units as a function of pressure. The effect of such intramolecular distance changes upon the absorption spectra of metal complexes has been well studied, especially for octahedral complexes in which intermolecular interactions have tended to be rather less important.[21] The increase in the energy of the ligand field bands with increasing pressure invariably observed for such complexes is readily understood in the context of the decreased metal–ligand distances occurring under pressure. This intramolecular effect is also presumably operative in complexes such as MGS; however, at least within the pressure range studied, the balance is apparently in favor of the intermolecular contribution. The shorter metal–metal distances in these cases undoubtedly play an important role in determining the direction of the pressure effect, but also of importance is the relative magnitude of the inter- and intramolecular distance charges occurring under pressure. The latter cannot be directly determined from the X-ray data obtained; however, based upon the results of compressibility measurements on nonmolecular solids such as AgCl, where the changes in lattice parameters do directly reflect the metal–chlorine distance changes, they are undoubtedly considerably smaller than the metal–metal distance changes observed herein. For example, for AgCl an overall decrease in Ag–Cl distance of only 5.5% in 100 kbars has been observed,[22] as compared to the 8.5% in the 100-kbar metal–metal distance change found for MGS (Figure 1).

The effect of increased pressure upon the conductivity of MGS is illustrated in Figure 4. In this case, data were obtained on both a polycrystalline sample (curve A) and a single crystal (curve B) with the single crystal wired for measurement along the "*c*" or metal–metal axis direction. Both sets of data indicate an initial increase in the conductivity with pressure which, on the basis of curve A, is apparently maintained up to *ca.* 100 kbars. This initial increase in conductivity correlates well with the results of earlier work on related $PtCl_4^{2-}$ complexes at ambient pressures and the conclusion that the conductivity of these complexes is highly dependent upon the metal–metal distance in the solid.[3] Indeed, as is indicated by the results obtained on the single crystal, the conductivity along the metal–metal axis direction at ~100 kbars must be well above the already significant ~10^{-3} ohm^{-1} cm^{-1} value exhibited by the polycrystalline sample. This is particularly remarkable in view of the rather small change in the metal–metal distance over this pressure range indicated by our X-ray measurements (Figure 1).

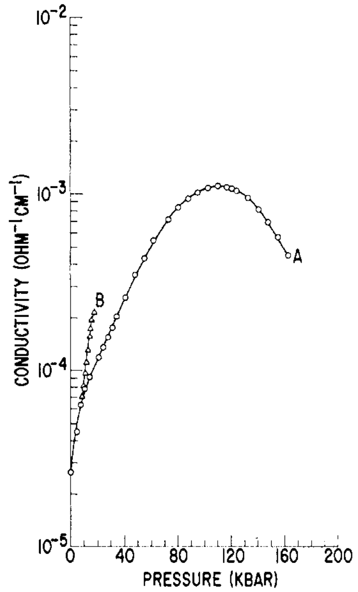

Figure 4.—The conductivity of $Pt(NH_3)_4PtCl_4$ as a function of pressure: (A) polycrystalline sample; (B) single crystal, "*c*" direction.

As is illustrated in Figure 5, much the same result was obtained for the related iridium(I) complex, $Ir(CO)_2(acac)$, in which the separation between the molecular units in the chain is close to that in MGS at ambient pressures. In this case, however, the maximum conductivity observed at high pressures is even greater than that exhibited by MGS and along the chain direction in the crystals may even be approaching quasimetallic character at these pressures.

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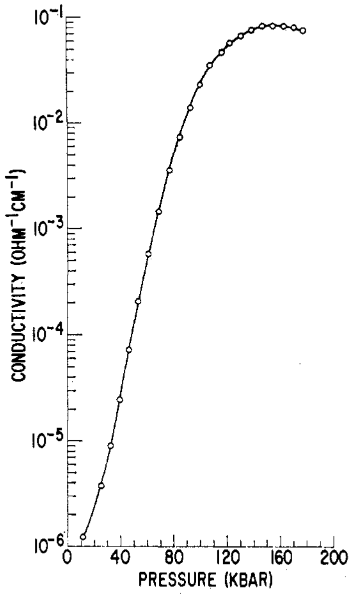

Figure 5.—The conductivity of $Ir(CO)_2(acac)$ as a function of pressure (polycrystalline sample).

Conductivity measurements were also carried out on polycrystalline samples of $Pt(en)_2PtCl_4$ and $Pd(NH_3)_4PdCl_4$; however, in neither case was it possible to characterize the conductivity behavior in an umambiguous fashion. In the case of $Pd(NH_3)_4PdCl_4$, the conductivity remained below the limits of measurement (*ca.* 10^{-7} ohm^{-1} cm^{-1}) throughout the pressure range surveyed. For $Pt(en)_2PtCl_4$ the conductivity initially increased with increasing pressure, albeit at a considerably slower rate than that observed for MGS, but at ~70 kbars, an irreversible phase change was evidenced, leading to a phase (or phases) whose conductivity decreased with increasing pressure. The fact that this was an irreversible phase change was evident both in the conductivities observed below 70 kbars upon unloading and in the X-ray powder photographs obtained for the resulting sample. Attempts to identify the product or products of this transformation on the basis of the X-ray diffraction pattern have thus far proven unsuccessful, although reaction products such as $Pt(en)Cl_2$, $PtCl_2$, and $Pt(en)_2Cl_2$ did not appear to be present.

For each of the other complexes studied the X-ray powder photographs of the samples before and after compression to *ca.* 170 kbars were identical, thus ruling out any irreversible phase changes in these cases. Moreover, on the basis of the high-pressure X-ray measurements performed on MGS up to *ca.* 125 kbars, which indicated a gradual and continuous change in lattice parameters throughout the pressure range, and the reversible and continuous character of the conductivity dependence upon pressure observed for both MGS and $Ir(CO)_2(acac)$, it appears that reversible phase changes can also be effectively ruled out for these complexes up to at least 170 kbars. Therefore, the fact that the conductivity of these complexes goes through a maximum and eventually decreases with increasing pressure at very high pressures appears to result from continuous changes in the structural parameters rather than any gross structural rearrangement.

Further information regarding this unusual conductivity behavior at high pressures was obtained, in the case of MGS, from a study of the temperature dependence of the conductivity as a function of pressure. In these measurements the temperature was cycled over the range 30–~150° at various pressures from 1 atm to 152 kbars. As is shown in Figure 6, in which the data from the unloading portion of the pressure cycle are presented, at each of these pressures the conductivity followed the usual exponential relationship $\sigma = \sigma_0 \exp(-\Delta E/kT)$, where σ_0 is the extrapolated value of the conductivity at $1/T = 0$ and ΔE is the thermal activation energy.

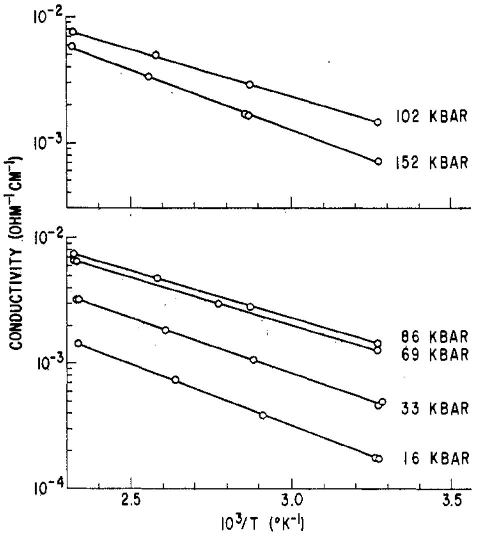

Figure 6.—The conductivity of $Pt(NH_3)_4PtCl_4$ as a function of temperature and pressure.

The values of ΔE and ln σ_0 derived from these data are plotted as a function of pressure in Figure 7. It is clear from these results that the origin of the inflection in the conductivity *vs.* pressure curve obtained for MGS is to be found in the activation energy term, which goes through a minimum at very close to the same pressure at which the conductivity reaches a maximum. The ln σ_0 curve, on the other hand, shows no inflection

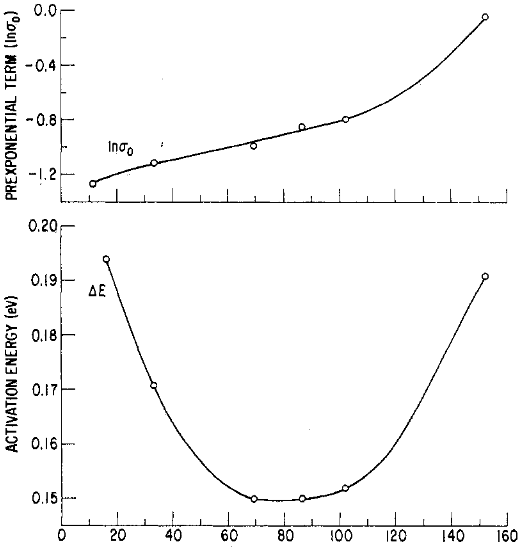

Figure 7.—Variation in ln σ_0 and the thermal activation energy for conduction (ΔE) in $Pt(NH_3)_4PtCl_4$ with pressure.

at this pressure but instead gradually rises with increasing pressure throughout the pressure range studied.

For an intrinsic, wide-band semiconductor σ_0 is directly proportional to the sum of the "hole" and "electron" mobilities, and to the extent that the effective masses of these carriers are independent of pressure, its variation with pressure can provide information regarding the dependence of these mobilities upon the internuclear distances in the solid.[23] Under these conditions the character of the ln σ_0 *vs.* pressure curve for MGS may be explained in terms of a gradual but continuous increase in the mobilities of the carriers in this complex with increasing pressure. This conclusion is consistent with the current band model for the electronic structure of MGS,[2,4a] in that the increased platinum orbital overlaps that would be anticipated from the observed decrease in metal–metal distances with pressure should lead to wider "d_{z^2}" and "p_z" bands and therefore higher mobilities. In this context the ΔE pressure dependence and thereby the maximum in the conductivity *vs.* pressure curve for MGS presumably reflects changes in the d_{z^2}–p_z band gap occurring under pressure and consequently contains information regarding the dependence of this band gap upon the internuclear distances in the solid.

The decrease in this band gap with increasing pressure can be readily understood in terms of the increase in band widths with decreasing metal–metal distance. On the other hand, the interpretation of the decrease in conductivity observed at very high pressures for both MGS and $Ir(CO)_2(acac)$ in terms of band gap changes obviously requires consideration of internuclear distance changes other than of the intermetallic type.

A similar reversal in the conductivity *vs.* pressure curve has been observed previously for ferrocene and was explained on the basis of electronic structure changes occurring within the ferrocene molecules caused by a decrease in the intramolecular distances.[24] The results of our high-pressure spectral studies have already shown that such intramolecular distance changes can also be important in determining the physical properties of the d^8 metal complexes under pressure. On the basis of these results and the molecular orbital calculations on MGS to be discussed in the following paper,[6] it appears likely that such intramolecular effects are indeed responsible for the conductivity behavior observed for MGS and $Ir(CO)_2(acac)$ at very high pressures.

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Studies of Intermolecular Interactions in Square-Planar d^8 Metal Complexes. II. A Molecular Orbital Study of Magnus' Green Salt

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The intermolecular interactions in Magnus' green salt (MGS) and their dependence upon some of the important structural parameters in the solid are explored using semiempirical molecular orbital theory and elementary band structure calculations. These studies indicate quite significant intermolecular effects at internuclear distance values appropriate to MGS, yet no significant covalent bonding between the platinum atoms in this structure. The substantial dependence of the electronic structure upon both the inter- and intramolecular distances in MGS evidenced by these calculations is discussed in light of the available experimental information on this and related square-planar d^8 metal complexes.

Introduction

In the preceding paper[1] the results of high-pressure physical measurements on Magnus' green salt, $Pt(NH_3)_4PtCl_4$ (MGS), and other d^8 metal complexes which exhibit columnar stacking in the solid state were interpreted in terms of pressure-induced internuclear distance changes. In order properly to evaluate these results in terms of the electronic structure changes occurring in these solids under pressure and, thereby, to obtain a better understanding of the structure–property relationships in this type of compound, a molecular orbital study of MGS was undertaken using the extended Hückel approach. The results of this study and of a simple band theory calculation carried out on MGS are described in this paper.

Because of the approximate nature of these calculations it is important to realize that the quantitative aspects of the results obtained cannot be taken too literally. However, we believe that these results do provide a reasonably accurate qualitative picture of the intermolecular interactions in MGS and the manner in which these interactions depend upon the important structural parameters in the solid.

Previous theoretical work on complexes of this type have been limited largely to qualitative applications of molecular orbital and elementary band theory involving no numerical computations. The first such application of molecular orbital theory in 1957 led to the suggestion that significant intermetallic bonding could occur within the linear chains of metal atoms in these structures, due to overlap of the filled d_{z^2}-like and empty p_z-like orbitals

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