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Studies of Intermolecular Interactions in Transition Metal Complexes. IV. A High-Pressure Study of Some Mixed-Valence Platinum and Palladium Complexes[1]

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The results of X-ray diffraction, spectral, and conductivity measurements carried out on linearly conductive complexes of the type $M(A)X_3$, where M = Pd, Pt, (A) = $(NH_3)_2$, $(C_2H_5NH_2)_4$, en, and X = Cl, Br, I, as a function of pressure are reported. The conductivity at high pressures was found to depend on the nature of M, A, and X and certain trends in conductivity with these parameters are noted. For several of the complexes continuous and reversible increases in conductivity by as much as 9 orders of magnitude in 140 kbars were observed. These findings and the results of spectral observations on the $Pt(C_2H_5NH_2)_4Cl_3 \cdot 2H_2O$ complex at *ca.* 30-kbar pressure are discussed in the context of the structural effects induced by the high pressure, as determined from the X-ray diffraction studies, and related to a reduction of the geometrical inequivalency in the metal coordination environments brought about by compression of the linear $(\text{- - -}M^{II}\text{- - -}X\text{-}M^{IV}\text{-}X\text{- - -})_n$ chains.

Introduction

The unusual stoichiometry and intense colors associated with the palladium and platinum complexes of the type $M(A)X_3$, where A = $(NH_3)_2$, $(C_2H_5NH_2)_4$, en, etc. and X = Cl, Br, I, have been of interest for some time. Early suggestions regarding the existence of Pd(III) and Pt(III) in these complexes[2] have been contradicted by subsequent structure determinations[3] which show square-planar coordinated M(II) ions and octahedrally coordinated M(IV) ions alternately arranged so as to give linear $[\text{- - -}M^{II}\text{- - -}X\text{-}M^{IV}\text{-}X\text{- - -}]_n$ chains (Figure 1) along one crystallographic direction. Typically the intrachain halogen atom is located about two-thirds of the distance between M(II) and M(IV) atoms.

These structural studies and the results of physical property measurements are consistent with a "class II mixed-valence compound"[4] description for the $M(A)X_3$ complexes. Thus, the compounds are diamagnetic[5] and exhibit solid-state spectra characteristic of the isolated constituent complex units superimposed on strong absorption bands in the visible region which have been assigned to M(II) → M(IV) intervalence charge-transfer transitions.[6]

Recently additional evidence for weak electronic interactions within the $[\text{- - -}M^{II}\text{- - -}X\text{-}M^{IV}\text{-}X\text{- - -}]_n$ chains has been obtained from electrical conductivity measurements.[7] Several of these complexes were studied in the form of single crystals and were found to behave as highly anisotropic semiconductors with room-temperature conductivities as high as 4.3×10^{-9} ohm^{-1} cm^{-1} along the chain direction in the crystal. The conductivity perpendicular to the chain direction was at least 300 times lower.

We have previously shown that the application of high pressure can produce substantial changes in the physical properties of such linearly conductive transition metal complexes by altering the interatomic distance relationships in the solid.[8] Through studies of the X-ray powder diffraction patterns as a function of pressure, these property changes can often be correlated with specific structural changes occurring in the solid, leading to detailed structure-property information of potential value in future synthesis work.

Particular interest in the $M(A)X_3$ complexes as candidates for such a high-pressure study stems from their unusual chain structure in which the environment about the M(II) and M(IV) atoms differs substantially only in the respective intrachain metal-halide distance. Compression along this chain direction should be felt mainly in the longer M(II)-X separations, thus reducing the inequivalency in the two coordination environments and lowering the barrier for electron delocalization within the chain. In the extreme situation, where the halide ion is equidistant from the two metal atoms, the metal valencies would become equivalent and the complex would be effectively transformed into a class III mixed-valence solid[4] with quasi one-dimensional metallic properties.

In this paper we report the results of some high-pressure X-ray diffraction, spectral, and conductivity measurements carried out on representatives of three different structural types of $M(A)X_3$ complexes, $[M^{II}(NH_3)_2X_2][M^{IV}(NH_3)_2X_4]$, where M = Pd or Pt and X = Cl or Br, $[Pt^{II}(en)X_2][Pt^{IV}(en)X_4]$, where X = Cl, Br, or I, and $[Pt^{II}(C_2H_5NH_2)_4][Pt^{IV}(C_2H_5NH_2)_4X_2]X_4 \cdot 4H_2O$, where X = Cl or Br. In the following paper paper, dc and ac conductivity and photoconductivity measurements carried out at ambient pressures are described which provide more information regarding the conduction process in these solids.

Experimental Section

Synthesis of $M(NH_3)_2X_3$ Complexes. The $Pd(NH_3)_2X_3$ (X = Cl, Br) complexes were prepared by direct halogenation of an ice-cold aqueous suspension of the corresponding $Pd(NH_3)_2X_2$ complex, which was prepared according to ref 5. Attempts to synthesize $Pd(NH_3)_2I_3$ by analogous procedures, as suggested by ref 7, were unsuccessful.

The corresponding Pt complex, $Pt(NH_3)_2Br_3$, was prepared, as in ref 3a, by evaporation of an aqueous solution containing equimolar amounts of $Pt(NH_3)_2Br_2$ (prepared by reaction of *trans*-$Pt(NH_3)_2Cl_2$ with KBr) and $Pt(NH_3)_2Br_4$ (prepared by direct bromination of $Pt(NH_3)_2Br_2$). The *trans*-$Pt(NH_3)_2Cl_2$ used for this synthesis was prepared from $Pt(NH_3)_4Cl_2$ (obtained from Matthey Bishop) according to ref 9.

Synthesis of $PdPt(NH_3)_4X_6$ Complexes. The chloride complex (X = Cl) was prepared as described in ref 5. The bromide derivative (X = Br) was prepared by boiling an aqueous solution of the chloride complex with an excess of KBr. The solution was cooled and evaporated slightly to yield dark greenish black crystals which were washed with water to remove excess halide salt. Attempts to prepare the

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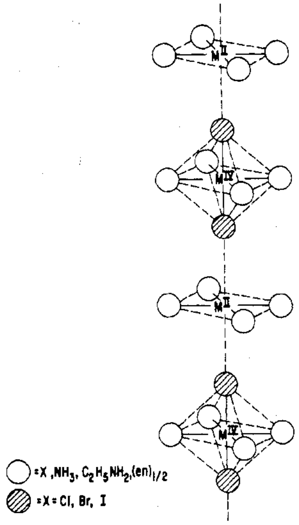

Figure 1. Stacking arrangement in the $M(A)X_3$ compounds.

bromide complex by direct mixing of $Pt(NH_3)_2Br_4$ and $Pd(NH_3)_2Br_2$ solutions were unsuccessful.

Synthesis of $Pt(C_2H_5NH_2)_4Cl_3{\cdot}2H_2O$ Complexes. Wolffram's Red Salt (X = Cl) was prepared according to ref 10. Reihlen's Green Salt (X = Br) was prepared by direct reaction of KBr with Wolffram's Red Salt.

Synthesis of $Pt(en)X_3$ Complexes. As a starting material for the synthesis of all $Pt(en)X_3$ complexes, $Pt(en)Cl_2$ was prepared according to ref 11. The method outlined in ref 12 for the preparation of $Pt(en)I_2$ from $Pt(en)Br_2$ was used to prepare both $Pt(en)Br_2$ and $Pt(en)I_2$ from $Pt(en)Cl_2$. Thus, $Pt(en)Cl_2$ was treated with aqueous $AgNO_3$, AgCl was removed by filtration, and the appropriate KX salt was added. Direct halogenation was used to prepare $Pt(en)X_4$ from $Pt(en)X_2$, where X = Cl or Br. The mixed-valence complexes $Pt(en)X_3$ (X = Cl, Br) were prepared by slow evaporation and cooling of an aqueous solution containing equimolar amounts of the corresponding $Pt(en)X_2$ and $Pt(en)X_4$ complexes. The method of ref 13 was used to prepare $Pt(en)I_3$ from reaction of $Pt(en)I_2$ with K_2PtI_6. An alternate method was also used to prepare $Pt(en)Br_3$ from $Pt(en)Br_2$ and $Pt(en)_2Br_4$ (prepared according to ref 12) based on a procedure from ref 13; no differences between the $Pt(en)Br_3$ prepared by the two different methods were apparent.

All compounds analyzed satisfactorily for the correct empirical formulas.

Conductivity Measurements at High Pressure. These measurements were carried out on polycrystalline samples at pressures up to 160 kbars using the high-compression belt apparatus.[14] A two-probe conductivity technique employing either Pt- or gold-wire pressure contacts was used in conjunction with a Keithly 610C electrometer for the dc conductivity measurements and a Wayne Kerr B224 bridge for the ac conductivity measurements. For the measurements as a function of both temperature and pressure, a special "sandwich heater cell" was used,[14] wherein the temperature was monitored by means of a chromel-alumel thermocouple located immediately adjacent to the sample. The temperature was varied from *ca.* 25 to 80°.

For each high-pressure experiment, the conductivity was measured for two complete cycles of pressure loading and unloading. The results were generally independent of the direction of pressure change and cycle, except for $Pd(NH_3)_2Br_3$ and $Pd(NH_3)_2Cl_3$. In both of these cases, the conductivity *vs.* pressure curve went through a maximum on the first pressure-loading cycle; the position of the maxima varied from run to run, but unloading and second-cycle curves were always reproducible and showed no indication of a maximum. The data presented in Figure 5 are derived from the unloading portion of the pressure cycle in these two cases.

Spectral and X-Ray Measurements at High Pressure. These measurements were made using a Bassett diamond-anvil press[15] which had been modified as described previously.[16] Pressures up to *ca.* 60 kbars were attained using this apparatus. For the spectral measurements, a 0.001 in. thick nickel gasket was inserted between the diamond anvils both to provide uniform sample pressure and to block light transmission outside the 0.040-in. diameter sample area. The spectral measurements were carried out on finely ground samples using a Cary 14 spectrophotometer equipped with a high-intensity source. Measurements were restricted to the range from 12 to 19 kK by available energy and by diamond absorption.

The same apparatus was used for the X-ray measurements except that a 0.005 in. thick nickel gasket was used to provide uniform pressure in the 0.025-in. diameter sample area. A pinhole camera arrangement was used to record the powder diffraction patterns under pressure using Mo Kα radiation. The samples were ground intimately with an equal weight of reagent grade NaCl. The pressure was determined from measurements of the (220) and (200) reflections due to NaCl using the pressure *vs.* compression values calculated by Decker.[17] The unit cell parameters for $Pd(NH_3)_2Cl_3$ were obtained from measurements of the (110), (200), (020), and (004) reflections of the orthorhombic unit cell.

Ambient-Pressure Spectral and X-Ray Measurements. X-Ray powder diffraction measurements using the Debye-Scherrer technique with Cu Kα radiation were made on each sample before and after the high-pressure conductivity experiments.

The single-crystal absorption spectrum of $Pt(C_2H_5NH_2)_4Cl_3{\cdot}2H_2O$ was recorded on a Beckman DK-2 spectrophotometer using a small crystal mounted over a slit cut in nickel foil.

Results

X-Ray Data. The X-ray powder diffraction pattern for each complex was examined both at ambient pressure and at ~60-kbar pressure (the approximate upper limit of the diamond-anvil cell) in order to determine qualitatively the effect of pressure on the structure. For all of the complexes except $Pt(C_2H_5NH_2)_4Br_3{\cdot}2H_2O$, the pattern obtained at high pressure was similar to the corresponding ambient-pressure pattern, aside from the expected increase in spacing of the diffraction lines corresponding to a uniform decrease in the unit cell dimensions. In the case of $Pt(C_2H_5NH_2)_4Br_3{\cdot}2H_2O$ an irreversible transformation to an as yet uncharacterized material was evidenced. The same transformation apparently occurs upon vigorous grinding of the sample with a mortar and pestle. Consequently, this compound was not included in the remainder of the high-pressure study.

For one of the complexes, $Pd(NH_3)_2Cl_3$, a detailed study of the change in lattice dimensions with pressure was made using NaCl as an internal pressure standard. The results are given in Figures 2 and 3 which show, respectively, the change in all three of the orthorhombic unit cell dimensions with pressure and in the intrachain Pd(II)-Pd(IV) distance ($c/2$) with pressure up to *ca.* 60 kbars.

Spectral Investigations. High-pressure spectral measurements in the visible-uv region were complicated both by very high sample absorbancy and by the necessarily small sample area of the diamind-anvil pressure apparatus employed. Indeed, with the exception of $Pt(C_2H_5NH_2)_4Cl_3{\cdot}2H_2O$, all of the compounds studied were either initially too highly absorbing or rapidly became so under pressure in the region between 12 and 31 kK. The one case for which meaningful spectral data could be obtained is shown in Figure 4.

The absorption spectrum of $Pt(C_2H_5NH_2)_4Cl_3{\cdot}2H_2O$ at approximately 30 kbars is compared with that of the single crystal at 1 atm. The single-crystal spectrum shows a shoulder at 16.0 kK, the same energy at which Yamada has reported a band polarized along the *c* axis.[6b] This band does

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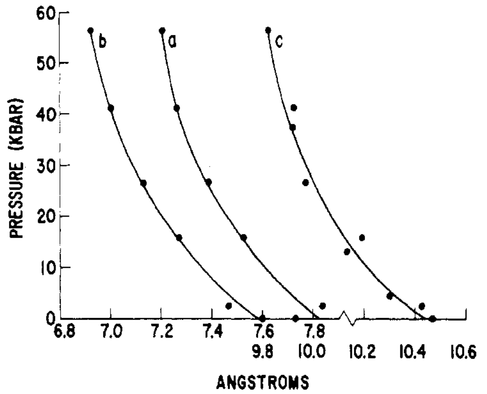

Figure 2. Lattice dimensions of $Pd(NH_3)_2Cl_3$ as a function of pressure.

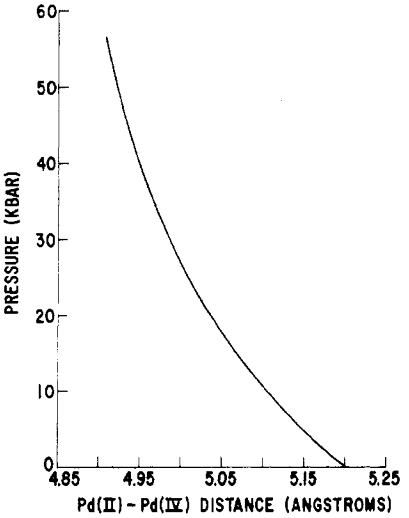

Figure 3. The Pd(II)-Pd(IV) intrachain distance in $Pd(NH_3)_2Cl_3$ as a function of pressure.

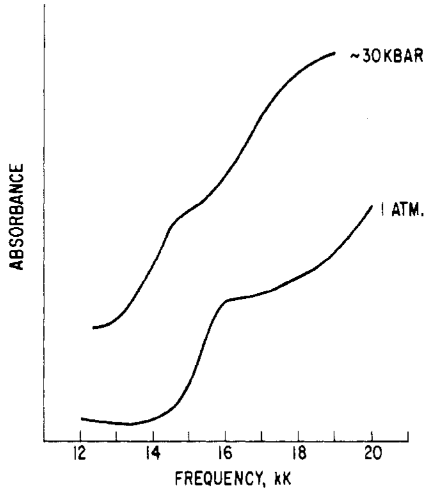

Figure 4. Absorption spectrum of $Pt(C_2H_5NH_2)_4Cl_3{\cdot}2H_2O$.

not occur in the spectra of the isolated complex units in solution and has been assigned to the intervalence $M(II)(d_{z^2}) \rightarrow M(IV)(d_{z^2})$ charge-transfer transition. This band shifts toward lower energy upon compression of the $[M\cdots X{-}M{-}X]_n$ chains.

Conductivity Measurements. Figure 5 shows the results of conductivity measurements as a function of pressure at room temperature for three $M(NH_3)_2X_3$ complexes (M = Pd or Pt, X = Br; M = Pd, X = Cl). Figure 6 shows similar results for the $Pt(en)X_3$ complexes, where X = Cl, Br, or I. In each case, the conductivity continuously increases with increasing pressure; this behavior was found to be both reversible and reproducible. X-Ray powder diffraction data obtained for each sample before and after the high-pressure experiment indicated that no irreversible phase changes had occurred. For the complexes $PdPt(NH_3)_4Cl_6$, $PdPt(NH_3)_4Br_6$, $Pt(C_2H_5NH_2)_4Cl_3{\cdot}2H_2O$, and $Pt(C_2H_5NH_2)_4Br_3{\cdot}2H_2O$ the conductivity remained below the limits of measurement up to 140 kbars.

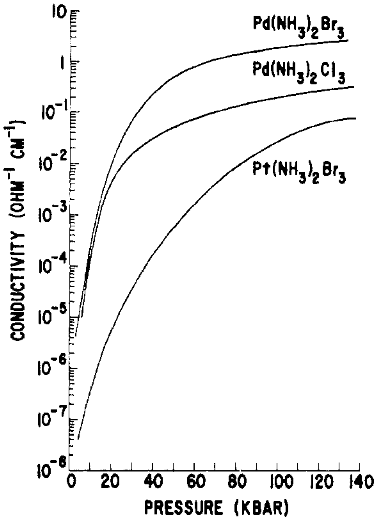

Figure 5. Conductivity of the $M(NH_3)_2X_3$ complexes as a function of pressure.

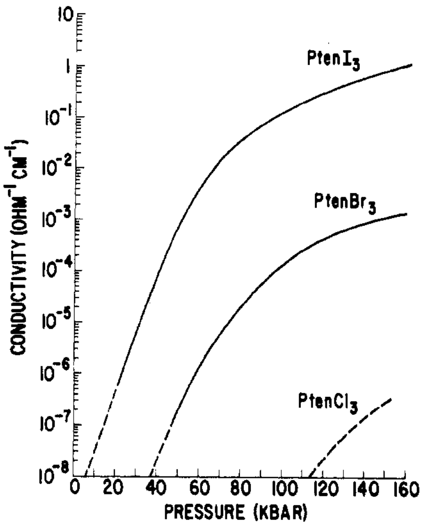

Figure 6. Conductivity of the $Pt(en)X_3$ complexes as a function of pressure.

In the case of $Pd(NH_3)_2Br_3$ the temperature dependence of the conductivity at high pressures was also investigated. Measurements were taken over the temperature ranges 30-78° at various pressures up to 140 kbars. The results show a linear log σ *vs.* $1/T$ relationship at each pressure investigated, consistent with a conductivity *vs.* temperature relationship of the form $\sigma = \sigma_0 \exp(-\Delta E/kT)$, where ΔE is the thermal activation energy for conduction. Figure 7 shows a plot of the derived values of ΔE as a function of pressure.

Discussion

Qualitative X-ray diffraction measurements carried out on each of the $M(A)X_3$ complexes up to ~60-kbar pressure in-

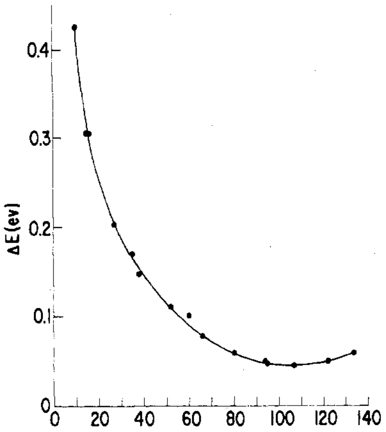

Figure 7. ΔE as a function of pressure for $Pd(NH_3)_2Br_3$.

dicate that, with the exception of $Pt(C_2H_5NH_3)_4Br_3 \cdot 2H_2O$, no first-order phase changes occur for any of these materials up to at least this pressure. For the complex $Pd(NH_3)_2Cl_3$, where detailed X-ray data were obtained, an overall decrease in the *a, b,* and *c* cell dimensions over this pressure range of, respectively, 8.0, 8.7, and 5.8% was observed. These values are in approximately the same range as those previously observed for the metal-chain complexes, $Pt(NH_4)PtCl_4$ and $Ir(CO)_2(acac)$,[8] and presumably reflect reductions mainly in the relatively long intermolecular separations in the solid under pressure.

The compression along the chain direction is given by the change in the *c* lattice dimension, which is just twice the M(II)-M(IV) distance within these chains. This distance is 5.21 Å at 1 atm and is composed of Pd(II)-Cl and Pd(IV)-Cl distances of 3.22 and 1.99 Å, respectively.[3a] Assuming that the principal interatomic distance change in this direction is in the considerably longer Pd(II)-Cl distance, this distance would be 2.87 Å at ~60 kbars. Although such a change is noteworthy, in the absence of an increase in the Pd(IV)-Cl distance, it is still considerably short of that which would be required to transform the system to the hypothetical Pd(III) state where the halide ion is equidistant from the two metal atoms. Moreover, a careful examination of the high-pressure X-ray diffraction patterns for $Pd(NH_3)_2Cl_3$ and the rest of the $M(A)X_3$ complexes revealed none of the substantial changes in relative positions and intensities that would be expected in the event of such a transition. It, therefore, appears that at least up to the limits of the X-ray measurements (~60 kbars), the class II → III transition does not occur for these complexes.

Nevertheless, as is evidenced by the spectral and conductivity results, the observed lattice dimension changes do indeed have substantial effects on the solid-state properties of these complexes. The spectral observations on the $Pt(C_2H_5NH_2)_4Cl_3 \cdot 2H_2O$ complex indicate a substantial red shift and a possible increase in intensity of the absorption band assigned to the intervalence charge-transfer transition. Here, the position of the *c*-polarized $Pt(II)(d_{z^2}) \rightarrow Pt(IV)(d_{z^2})$ transition at ~30 kbars appears to be approximately 14.6 kK, or 1.4 kK lower than that observed in the crystal at 1 atm. These spectral changes presumably reflect the gradual reduction in the inequivalence of the M(II) and M(IV) coordination environments effected by compression along the chain direction and consequently a smaller energy separation for the d_{z^2} orbital energy levels on the two sites. This is illustrated in Figure 8 which shows, qualitatively, the broadening of the M and X energy levels into bands and gradual merging of the two M d_{z^2} bands that would be anticipated in the event of such a compression along the M-X chain direction.

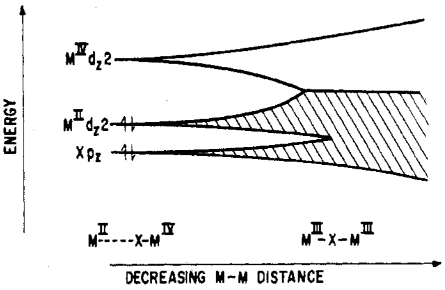

Figure 8. Energy level description for $M(A)X_3$ complexes.

The most remarkable effects of pressure are seen in the conductivity behavior. At ambient pressures and temperatures, the conductivity of these complexes is quite low ($<10^{-8}$ ohm^{-1} cm^{-1}), even along the $(M\text{-}X\text{-}M)_n$ chain direction in the single crystals. It is generally even lower for the samples in polycrystalline form, as studied in the present investigation. However, as is illustrated in Figures 5 and 6 these conductivities increase quite rapidly under pressure and even at ~5 kbars are considerably higher than the highest values observed for any of the single-crystal samples at 1 atm.[7] This conductivity continues to increase for most of the complexes studied to the limits of the high-pressure measurements, ~140 kbars. The overall change in conductivity over the range 1 atm to ~140 kbars is as large as 9 orders of magnitude for several of these complexes. This is considerably in excess of that which has previously been observed in high-pressure work on other inorganic or organic materials.

The actual conductivity at high pressure depends quite markedly on the particular compound and among the complexes studied an apparent trend with M, A, and X is indicated. In particular, among the isostructural $M(NH_3)_2X_3$ complexes the replacement of M = Pd by M = Pt causes a decrease in the conductivity at high pressures, whereas replacement of Cl by Br increases the conductivity. The trend I > Br > Cl is maintained in the $Pt(en)X_3$ complexes which are in general less conductive at high pressures than the corresponding $M(NH_3)_2X_3$ derivatives.

The gradual leveling off in the conductivity increase above ~100 kbars is most pronounced for the $M(NH_3)_2X_3$ complexes but is also noticeable in the case of the $Pt(en)X_3$ derivatives. This probably reflects, in part, the reduced compressibility along the chain axis at very high pressures, as is indicated by the high-pressure X-ray data for $Pd(NH_3)_2Cl_3$ (Figure 3). It is also possible that conductivity-decreasing effects like those proposed previously for the metal-chain complexes[8] arising from internuclear distance changes other than those within the $(M\text{-}X\text{-}M)_n$ chains are beginning to make a significant contribution at these pressures.

In order to investigate the further possibility that we have, in fact, reached a one-dimensionally metallic M(III) state at these higher pressures, a study of the effect of temperature on the high-pressure conductivity was undertaken for the most conductive of these complexes, $Pd(NH_3)_2Br_3$. The results (Figure 7) show a substantial reduction in the activation energy for conduction with pressure, but there is no indication of a change in sign as would be expected for the transition to a metallic state. Indeed the activation energy appears to reach a broad minimum at ~106 kbars for this complex indicating that a further increase in pressure beyond 140 kbars will probably not be effective in driving this transition to completion. The increase in activation energy at the highest pressures does seem to imply the existence of a secondary pressure effect, such as could arise from intramolecular distance changes, which may prevent the ultimate realization of the class II → III transition.

In summary, the results of this study indicate that the solid-state properties of the $M(A)X_3$ complexes are extraordinarily sensitive to pressure, presumably due to the effect of pressure in reducing the geometric inequivalency in the environment about the metal atoms while at the same time increasing the intrachain metal-halogen orbital overlaps. In the context of the energy level diagram in Figure 8, at high pressures the system is effectively being driven toward a one-dimensionally metallic M(III) state whose ultimate attainment, however, is apparently prevented by the action of secondary effects which may arise from extrachain internuclear distance changes. The application of high pressures also serves to raise the level of conductivity of the $M(A)X_3$ complexes into a more easily measurable range, revealing apparent trends in conductivity with the M, (A), and X groups. These trends are further investigated in the following paper which deals with the electrical properties of these complexes at ambient pressures.

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Registry No. $Pd(NH_3)_2Br_3$, 51017-61-9; $Pd(NH_3)_2Cl_3$, 51064-32-5; $Pt(NH_3)_2Br_3$, 50790-39-1; $Pt(en)I_3$, 33907-25-4; $Pt(en)Br_3$, 33907-32-3; $Pt(en)Cl_3$, 50600-56-1; $Pt(C_2H_5NH_2)_4Cl_3 \cdot 2H_2O$, 50600-57-2.

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Studies of Intermolecular Interactions in Transition Metal Complexes. V.[1] Electrical Properties of Some Mixed-Valence Platinum and Palladium Complexes

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The results of dc and ac conductivity measurements and a photoconductivity study on some one-dimensionally conductive mixed-valence complexes of the type $M(A)X_3$, where M = Pd, Pt, (A) = en, $(NH_3)_2$, and X = Cl, Br, I, are reported. These results suggest that the conventional band-type conduction model is not appropriate for discussing electron transport in these materials and that a more localized description of their electronic structure is required. A tentative hopping-type mechanism for the electrical conductivity is presented and used to discuss the observed trends in conductivity with M, (A), and X as well as the ac conductivity and photoconductivity results.

Introduction

Electron-transport phenomena in one-dimensional chain complexes is currently a subject of intense interest in solid-state physics.[2] This interest has been centered largely on complexes which contain linear chains of directly interacting metal ions and display highly directional, pseudometallic solid-state properties, such as $K_2Pt(CN)_4Br_{0.3} \cdot xH_2O$. We describe herein the results of some electrical measurements on another type of linear-chain mixed-valence complex containing Pt and Pd, which also exhibits highly anisotropic solid-state behavior. These are compounds of the type $M(A)X_3$, where M = Pd, Pt, (A) = $(NH_3)_2$, en, and X = Cl, Br, I.

In the preceding paper in this series[1] the physical properties of these complexes at high pressures were described. The present paper focuses on the electrical properties of these materials at ambient pressures and on the nature of the one-dimensional electron-transport process.

Previous work on these compounds has centered mainly on their unusual spectral properties and has revealed strong polarized absorption bands in the visible region of the solid-state spectra which have been assigned to intermolecular charge-transfer transitions.[3] Recently electrical conductivity measurements were reported[4] for several examples of this type of complex, indicating highly anisotropic behavior with the highest conductivity in the direction of the linear chains. These conductivities were thermally activated, with activation energies on the order of 0.3 eV. The values for room-temperature conductivity depended upon the nature of M and X; however, a detailed investigation of this dependence and the electron-transport mechanism was prevented by the limited number and low conductivity of the complexes chosen for study. Our high-pressure study[1] of these materials revealed a similar dependence of the conductivity on the nature of M, A, and X, although possible rearrangements in the conductivity order due to differing compressibilities among the complexes must be considered.

In addition to the interest in characterizing this solid-state behavior and its dependence on structural parameters in more detail, a better understanding of the electron-transport process in these linear-chain structures may also be useful in the study of redox reactions involving Pd and Pt complexes. Indeed, the binuclear halide-bridged structures which have been proposed as intermediates in electron-transfer reactions between Pt(II) and Pt(IV) complexes in solution[5] closely resemble the arrangement of complex units within the linear chains of the $M(A)X_3$ complexes. Hope-

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