tion 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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(1) Part IV: L. V. Interrante, K. W. Browall, and F. P. Bundy, *Inorg. Chem.*, **13**, 1158 (1974).

(2) I. F. Shchegolev, *Phys. Status Solidi A*, 12, 9 (1972); H. R. Zeller, "Advances in Solid State Physics," Vol. XIII, Pergamon Press, New York, N. Y., 1973.

(3) (a) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **29**, 421 (1956); (b) *ibid.*, 12, 894 (1956); (c) P. E. Fanwick and D. S. Martin, Jr., *Inorg. Chem.*, 12, 24 (1973).

(4) T. W. Thomas and A. E. Underhill, *J. Chem. Soc. A*, 512 (1971).

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 494-497.

fully, through studies of the electron-transport process in the solid-state system, information relevant to the detailed understanding of the electron-transfer reaction in solution can be obtained.

In this paper, we report the results of ac and dc conductivity measurements on both single-crystal and polycrystalline samples and the results of a photoconductivity study. These measurements reveal new information regarding the electron-transport process and the origin of the observed trends in conductivity with the structural parameters M, A, and X.

Experimental Section

Preparation of Materials. The details of the preparation of all of the compounds used in this study have been reported previously.[1] All compounds analyzed satisfactorily for the correct empirical formulas. Single crystals of $Pt(NH_3)_2Br_3$ which were up to several millimeters long and 0.1 mm × 0.1 mm in cross section were prepared by slow cooling an aqueous solution containing equimolar amounts of $Pt(NH_3)_2Br_2$ and $Pt(NH_3)_2Br_4$. Single crystals of $Pd(NH_3)_2Cl_3$ as large as 2 mm long and 0.2 mm × 0.1 mm in cross section were prepared by dissociation of $Pd(NH_3)_2Cl_4$ according to the method of Cohen and Davidson.[6] Attempts to prepare single crystals of $Pd(NH_3)_2Br_3$ by the above techniques, as well as by silica gel growth procedures, were unsuccessful. Numerous attempts were also made to prepare single crystals of the $Pt(en)X_3$ complexes, where X = Cl, Br, I, by growth from gels, using a circulating crystallizer, and by slow cooling, with only limited success. The best crystals of $Pt(en)Cl_3$ and $Pt(en)Br_3$, 0.4 mm long and 0.2 × 0.04 mm in cross section, were grown by slow cooling. Single crystals of $Pt(en)I_3$ of a size suitable for conductivity measurements could not be obtained.

Dc Conductivity Measurements. Four-electrode dc conductivity measurements were made on both polycrystalline samples in the form of pellets pressed at 85,000 psi and on single crystals. Electrical contact to the sample was made with 2-mil platinum wire in the case of pellet samples and 0.5-mil gold-coated tungsten wire in the case of single crystals; the wires were attached with silver conducting paint. The current through the sample *via* the end contacts was determined by measuring the voltage drop across a standard resistor in series with the sample. A 6-V mercury battery was used to provide currents ranging from 10^{-7} to 10^{-12} A. Measurement of the voltage drop across the two voltage contacts allowed calculation of the sample resistance. All voltage measurements were made using a Keithley 610C electrometer. Measurements were carried out *in vacuo* at pressures $<10^{-5}$ Torr as a function of temperature. Activation energies for conduction were determined from the slope of straight-line plots of log σ *vs.* $1/T$, where σ is conductivity and T is absolute temperature, using the method of least squares for a best fit. The data for each sample were in good agreement with a relationship of the form $\sigma = \sigma_0 \exp(-\Delta E/kT)$. Because of the difficulty in measuring the very high resistance of most of the samples at low temperatures, the room-temperature conductivities of all samples except $Pd(NH_3)_2Br_3$ were determined by extrapolation of data obtained at elevated temperatures using the straight-line log σ *vs.* $1/T$ relationship.

Ac Conductivity Measurements. Two-probe ac conductivity measurements were made on single crystals using silver paint or Aquadag electrodes and gold-coated tungsten wire as for the dc measurements. A General Radio Type 1615A capacitance bridge equipped with an audio oscillator and detector was used to make ac measurements as a function of both frequency and temperature. These measurements were carried out in air in a temperature-controlled oven. No dependence of the results upon the electrode material was observed.

Photoconductivity. The photoresponse of single-crystal samples was measured using a two-probe dc technique. Direct resistance measurements on samples with silver paint and Aquadag electrodes were made with a Keithley 610C electrometer having an input resistance $>10^{14}$ ohms. A set of twelve Monopass filters was used to isolate regions of the spectrum from 12.5 to 25 kK generated by 75-W Xe arc and 200-W quartz–iodine lamp sources. Measurements were made both with and without a No. 4602 glass filter (with <1% transmission below 10 kK). The observed photoresponse was corrected for dark current and for the effects of wavelength-dependent heating and light intensity. A miniature thermistor was mounted next to the sample for temperature measurement and an ISCO Model 5R spectral radiometer was used to measure the incident light intensity. The photoresponse increased as the incident light intensity increased and decreased as the temperature increased at any given wavelength.

Thermo-emf Measurements. Thermo-emf measurements were made on polycrystalline pressed pellet samples sandwiched between two massive copper blocks and on single-crystal samples in a specially designed apparatus. The single-crystal device consisted of a thin insulating sheet which could be mounted on a temperature-controlled block and which had cemented on it two small temperature-controlled copper blocks separated by 0.4 mm; a needle-shaped crystal could be cemented between the two blocks with silver conducting paint, thus making electrical and thermal contact. Temperature differentials of up to 40° for the polycrystalline samples and up to 15° for the single-crystal samples were applied while the resulting voltage between the hot and cold ends of the sample was measured with a Keithley 610C electrometer.

Results

Due to problems with insolubility, hydrolytic instability, and slow rates of dissolution and recrystallization, considerable difficulty was encountered in obtaining single-crystal samples of the $M(A)X_3$ complexes of appropriate size and quality for electrical property studies. In the case of the $M(NH_3)_2X_3$ derivatives, only $Pd(NH_3)_2Cl_3$ and $Pt(NH_3)_2Br_3$ were obtained in the form of single crystals suitable for four-probe conductivity measurements. Here the crystals were rectangular parallelepipeds with well-formed faces and no visible defects.

For the $Pt(en)X_3$ complexes, single crystals of $Pt(en)Cl_3$ and $Pt(en)Br_3$ were obtained as thin platelets, ($\leqslant 0.04$ mm thick) suitable only for two-probe conductivity measurements along the chain direction in the solid. Due to the small cross section and the high resistivity of these samples, only an upper limit for the room-temperature conductivity could be set in the case of the $Pt(en)Cl_3$ complex.

All of the crystals prepared were examined under crossed polaroids with a microscope and, in several cases, by X-ray precession techniques to determine crystal quality and orientation. Measurements were carried out on two or more high-quality single crystals of different sizes from different preparations to determine the reproducibility of the conductivity data; in each case good agreement was obtained. Similar tests for reproducibility were carried out in the case of the pressed pellet samples, which were all studied using four-probe techniques.

The results obtained on the various samples studied are summarized in Table I and examples of the resistivity temperature dependence are illustrated in Figures 1 and 2. The data show, in general, a lower resistivity (higher conductivity) and lower activation energy for single-crystal as compared to the pellet samples. Such results are typical for highly anisotropic materials and presumably reflect, in part, the conductivity parameters "averaged" over all directions in the crystal.[7] Due to this factor and the grain boundary effects which usually arise in the case of polycrystalline samples, such data are useful only to indicate qualitative trends among complexes of similar structures and with a similar conductivity mechanism.

The first such trend to be noted is the considerably higher resistivity and higher activation energy for $Pt(en)X_3$ complexes as compared with those of the $M(NH_3)_2X_3$ type. This presumably reflects the relatively longer M(II)–M(IV)

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(6) A. J. Cohen and N. Davidson, *J. Amer. Chem. Soc.*, 73, 1955 (1951).

(7) P. L. Kronick and M. M. Labes, *J. Chem. Phys.*, 35, 2016 (1961); F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967, p 168 ff.

Table I. Results of Dc Conductivity Measurements

Compd	Single crystal		Pressed pellet	
	ΔE, eV	$\rho_{25°}$, ohm cm	ΔE, eV	$\rho_{25°}$, ohm cm
$Pd(NH_3)_2Cl_2 \cdot Pd(NH_3)_2Cl_4$	0.35 $(0.33)^a$	5.1×10^8 $(2.3 \times 10^8)^a$	0.42 $(0.44)^a$	1.4×10^9 $(4.8 \times 10^8)^a$
$Pd(NH_3)_2Br_2 \cdot Pd(NH_3)_2Br_4$			0.3	2×10^7
$Pt(NH_3)_2Br_2 \cdot Pt(NH_3)_2Br_4$	0.22	2.9×10^8 $(>10^{12})^a$	0.52	3.4×10^9
$Pd(NH_3)_2Cl_2 \cdot Pt(NH_3)_2Cl_4$				$>3 \times 10^{10}$ $(3.2 \times 10^{10})^a$
$Pt(en)Cl_2 \cdot Pt(en)Cl_4$		$>10^{11}$	1.7	$\sim 1 \times 10^{15}$
$Pt(en)Br_2 \cdot Pt(en)Br_4$	0.67	1×10^{10}	1.2	2×10^{12}
$Pt(en)I_2 \cdot Pt(en)I_4$			0.69	1×10^9

[a] Results of ref 4.

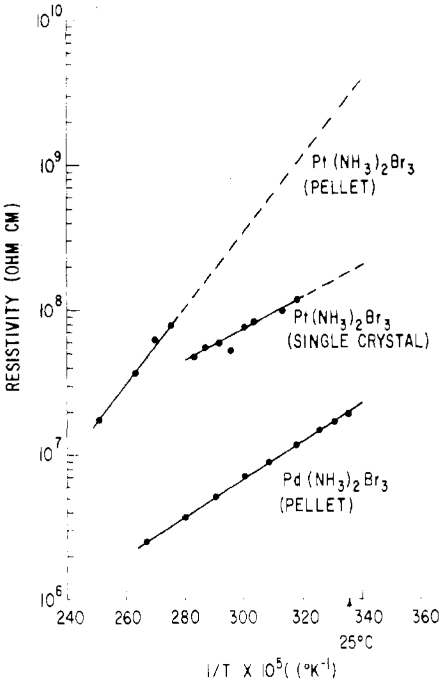

Figure 1. Resistivity of $M(NH_3)_2Br_3$ complexes.

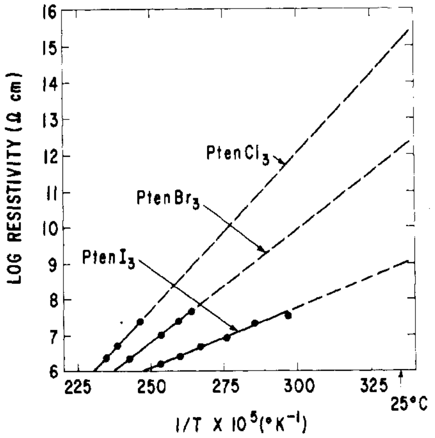

Figure 2. Resistivity of $Pt(en)X_3$ complexes.

separations in the former compounds, as evidenced by single-crystal X-ray studies.[8]

Within the isostructural $Pt(en)X_3$ series of complexes, changing the halide ion has a considerable effect on both resistivity and activation energy with a trend toward decreasing resistivity and decreasing activation energy in the order $Cl > Br > I$. A similar trend is apparent among the structurally analogous $M(NH_3)_2X_3$ complexes, which also show decreased resistivity and decreased activation energy for the Pd as compared to the Pt derivatives. The same trends were noted in conductivity measurements on these complexes at ultrahigh pressures.[1]

The results of two-probe ac resistivity measurements as a function of both frequency and temperature are compared with results of dc resistivity measurements in Figure 3 for the case of $Pd(NH_3)_2Cl_3$ single crystals. The ac resistivity is frequency dependent over the range studied, from 100 to 10,000 Hz, and is tending toward the higher dc resistivity as the ac frequency decreases.

Figure 4 shows the photoconductivity of $Pd(NH_3)_2Cl_3$ single crystals as a function of wavelength in the region from 12.5 to 25 kK. The photosensitivity, corrected for wavelength-variable heating and light intensity effects, is very weak, with an approximate quantum yield of 4×10^{-6} electron liberated per incident quantum but does show a definite wavelength dependence, with a broad maximum at 25 kK. A qualitative investigation revealed no evidence of strong photoconduction below 10 kK.

Attempts to measure the thermo-emf of both single-crystal and pellet samples of these complexes did not yield definitive results. Spurious voltages and polarization effects were noted, especially at the lower temperatures (25°), presumably due to the high resistance of the samples. At temperatures above 60°, indications of a positive thermo-emf were detected for the case of single crystals of $Pd(NH_3)_2Cl_3$ indicating possible p-type conductivity behavior; however, owing to the experimental uncertainties a quantitative measure of the thermo-emf could not be obtained.

Discussion

The conductivity behavior of the $M(A)X_3$ complexes has been discussed previously in the context of a one-dimensional intrinsic band model[4] analogous to that used by Miller[9] for $Pt(NH_3)_4PtCl_4$ (Magnus' Green Salt, MGS), involving overlap of the d_{z^2} orbitals on the metals with p_z orbitals on the bridging halide ion. The data we have obtained, along with the results of earlier spectral measurements, indicate that the intrinsic band model may not be the most appropriate one to use for discussing the conduction mechanism in these complexes.

On the basis of the intrinsic band model, a direct relationship between the thermal activation energy for conduction and the $M(II)(d_{z^2}) \rightarrow M(IV)(d_{z^2})$ "band gap" of the form $\Delta E = {}^1\!/_2 E_{gap}$, would be anticipated.[10] The measured thermal activation energies for the single-crystal samples we have

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[8] T. D. Ryan and R. E. Rundle, *J. Amer. Chem. Soc.*, 83, 2814 (1961); K. W. Browall, L. V. Interrante, and J. S. Kasper, to be submitted for publication.

[9] J. R. Miller, *J. Chem. Soc.*, 713 (1965).

[10] F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967, p 19 ff.

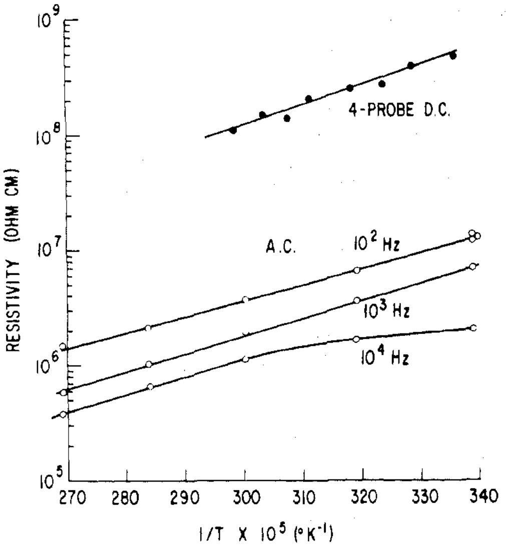

Figure 3. Comparison of dc and ac conductivity data for $Pd(NH_3)_2Cl_3$ single crystals.

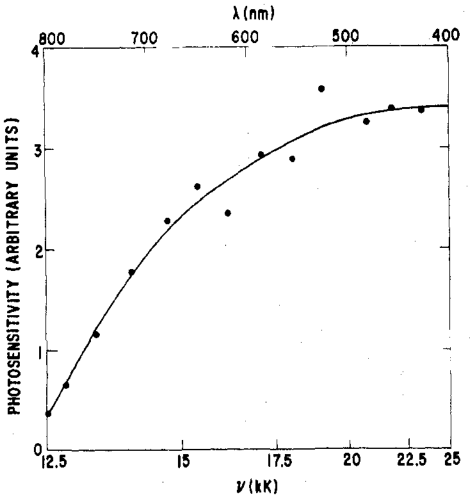

Figure 4. Photoconductivity of $Pd(NH_3)_2Cl_3$ single crystals.

studied (Table I) would indicate "band gaps" which are on the order of 1 eV or less. Solid-state spectral measurements,[3a,b] on the other hand, indicate that the $M(II)(d_{z^2}) \rightarrow M(IV)(d_{z^2})$ transition occurs at considerably higher energies (1.5-2.5 eV) for these same complexes. For example, in the case of $Pd(NH_3)_2Cl_3$, a *c*-polarized absorption band which has been attributed to the $M(II)(d_{z^2}) \rightarrow M(IV)(d_{z^2})$ charge-transfer transition occurs at about 1.65 eV, whereas on the basis of the conductivity activation energy a band gap of 0.70 eV would be anticipated. Moreover, at 0.70 eV, which corresponds to the near-infrared region of the spectrum, there is no evidence for any strong absorption bands.

The observed photoconductivity data for single crystals of $Pd(NH_3)_2Cl_3$ also fail to corroborate a conventional band model description. Qualitative observations made in the near-infrared region using a 200-W quartz-iodine source indicate little or no photoresponse. A measurable photoconductivity is observed in the visible region, at 25 kK, but the extremely low quantum yield (4×10^{-6}) is not at all characteristic of a direct band-gap excitation in a wide-band semiconductor. Such low quantum yields are found in certain molecular solids where low carrier mobilities, severe trapping effects, secondary carrier generation processes, and various other effects dominate the photoconduction behavior.[11]

For wide-band semiconductors in single-crystal form, there is generally little frequency dependence of the conductivity, and, indeed, previous work on the related metal-chain complex, MGS,[12] shows no indication of such an effect. The strong frequency dependence of the conductivity shown in Figure 3 for $Pd(NH_3)_2Cl_3$ crystals is, however, similar to the behavior of various amorphous materials and low-mobility crystalline solids where the conduction mechanism presumably involves hopping of carriers between essentially localized states.[13] In these cases, the frequency-dependent conductivity usually conforms to the relationship $\sigma(\omega) = \sigma' + \sigma''(\omega)$, where σ' is the dc conductivity and $\sigma''(\omega)$ is the additional frequency-dependent conductivity given by $\sigma'' = A\omega^n$, where A and n are empirical constants and ω is the frequency. An analysis of the ac conductivity data for $Pd(NH_3)_2Cl_3$ indicates good agreement with this relationship, where, for example, at 60°, $n = 0.25$ and $A = 8 \times 10^{-8}$. Systems of this type generally reveal a temperature-dependent activation energy for ac conductivity which approaches the dc conductivity activation energy at higher temperatures. In the case of $Pd(NH_3)_2Cl_3$, there is no indication of a temperature-dependent activation energy except at the highest frequency investigated, 10^4 Hz, below 60°. Indeed, the log σ *vs.* $1/T$ relationship is quite linear, with the one exception, over the entire temperature and frequency range. However, due to experimental limitations, the temperature range may be sufficiently small so that such a nonlinearity could have been missed.

In view of these observations, models other than the intrinsic band model must be considered for the conduction mechanism in the $M(A)X_3$ complexes. One such model is shown in Figure 5. This model illustrates the generation and motion of localized carrier species *via* a phonon-assisted electron-transfer process. In a-d, positively and negatively charged carriers are created *via* a series of combined electron- and ion-transfer steps. The halide ion motion, indicated by small arrows, serves to lower the barrier for electron transfer by rendering the environment about the metal ions more nearly equivalent. The "carriers" in this mechanism are clusters of three halide-bridged metal ions (c and d) with a formally trivalent metal ion at the center. These carriers could be generated in an intrinsic manner, as illustrated in Figure 5, or could arise from M(III) ions already present at defect sites in the structure. Such an alternative carrier generation process involving a M(III) ion present at a chain terminus, due to, for example, a small deviation in stoichiometry, is illustrated in Figure 6. In either case, the motion of the carriers, once created, is the same. This motion, since it involves the exchange of halide ions, is in itself a thermally activated process and, thereby, has associated with it a certain activation energy which is determined, in part, by the M-X stretching force constant. Indeed, comparison of the M-X stretching frequencies for the corresponding octahedral MX_6^{2-} complexes reveals an order of decreasing stretching frequency with M and X (Pt > Pd; Cl > Br > I) which is the same order as that of the activation energy for conduction among the $M(A)X_3$ complexes.

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(11) Reference 10, pp 23-28, 514-516.

(12) J. P. Collman, L. F. Ballard, L. K., Monteith, C. G. Pitt, and L. Slifkin in "International Symposium on Decomposition of Organo-Metallic Compounds to Refractory Ceramics, Metals and Metal Alloys," K. S. Mazdiyasni, Ed., University of Dayton Research Institute, Dayton, Ohio, 1968, pp 269-283.

(13) M. A. Abkowitz and A. I. Lakatos, *J. Chem. Phys.*, **57**, 5033 (1972); A. I. Lakatos and M. Abkowitz, *Phys. Rev. B*, **3**, 1791 (1971).

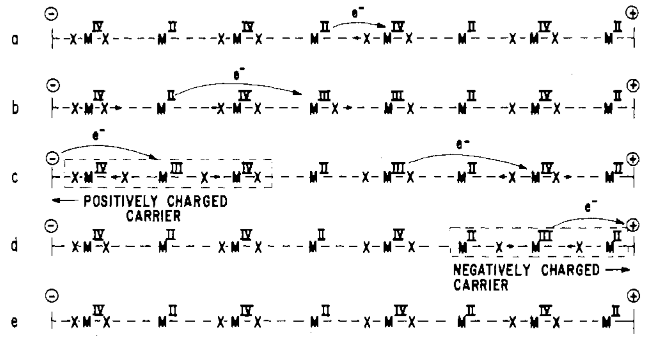

Figure 5. A hopping process for the conductivity in the mixed-valence complexes.

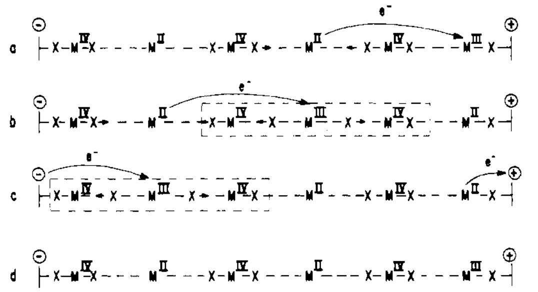

Figure 6. A possible "impurity" mechanism for the conductivity in the mixed-valence complexes.

Another factor which may be of importance in determining the conductivity order among these complexes is the degree of M-X orbital overlap which, in the context of the conduction mechanism illustrated in Figures 5 and 6, will influence the probability of electron transfer *via* a tunneling process or the height of the activation energy barrier for electron hopping.[14] This should vary roughly as the size of the interacting M and X orbitals which should increase in the order Cl $<$ Br $<$ I. However, on this basis we would anticipate that the Pd complexes should be less conductive than the Pt derivatives, which is contrary to the experimental findings, indicating that orbital overlap considerations alone are not sufficient to explain the observed conductivity behavior of the $M(A)X_3$ complexes.

The photoconductivity results obtained for $Pd(NH_3)_2Cl_3$ may also be understood in the context of such a conduction process. Irradiation with light of energy appropriate to the $M(II)(d_{z^2}) \rightarrow M(IV)(d_{z^2})$ energy level separation (~13-25 kK in the visible region) in this case would create two M(III) ions in the environment of an M(II) and M(IV) ion, respectively. The requirement that these ions must undergo vibrational relaxation in a specific manner to yield carriers, along with the probable low mobility of these carriers, could certainly account for the low quantum yield observed. One consequence of the proposed mechanism is that M(III) ions, either in intrinsically generated carriers or at extrinsic impurity sites, should be present in significant concentrations in these solids and might be detectable by esr spectroscopy. Preliminary esr measurements on single-crystal samples of the $Pd(NH_3)_2Cl_3$ complex suggest that this is indeed the case.[15] In particular, a weak, anisotropic signal has been observed at liquid helium temperatures whose esr parameters correspond closely with those previously reported by Krigas and Rogers[16] for the presumed $Pd^{III}Cl_5^{2-}$ radical in γ-irradiated crystals of K_2PdCl_4. However, more work is needed to characterize fully this paramagnetic species in the $Pd(NH_3)_2Cl_3$ crystals and to determine its relationship to the conductivity properties reported herein.

The results obtained in this investigation thus argue against the use of an intrinsic band model in accounting for the conductivity properties of the $M(A)X_3$ complexes at ambient pressures; instead an alternate hopping-type process is suggested. At higher pressures this may well give way to a band-type conduction process, as the metal d_{z^2} and ligand p_z orbital interactions increase under compression;[1] however, at ambient pressures the available evidence indicates that the degree of intermolecular interaction in these solids is quite weak, necessitating the use of a more localized description for the electronic structure.

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Registry No. $Pd(NH_3)_2Cl_2 \cdot Pd(NH_3)_2Cl_4$, 51064-32-5; $Pd(NH_3)_2Br_2 \cdot Pd(NH_3)_2Br_4$, 51017-61-9; $Pt(NH_3)_2Br_2 \cdot Pt(NH_3)_2Br_4$, 50790-39-1; $Pd(NH_3)_2Cl_2 \cdot Pt(NH_3)_2Cl_4$, 50600-81-2; $Pt(en)Cl_2 \cdot Pt(en)Cl_4$, 50600-56-1; $Pt(en)Br_2 \cdot Pt(en)Br_4$, 33907-32-3; $Pt(en)I_2 \cdot Pt(en)I_4$, 33907-25-4.

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(14) Reference 10, p 421 ff.

(15) Private communication from Dr. G. Watkins, General Electric Corporate Research and Development.

(16) T. Krigas and M. T. Rogers, *J. Chem. Phys.*, **54**, 4769 (1971).