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Electric Conduction Studies on Mixed-Valence Complexes of Platinum and Palladium

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Mixed-valence complexes of the type $[M(A_2)_2]\cdot[M(A_2)_2X_2]Y_4$, where M = Pt or Pd, (A_2) = ethylenediamine(en) or trimethylenediamine(tn), X = Cl, Br or I, and Y = ClO_4 or BF_4 are crystallized in needles, containing $-M^{IV}-X\cdots M^{II}\cdots X$ chains [1–6]. They have intense reflectance absorptions in the polarized spectral parallel to the chain in the visible region, which were attributed to the intervalence electronic transition from M(II) to M(IV) in the one-dimensional chain [2]. They are expected as anisotropic semiconductors with the highest conductivity along the needle.

Electric conductivity of polycrystalline and single-crystal samples of the mixed valence compounds with the general formula, $[M(A_2)X_2][M(A_2)X_4]$, were measured by Thomas and Underhill [7] and Interrante *et al.* [8] where M = Pd, Pt; A_2 = en, $(NH_3)_2$; and X = Cl, Br. The results were discussed in terms of different mechanisms by these authors [7, 8]. In order to obtain more data to elucidate the mechanism of the conductance of this sort, in this study we have measured dc conductivities of single-crystals of a series of compounds of the type $[M(A_2)_2][M(A_2)_2X_2]Y_4$.

Experimental

Single crystals of platinum(II,IV) complexes were prepared as described previously [2]. Well formed crystals of dimensions up to 0.2 × 0.04 × 3 mm^3 were obtained by recrystallization in aqueous solution. Dc conductivity measurements in the temperature range below 100 °C were possible along the needle axis only by the two-probe method, since the crystal easily cleaved along a plane perpendicular to the needle axis. A steady potential was applied across a sample and a standard resistance in series. Measurement of the voltage drop across the standard resistance allowed the calculation of the sample resistance. The sample was maintained in a vacuum in a temperature-controlled furnace during measurements. Silver paste was used as the electrode material. The complexes behaved as ohmic semiconductors. Aquadag was used in place of silver paste for some measurements to confirm that the measured conductivities were not affected by such materials.

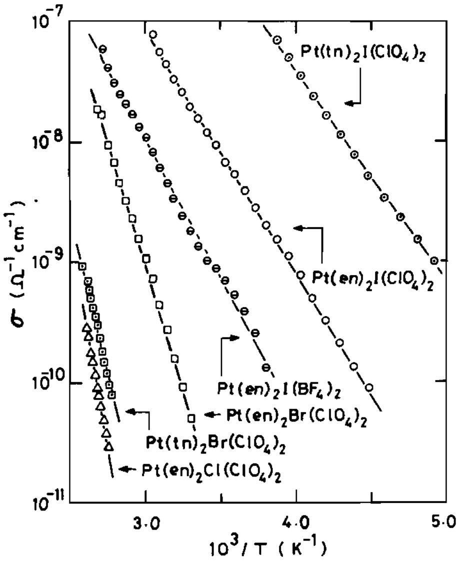

Fig. 1. Conductivity of the $[Pt(A_2)_2][Pt(A_2)_2X_2]Y_4$ complexes as a function of temperature.

Crystals of palladium complexes were obtained only as fine needles unsuitable for single-crystal measurements. Therefore conduction measurements were made on compressed powder samples, which were all studied using four-probe techniques.

Results and Discussion

Figure 1 shows the results of the conductivity measurements as a function of temperature for platinum complexes. In each case, the conductivity obeys the equation $\sigma = \sigma_0 \exp(-E/kT)$, where E is the activation energy and σ_0 is the pre-exponential factor independent of temperature. The values obtained by the method of least squares are summarized in Table I, together with the room temperature conductivities. Also listed in this table are the related optical and structural data [2, 5]. The results demonstrate that the effect of varying the halogen or the metal on conduction properties is much greater than that of the diamine ligand or the counter ion. Qualitative features are quite consistent with the structural and optical information as follows. The activation energy E decreases as the atomic distance

TABLE I. Results of Conductivity Measurements, Peak Positions of Reflectance Spectra and Distance Ratios.

Compound	σ (25 °C $(\Omega^{-1}\ \mathrm{cm}^{-1})$	σ_0 $(\Omega^{-1}\ \mathrm{cm}^{-1})$	E (eV)	$h\nu_{max}$ [a] (eV)	η [b]
(a) Single Crystals					
$[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2Cl_2}](\mathrm{ClO_4})_4$	2.0×10^{-15}	2.0×10^{8}	1.36	2.82	0.75
$[\mathrm{Pt(tn)_2}][\mathrm{Pt(tn)_2Br_2}](\mathrm{ClO_4})_4$	2.0×10^{-14}	5.9×10^{6}	1.21	2.05	0.86
$[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2Br_2}](\mathrm{ClO_4})_4$	3.0×10^{-11}	5.4×10^{3}	0.84	1.88	
$[\mathrm{Pt(tn)_2}][\mathrm{Pt(tn)_2I_2}](\mathrm{ClO_4})_4$	7.0×10^{-7}	1.1	0.37	1.53	
$[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2I_2}](\mathrm{ClO_4})_4$	1.4×10^{-8}	3.2×10^{-1}	0.42	1.53	0.93
$[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2I_2}](\mathrm{BF_4})_4$	1.6×10^{-9}	8.1×10^{-2}	0.46	1.53	
(b) Pressed Pellets					
$[\mathrm{Pd(en)_2}][\mathrm{Pd(en)_2Cl2}](\mathrm{ClO_4})_4$	2.0×10^{-12}	1.2×10^{2}	0.81	1.94	
$[\mathrm{Pd(en)_2}][\mathrm{Pd(en)_2Br_2}](\mathrm{ClO_4})_4$	1.2×10^{-8}	2.8	0.49	1.61	
$[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2I_2}](\mathrm{ClO_4})_4$	3.0×10^{-9}	1.1	0.51	1.53	

[a] Reference 2. [b] Reference 5. η denotes the ratio of the interatomic distances, Pt(IV)–X/Pt(II)–X, where X= Cl, Br, and I.

ratio η = [Pt(IV)–X]/[Pt(II)–X] approaches unity, *i.e.*, the oxidation states of Pt(II) and Pt(IV) are more averaged [5]. The decreasing trend of E (Cl > Br > I and Pt > Pd) is the same as the decreasing trend of the maximum position ν_{max} of the visible spectra which was assigned to the intervalence electronic transition [2]. This agreement suggests that the conduction process and the intervalence absorption have a common origin and that the conduction process is electronic in nature.

Conduction may occur by a one-dimensional intrinsic band model firstly proposed by Thomas and Underhill [7], or by a hopping mechanism, as discussed by Interrante and coworkers [8]. In the former model, the conduction and the valence bands would originate from the empty d_{z^2} orbital of M(IV) (more strictly, a molecular orbital formed wih the M(IV) d_{z^2} and the halogen p_z orbitals) and the filled M(II) d_{z^2} orbital, respectively. In general the intrinsic band model of semiconductors predicts that the activation energy is equal to one half of the band gap energy. For the single-crystal platinum complexes, one can see in Table I that the approximate relation $2E \cong h\nu_{max}$ is observed in chloro and bromo complexes, but in iodo complexes 2E (0.74 ~ 0.92 eV) is much lower than $h\nu_{max}$ (1.53 eV). This discrepancy is probably due to the broad spectra in iodo homologs [2]. Recently, Papavassilou and Zdetsis [9] measured the single-crystal spectra of $[\mathrm{Pt(pn)_2}][\mathrm{Pt(pn)_2X_2}](\mathrm{ClO_4})_4$ (X = Cl, Br or I, and pn = 1,2-diaminopropane) and determined the gap frequency ν_{gap} by using the Lorentzian equation. In each compound ν_{gap} is lower than ν_{max} and the difference between ν_{gap} and ν_{max} is very large in the case of the iodo compound compared with those of the bromo and chloro compounds: $h\nu_{gap}$ = 1.13 eV and $h\nu_{max}$ = 1.50 eV. When this correlation between ν_{gap} and g_{max} is applied to the present results, $h\nu_{gap}$ would be 1.1 eV and hence the quantitative discrepancy between the activation energy and the intervalence absorption is greatly reduced. Thus, the conduction process is considered to be dominantly characterized by a band type carrier excitation. For more precise discussion on the conduction mechanism, further experimental results such as direct measurements of the carrier mobility are needed.

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