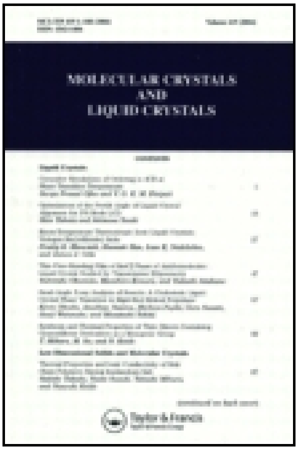

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One Dimensional Electric Conduction Mechanism in Mixed-Valence Complexes

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ONE DIMENSIONAL ELECTRIC CONDUCTION MECHANISM IN MIXED-VALENCE COMPLEXES

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The d.c. conductivity σ along the chain of $-M(II)-XM(IV)X-$ was observed with crystals of $[M(II)(AA)_2]\cdot[M(IV)(AA)_2X_2]Y_4$; M=Pt, Pd, Ni, X=Cl, Br, I, (AA)=(en), (tn), $Y=ClO_4, BF_4$. Systematic change of σ from 10^{-8} to 10^{-15} $(\Omega\text{-cm})^{-1}$ with M and X was characterized by an inter-ionic distance δ as $\sigma \propto \exp[-\alpha\delta]$. Its temperature change is expressed as $\sigma(T)=\sigma_0 \exp[-\Delta E/kT]$ with $\Delta E=0.4$ to 1.4 eV, which is in $h\nu>2\Delta E$ relation for the specturm absorption. Hydrostatic pressure on single crystal induces lattice contraction and σ enhancement of $10^{3\pm1}$ times only by 7 kbar, suggesting dominant role of the orbital overlapping on σ. ESR singnal of $g_{av}=2.15\pm0.03$ was observed for M=Pt, and its anisotropy with c-axis as $g_\perp>g_{//}$ indicates dz^2 band contribution. The signal intensity change down to 77 K provides the carrier activation energy $\Delta\varepsilon=12\pm1$ meV (X=I) and scarce activation number 1 per 10^4 Pt ion. Hence the conduction is considered as dominantly regulated by hopping process among the localized dz^2 states with phonon assisted tunneling.

INTRODUCTION

For complexes containing transitional element (M=Pt, Pd, or Ni), an overlapping of the dz^2 orbitals may have important role in the chemical bonding, and it brings not only crystal anisotropy forming linear chain structure but also sometimes one-dimensional electrical conductivities so significant as metallic or semi-metallic in case of the well known Krogmann's salts (KCP) or the Magnus green salts. As temperature decrease, the one-dimensional metallic state becomes unstable and transforms into semiconducting state characterized by electronic localization character due to the CDW (or SDW) occurence and ionic lattice distortions. This low temperature phase can be understood from a view point of partial mixed valence state with M^{2+} and M^{4+} as has been discussed for KCP [1].

Another type of the mixed valence complexes has been investigated where the M atom is linearly chained via halogen X ion as M(II)-X-M(IV)-X-M(II). Also in this case the dz^2 orbital-overlapping takes place through hybridization with the pz orbital of the X ion. Subsequently, electronic transition between M(II) and M(IV) sites can be easily induced and intense visible light absorption is observed (the class II) with considerable extent of electrical conductivities [2].

An interesting point regarding to this structure is that the difference between M(II) and M(IV) site is only characterized by the X ion location. If X comes just to the midpoint of the both M sites, all the M ion becomes equivalent M(III) state and similar situation with the Krogmann's salt may be expected with large conductivities. Accordingly the X ion motion due to thermal phonons must be taking into considerations for the conduction mechanism of this kind of complexes. From these viewing points, a series of this kind complexes are investigated in several physical quantities, and the conduction mechanism is discussed.

SAMPLES

The complexes of the type $[M(II)(A\text{-}A)_2][M(IV)(A\text{-}A)_2X_2]Y_4$ with M=Pt, Pd, Ni, X=Cl, Br, I, $(A\text{-}A)=NH_2(CH_2)_2NH_2$; (en), $NH_2(CH_2)_3NH_2$; (tn), $Y=ClO_4$ or BF_4 were prepared by M(2+) and M(4+) mixing [3]. Considerably large single crystals grow into needle-like along c-axis, which corresponds to the chain direction, from aqueous solution, especilly for M=Pt. The X-ray crystal analysis [4] and spectrum absorption measurements [5] have been carried out, and the results of the atomic distance ratio: η =M(IV)-X/M(II)-X and the spectrum peak energy: hν are presented in table I.

CONDUCTIVITIES

The dc conductivity was mearsured [6] in vacuum with temperature decrease from 100°C (in higher temperatures the crystal becomes unstable), and the σ(25°C) was observed in wide renge of 10^{-8} to 10^{-15} $(\Omega\text{-cm})^{-1}$ as given in table I. The temperature dependence of the conductivity $\sigma(T)$ was found to be well expressed by the semiconducting character with themral activation eneray ΔE as

$$\sigma(T) = \sigma_0 \cdot \exp\,[-\Delta E/k_B T] \qquad (1)$$

The parameters σ_0 and ΔE for each complex have been reported [6] and the ΔE is cited in table I. Here we find a systematic tendency over all quantities presented, with the order of X=Cl→Br→I and M=Pt→Pd→Ni. This qualitative character can be understood by the following process. With this order, η becomes large and the X ion is closer to the M(II)-M(IV) midpoint, then the two M ion character will be more uniformed. Subsequently hν and ΔE, relating to the energy difference between dz^2(II) and dz^2(IV) becomes smaller [14], and σ will be enhanced.

For quantitative analysis, the conduction mechanism must be considered. The orbital overlapping at the gap between M(II) and X ion-spheres will play most important role for the electron transport through the chain, then the gap distance δ is estimated from the lattice parameters:

Table 1 Electrical and optical data of $[M(en)_2][M(en)_2X_2](ClO_4)_4$

M X		Pt pellet(500kg/cm^2)	single crystal	Pd		Ni	
Cl	σ(25°C)		$2\times10^{-15}[\Omega\text{-cm}]^{-1}$	2.0×10^{-12}		1.3×10^{-8}	
	2ΔE		2.70[eV]	1.62		1.15	
	hν	2.8[eV]		1.94		2.05	
	η		0.75		0.77		
Br	σ(25°C)		3.0×10^{-11}	1.2×10^{-8}			
	2ΔE		1.68	0.98			
	hν	1.88		1.61(broad)			
	η		0.86$^{b)}$		0.96		
I	σ(25°C)	3.0×10^{-9}	1.8×10^{-8}				
	2ΔE	1.02	0.84				
	hν	1.53(broad)					
	η		0.92$^{a)}$				

a) by Endres et al[13] , and all other data by ours [4,5,6]
b) only this η is with (tn) in replace of (en).

a and η, and ion radius r as,

$$\delta = \frac{a}{2(1+\eta)} - [r(II) + r(X)] \qquad (2)$$

The parameter a=M(II)-M(II) is given from the crystal analysis [4] as 10.806 Å (X=Cl, AA=en), 11.002 (Br, tn), 11.638 (I, en) for M=Pt, and 10.697 (Cl, en), 10.787 (Br, en) for M=Pd. The radius r for each ion was given by Shanon etal [7]. With use of these data, the distance δ was computed from eq. 2, and almost linear correspondence between δ and η was found for these complexes.

Resultantly, the conductivity σ(25°C) is plotted against the gap distance δ in Fig. 1. Here it is found that σ is well ruled by the distance in a form of $\sigma \propto \exp[-\alpha\delta]$ through this kind of complexes. This result may suggest that the conduction is due to the wave function peneteration through the potential barrier between the M(II) and X+M(IV) state likely as the tunneling process.

WITH PRESSURES

From the fact, σ enhancement is expected by high pressure applications. Hydrostatic pressure was applied on the single crystals of M=Pt, X=I, and enormous enhancement of about $10^{3\pm1}$ times was observed only by 7 K bar (see Fig. 2). This is about 10^2 times larger than the observed with powder pellet samples. Silicone oil was used for transmission, from which the crystal surface was protected by paraffin coating [8]. As seen in Fig. 2 several repeat of the pressure cycle diminished the hysteresis and reproducible $\sigma(p)$ was obtained. In consequence, an exceedingly large coefficient of $\partial \ln\sigma/\partial p = 1.0 \pm 0.3$/kbar was determined. The lattice parameter: a was also measured under this pressure, and the contraction was really

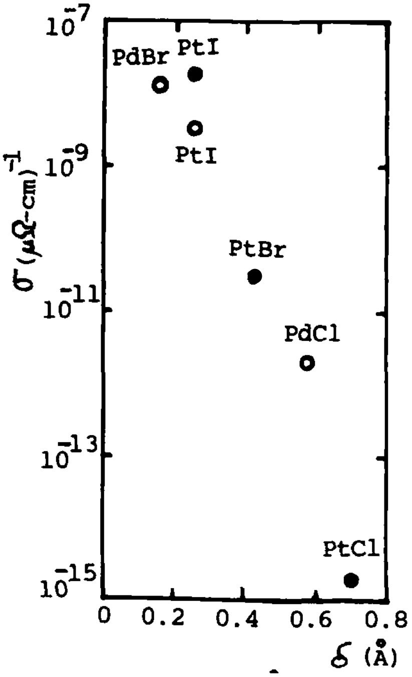

FIGURE 1 Conductivity to the gap distance relation over the complexes, ● with single crystal and ○ with powder pellet.

observed as shown in Fig. 3, where $\partial a/\partial p=2.5\times10^{-2}$Å/kbar was elucidated. From these result $\partial n\sigma/\partial a$ is computed as 40± 12/Å, and it turns out that this magnitude is comparable with the coefficient $\partial \ln\sigma/\partial\delta$ found in Fig. 1. Accordingly it is considered that the contraction under pressure takes place dominantly at the most weak bonding of M(II)-X.

The σ-T relation was measured under the pressure and the dependence of the $\sigma_0(p)$ and $\Delta E(p)$ was investigated as shown in Fig. 4, where we find that $\sigma_0(p)$ is more sensitive than $\Delta E(p)$. This result can be understood as follows.

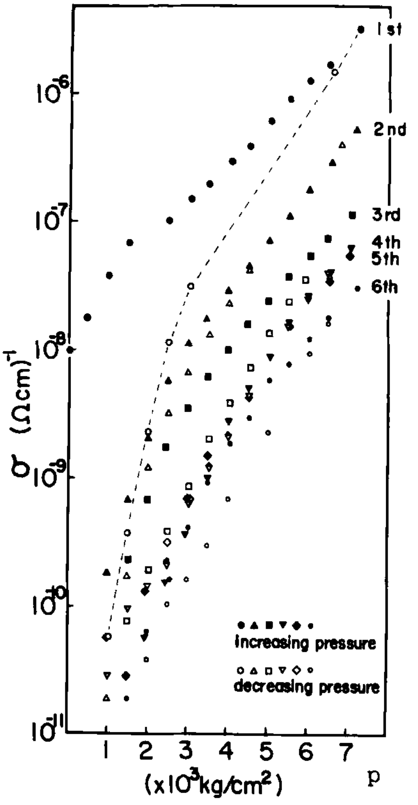

FIGURE 2 The dc conductivity with pressure cycles(1st-6th)

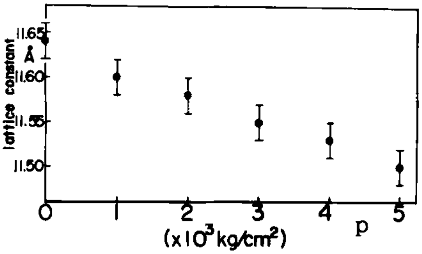

FIGURE 3 Lattice constant along c-axis under pressures.

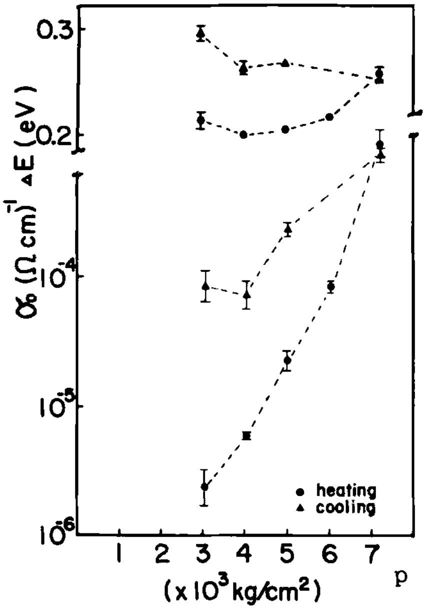

FIGURE 4 Changes of conduction parameters σ_0 and ΔE with pressure.

In this rather weak pressure range, the electronic states will be little influenced, but the most flexible bonding at M(II)-X is contracted and the orbital-overlapping factor $\exp[-\alpha\delta]$ in the σ_0 will be enhanced.

ESR MEASUREMENTS

As denoted in table I, the absorption spectrum shows much broadening for the case of $\sigma \sim 10^{-8}$ $(\Omega\text{-cm})^{-1}$. Then it is suggested that the relevant electronic state dz^2 will be wide spreaded as forming energy bands [9]. In case of a free electron band, direct excitation requires a relation $h\nu=2\Delta E$, but in table I, $h\nu>2\Delta E$ prevails and the tendency is more significant as σ larger. As one of the reason, previously we mentioned about the difference, in broad spectrum, between the measured peak energy $h\nu$ and the spectrum edge $h\nu_g$ which should correspond to the $2\Delta E$ [6].

In order to investigate this problem more directly, electron spin resonance (ESR) measurements were carried on the (M=Pt) crystals with temperature change down to 77 K. The signal was observed with single crystals and also powders as shown in Fig. 5. It showed a sinusoidal anisotropy (see Fig. 6) in the g shift by rotating the H field in the a-c plane as given in Fig. 6 for X=I, $g_{//}c=2.049$ and $g_{\perp}c=2.158$. By the character of $g_{\perp}>g_{//}$, this signal was considered as due to unpaired electron in the dz^2 state. Hyperfine splittings were observed with temperature decrease and definite H-directions, and the details will be in a forthoming paper. By integrating the spectrum intensity, spin rumbers N(/cc) was calculated with the reference of DPPH and Cu^{2+} samples, and its temperature dependence is plotted in Fig. 7. Here we find $N=N_0\exp[-\Delta\varepsilon/kT]$ relation. The spin activation energy $\Delta\varepsilon$ was estimated at 12±1 meV for X=I and 22±1 meV for Cl. With use of this $\Delta\varepsilon$, the number of activation centre: No is calculated as $No=10^{17\pm1}$/cc by applying N, T data to eq. 3. Since the Pt ion number is 2.8×10^{21}/cc in this compound, the carrier activation centre is about 1 per 10^4 Pt site in the chain. From this scarcity, the centre seems to be located at structure dislocations or

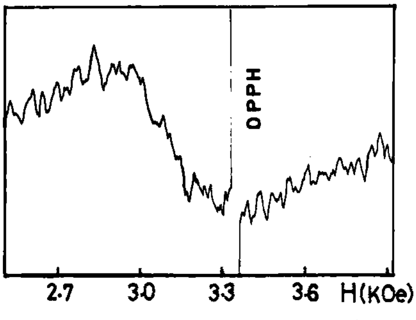

FIGURE 5 ESR spectrum for $Pt(en)_2I(ClO_4)_2$ powder at 300K, g=2.152±0.02

thermal defects in the chain such as –M(II)–XM^e(III)–XM^e(III)–XM(IV)X. In regard of this site-formation or carrier activation at the site, the X ion motion plays important role, since the M(III)X–M(III)X is created by the X ion displacement.

CONDUCTION MECHANISM

Paraskevaidis etal [10] computed the optical mode oscillation frequency $h\omega$ in the M-X-M chain from the force constants determined by taking into account the resonance Raman and infrared spectra for similar kind of compound, and the $h\omega$ was given as 316, 341 cm^{-1} for X=Cl and 179, 212 cm^{-1} for X=Br. In comparison of our obtained $\Delta\varepsilon$ with these values, we find them in similar magnitude. Hence the above mentioned carrier activation mechanism assisted by X ion displacement seems to be reasonable, since most of the carrier activation energy will be related to displace the X ion at the defect site.

When this $\Delta\varepsilon$ is compared with coduction activation energy ΔE, it is found quite smaller by factor of 10 or 10^2. Accordingly it is concluded that the dominant part of the ΔE takes place not in the carrier activation process, but in the successive transport process among localized state in the dz^2(IV) band [11]. This result can be understood followingly; the electronic potential around the Pt ion is sensitively modified by the X ion displacement in terms of polarization energy $e\psi=e/r-e/\kappa r$ where κ is dielectric constant of this ionic medium, and then the thermal oscillation in the chain induces nonperiodical potentials. In consequence, the Anderson localization will take place [11] in the bottom edge of the empty dz^2(IV) band and the small density carriers transfer among these localized states by hopping with the ΔE

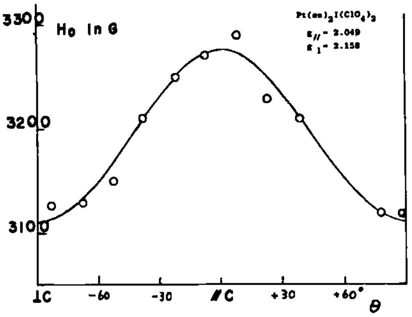

FIGURE 6 ESR signal-shift anisotropy with θbetween H and c-axis in a-c plane.

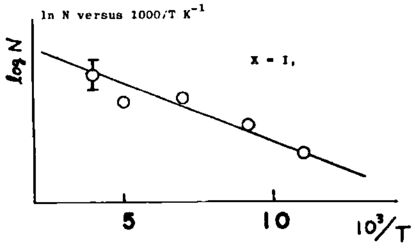

FIGURE 7 Spin numbers N(/cc) change with temperature T.

activation and barrier tunneling process as shown in Fig. 8.

From this viewing point the relation $h\nu>2\Delta E$ can also be understood as follows. In case of the optical absorption the transition is adiabatic; without any X ion motion, then $h\nu$ is expressed directly as $=I-A$. Alternatively the conduction process is isothermal and followed by ion polarization, then the $2\Delta E$ is different from $h\nu$ by $2e\psi$. This X ion polarization suppress the barrier potential for electron transfer by tunneling as shown in Fig. 8, and enhances the conductivity σ. Therefore, we can understand the character of $h\nu>2\Delta E$ with large σ in table I.

This carrier transfer process (Fig. 8) seems to be supported by the following evidence. The conduction parameters σ_0 and ΔE has been determined for these complexes [6] and plotted in Fig. 9, where the points estimated from other investigators' data [11] for simillar kind of complexes are also presented. Here we find a strong correlation like as $\log\sigma_0\propto\Delta E$ through the complexes, and this relation may be ascribed to the model in Fig. 9 as follows. The transport mobility μ due to tunneling process should be strongly dependent on the barrier height above the activation energy level ΔE, and also on the thickness d, likely as $\mu\propto\sigma_0\propto \exp[-k(V_0-\Delta E)\cdot d(V_0-\Delta E)]$, whence the $\ln\sigma_0$ should increase with ΔE. Similar character in aromatic substances was first tried to account for by Many etal [12] with this mechanism.

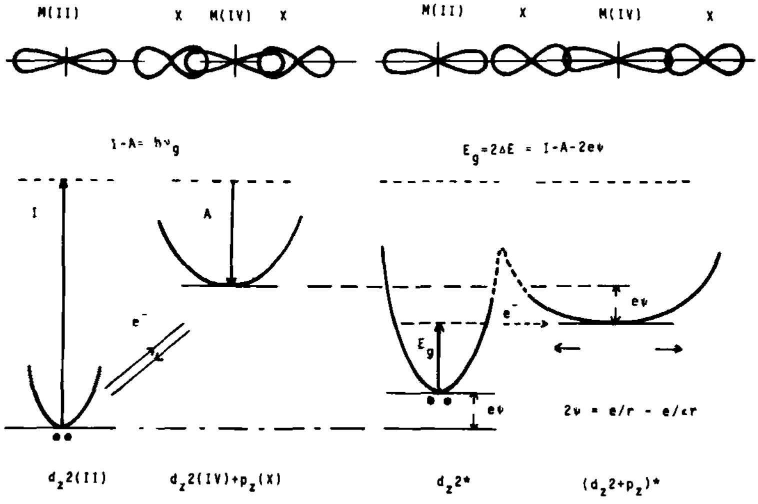

FIGURE 8 Electron transition and transfer mechanism in the M-X-M chain.

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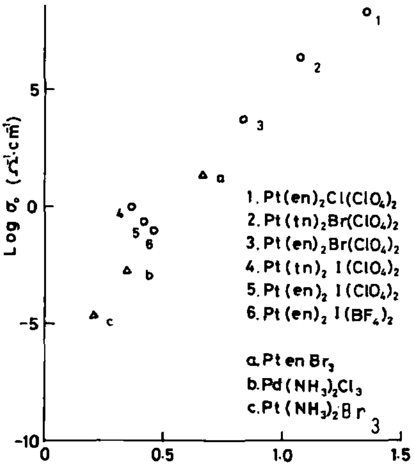

FIGURE 9 Correlation between σ_0 and ΔE in $\sigma(T)=\sigma_0\exp\{-\Delta E/kT\}$ through the complexes.