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X-Ray Photoelectron Spectra and Electrical Conductivities of One-dimensional Halogen-bridged Pd(II)-Pt(IV) and Ni(II)-Pt(IV) Mixed-valence Complexes

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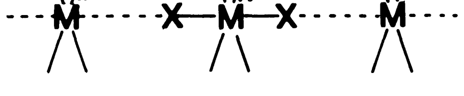
The X-ray photoelectron spectra have been measured for the one-dimensional halogen-bridged metal-alternated mixed-valence complexes, $[Pd^{II}(en)_2][Pt^{IV}X_2(en)_2](ClO_4)_4$ (X=Cl, Br, and I) and $[Ni^{II}(en)_2][Pt^{IV}X_2(en)_2](ClO_4)_4$(X=Cl and Br), along with their parent complexes, $[Pd(en)_2]Cl_2$, $Ni(en)_2Cl_2$, and $[PtCl_2(en)_2]Cl_2$. As the bridging halogen changes from Cl to I, the binding energies of the Pt(IV)4f levels become lower while those of M(II) (M=Pd and Ni) levels become higher, each gradually approaching to the M(III) binding energies (M=Pt, Pd, or Ni), respectively. Comparing the binding energies of the Pt(IV)4f levels in these hetero-metal mixed-valence complexes with those previously reported for the homo-metal halogen-bridged Pt(II)-Pt(IV) mixed-valence complexes having the same bridging halogens, the reductive trend of the oxidation states of Pt(IV) is found to be significantly suppressed by the metal alternation. In accord with this result, the activation energies obtained from the electrical conductivities are fairly larger than those of the homo-metal Pt(II)-Pt(IV) mixed-valence complexes. Their magnitudes are in the order of Pd^{II}-Pt^{IV}>Ni^{II}-Pt^{IV}>Pt^{II}-Pt^{IV}, suggesting that the electron-electron repulsion energy on M(II) ions plays an important role in mixed-valence states.

Various kinds of halogen-bridged one-dimensional M(II)–M(IV) mixed-valence complexes of Pt, Pd, and Ni have created a greater current interest in the field of low-dimensional chemistry and physics.[1–4] So far, we have prepared about one hundred compounds with a general formula of $[M^{II}(AA)_2][M^{IV}X_2(AA)_2]Y_4$ (M=Pt, Pd and Ni; X=Cl, Br and I; $(AA)_2$=(diamines)$_2$, linear-tetramines, and tetraaza-macrocycles; Y=ClO_4, BF_4 *etc.*).[5–9] Although these complexes exhibit a considerable variety of semiconducting properties, they can be well characterized by a common feature; the electrical,[10–12] optical,[13–15] and vibrational properties[16–18] are closely correlated with the degree of the oxidation states of the M(II) and M(IV) ions. This has been clearly demonstrated by the X-ray photoelectron spectra[19–22] and XANES.[23] From the results of the X-ray diffraction measurements,[24–31] the oxidation states of metal ions were found to be systematically dependent on the ratio between M(IV)–X and M(II)···X distances, which is influenced by the kinds of metals, bridging halogens, counter ions, and in-plane ligands.



For example, as the bridging halogen ions change from Cl to I, the ratio between M(IV)–X and M(II)···X distances approaches unity.[31] At the same time, the oxidation states of the M(II) and M(IV) metal ions almost become tervalent states. These characteristic behaviors have been theoretically elucidated by energy-band calculations by Whangbo and Foshee[32] using the extended Hückel method and recently by Nasu[33–35] on the basis of an extended Peierls-Hubbard model. According to Nasu's model, the oxidation states of metal ions are determined by three physical parameters: the distortion energy due to the displacement of a halogen ion from the midpoint between adjacent metal ions, the transfer energy between metal ions, and the electron–electron (e–e) repulsion energy on metal ions. In a preceding paper,[36] it has been confirmed that the metal (M) and halogen ions (X) dependences on intervalence charge transfer transitions along the chains can be interpreted in terms of these parameters, including the e–e repulsion energy on the adjacent metal ions.

In order to obtain more detailed information regarding the mixed-valence states in one-dimensional complexes of this type, we have measured the X-ray photoelectron spectra and single-crystal electrical conductivities of the hetero-metal mixed-valence complexes, $[Pd(en)_2][PtX_2(en)_2](ClO_4)_4$(X=Cl, Br, and I) and $[Ni(en)_2][PtX_2(en)_2](ClO_4)_4$ (X=Cl and Br) (hereafter, they are abbreviated to Pd(II)–X–Pt(IV) and Ni(II)–X–Pt(IV)). The X-ray photoelectron spectra of their parent complexes, $[Pd(en)_2]Cl_2$, $Ni(en)_2Cl_2$[37] and $[PtCl_2(en)_2]Cl_2$ have also been measured as references. The metal alternation is expected to add two different types of energy to the one-dimensional M–X–M system. One is due to the alternating ionization energies and the other is due to the alternating electron–electron repulsive energies on metal sites.

Experimental

Materials. The M(II)–X–Pt(IV) complexes were synthesized by methods previously described.[5,8,38] Single crystals of the Pd(II)–X–Pt(IV) complexes were grown from dilute perchloric acid solutions, while those of the Ni(II)–X–Pt(IV) complexes were obtained from aqueous solutions containing $NaClO_4$.

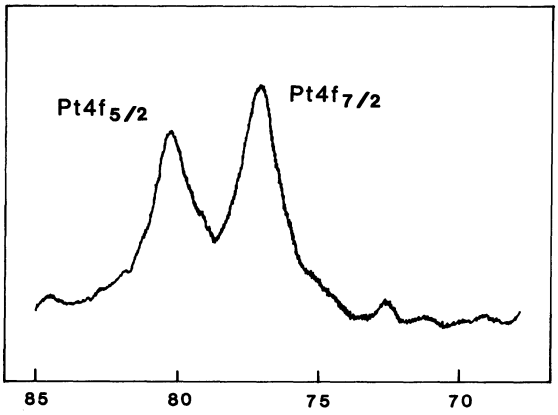


Fig. 1. X-Ray photoelectron spectra of Pt4f in [Pd$(en)_2$][$PtCl_2(en)_2$]$(ClO_4)_4$.

X-Ray Photoelectron Spectra. The X-ray photoelectron spectra were obtained on a SHIMADZU ESCA 750 using Mg*Kα* exciting radiation at room temperature, the source vacuum being ≈10^{-7} Torr.† The spectra were calibrated by the emission from the Cls line (285.0 eV). The absolute energy of emitted electrons, however, may not be so meaningful in the present study because it is not free from possible systematic errors due to charging-up. Thus, in this paper, we will refer only to a relative energy with respect to the reference signals for the parent complexes.

Electrical Conductivities. Single-crystal d.c. conductivities along the needle axis were measured in a temperature range below 100 °C by the two-probe method. Silver paste was used as the electrode material.

Results and Discussion

As a probe for an examination of the oxidation states of metal ions in metal-alternated mixed-valence complexes, we measured the binding energies of Pt(IV)4f, Pd(II)3d, and Ni(II)2p levels in the Pd(II)-X-Pt(IV), Ni(II)-X-Pt(IV) and their parent complexes. In Fig. 1, the X-ray photoelectron spectrum of Pt(IV)4f levels in the Pd(II)-Cl-Pt(IV) complex is shown as an example. The peak energies of the doublet correspond to the binding energies of the $4f_{7/2}$ and $4f_{5/2}$ levels of Pt(IV). All the Pt(IV)4f spectra observed in the metal-alternated mixed-valence complexes, including the reference complexes, are quite similar, but the magnitudes of their binding energies show a characteristic dependence on the kind of the constituent metal and halogen ions. The observed binding energies of the Pt(IV)$4f_{7/2}$ and Pd(II)$3d_{5/2}$ levels for the Pd(II)-X-Pt(IV) complexes and for the Pt(IV)$4f_{7/2}$ and Ni(II)$2P_{3/2}$ levels of the Ni(II)-X-Pt(IV) complexes are listed in Table 1, along with those for reference states of the parent complexes.

Table 1. Binding energies /eV

(i) Pd(II)-Pt(IV)		
	$Pd3d_{5/2}$	$Pt4f_{7/2}$
$[Pd^{II}(en)_2]Cl_2$	338.6	—
$[Pt^{IV}Cl_2(en)_2]Cl_2$	—	75.8
$[Pd(en)_2][PtCl_2(en)_2](ClO_4)_4$	338.6	75.8
$[Pd(en)_2][PtBr_2(en)_2](ClO_4)_4$	338.7	75.6
$[Pd(en)_2][PtI_2(en)_2](ClO_4)_4$	338.9	75.4
(ii) Ni(II)-Pt(IV)		
	$Ni2p_{3/2}$	$Pt4f_{7/2}$
$Ni^{II}(en)_2Cl_2$	855.6	—
$[Ni(en)_2][PtCl_2(en)_2](ClO_4)_4$	856.1	75.8
$[Ni(en)_2][PtBr_2(en)_2](ClO_4)_4$	856.4	75.6

In this table, it is immediately noticed that the binding energy of the Pt(IV)$4f_{7/2}$ level shifts to a lower energy while those of the Pd(II)$3d_{5/2}$ and Ni(II)$2p_{3/2}$ levels shift to higher energies by changing halogen ions in order of X=Cl, Br, and I. Such a trend is the same as that previously observed for homo-metal M(II)-M(IV) mixed-valence complexes.[19-22] This can be interpreted in terms of the difference of magnitudes of the charge-transfer dependence on the ionic radius of the bridging halogens.[36] The energy shifts of the Pt(IV)$4f_{7/2}$ level in the metal-alternated Pd(II)-X-Pt(IV) complexes from the reference energy of $[Pt^{IV}Cl_2(en)_2]Cl_2$ yield 0.0, −0.2, and −0.4 eV for X=Cl, Br, and I, respectively. These values are remarkably smaller than −0.3, −0.7, and −1.0 eV for the Pt(IV)$4f_{7/2}$ level in the homo-metal Pt(II)-X-Pt(IV) complexes.[19] Such a suppression of the reductive trend of the Pt(IV)4f binding energy due to the alternated substitution of Pd ions indicates that the alternated core-potentials in the Pd-X-Pt chain structure give a fairly large effect on the mixed-valence states constituted by the metal d electron. Since there is a considerable energy difference between the Pd-4d and Pt-5d levels, the 4d-5d

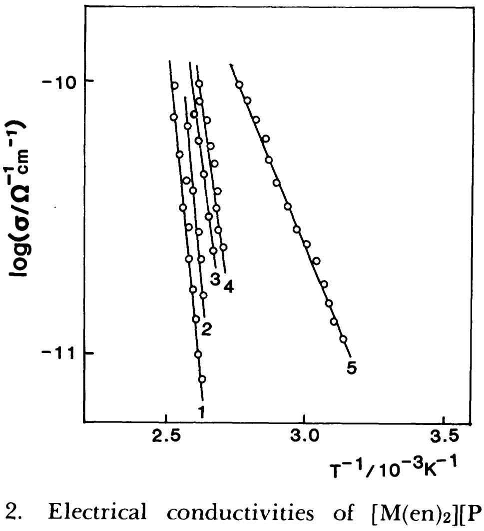


Fig. 2. Electrical conductivities of $[M(en)_2][PtX_2(en)_2](ClO_4)_4$.
1) $[Pd(en)_2][PtCl_2(en)_2](ClO_4)_4$, 2) $[Ni(en)_2][PtCl_2(en)_2](ClO_4)_4$, 3) $[Pd(en)_2][PtBr_2(en)_2](ClO_4)_4$, 4) $[Ni(en)_2][PtBr_2(en)_2](ClO_4)_4$, 5) $[Pd(en)_2][PtI_2(en)_2](ClO_4)_4$.

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† 1 Torr≈133.322 Pa.

TABLE 2. ELECTRICAL CONDUCTIVITIES (σ) AND ACTIVATION ENERGIES (ΔE) OF $[M^{II}(en)_2][M^{IV}X_2(en)_2](ClO_4)_4$

	X	Ni(II)-Ni(IV)a)	Pd(II)-Pd(IV)b)	Pt(II)-Pt(IV)b)	Ni(II)-Pt(IV)	Pd(II)-Pt(IV)
σc)	Cl	1.3×10^{-8}	2.0×10^{-12}	2.0×10^{-15}	3.2×10^{-17}*	4.0×10^{-18}*
ΔEd)		0.5	0.8	1.4	1.8	2.1
σc)	Br	—	1.2×10^{-8}	3.0×10^{-11}	8.4×10^{-14}*	1.4×10^{-15}*
ΔEd)		—	0.5	0.8	1.3	1.3
σc)	I	—	—	1.8×10^{-8}	—	4.5×10^{-11}
ΔEd)		—	—	0.4	—	0.6

a) Ref. 6, b) Ref. 12, c) $\Omega^{-1}\,cm^{-1}$, d) eV The * mark denotes the values of the room-temperature electrical conductivities obtained by an extrapolation.

charge transfer in the Pd(II)-X-Pt(IV) complexes is thought to be considerably smaller compared with the resonance 5d-5d charge transfer in the Pt(II)-X-Pt(IV) complexes. The decrease in the charge transfer, therefore, provides for the smaller energy shift of the Pt(IV)$4f_{7/2}$ level, indicating that the oxidation state of the Pt(IV) species remains close to the quadrivalent state. A similar interpretation can hold for the change in the Pt(IV)$4f_{7/2}$ binding energy in the Ni(II)-X-Pt(IV) complexes. Thus, it may be concluded that the metal alternation in the mixed-valence complexes leads to a suppression of the mixing of d_{z^2} orbitals between adjacent metal ions.

The metal alternation effect is expected to cause a change in the semiconducting properties of the mixed-valence complexes. The experimental results of the electrical conductivities of M(II)-X-Pt(IV) complexes along the chain are presented as a function of temperature in Fig. 2. Their behaviors suggest a hopping-type of electron-conduction with a thermal-activation energy ΔE. Upon assuming this conduction mechanism, estimated activation energies can be determined as summarized in Table 2, together with conductivities at room temperature. For complexes indicated by an * mark, we used room-temperature conductivities obtained by extrapolation. In this table, for comparison, we also list data concerning the homo-metal M(II)-M(IV) mixed-valence complexes of Pt, Pd, and Ni.

It is found that the activation energies decrease in the order of Cl>Br>I for X in both Pd(II)-X-Pt(IV) and Ni(II)-X-Pt(IV) complexes. This tendency is also coincident with those observed in homo-metal mixed-valence complexes. Such a ΔE behavior can be qualitatively interpreted in terms of a small polaron model,39) whose activation energy is closely correlated with the degree of the charge transfer between M(II) and M(IV) ions; the smaller the charge transfer, the larger the binding energy of the polaron. This may be the reason why the activation energies are in the order of Cl>Br>I.

It is interesting to note that the activation energies in changing metal ions increase in the order of Pd(II)-Pt(IV)>Ni(II)-Pt(IV)>Pt(II)-Pt(IV) for the same bridging halogen ions. The relation, M(II)-X-Pt(IV)>Pt(II)-X-Pt(IV) (M=Pd and Ni), that is, the activation energies of the metal-alternated complexes are larger than those of the regular Pt(II)-Pt(IV) mixed-valence complexes, may be naturally understood assuming a smaller charge-transfer energy in the metal-alternated complexes, as described before regarding the M-dependence of the Pt(IV)$4f_{7/2}$ binding energy. However, the order of Pd(II)-X-Pt(IV)> Ni(II)-X-Pt(IV) is rather peculiar because the ionization energy of a Ni ion is much larger than that of a Pd ion and, thereby, it gives a smaller charge transfer, suggesting an opposite relation regarding the activation energy to the experimental results. In order to interpret such a characteristic nature of the metal-alternated complexes, we have to take into account another contribution arising from metal alternation. In the M(II) species of M(II)-X-M(IV) complexes, electron-electron (e-e) repulsion energy is much larger for M=Ni(II) than for M=Pd(II). This surpassed the effect brought about by a change in the ionization energy, resulting in the observed relation concerning ΔE, Pd(II)-X-Pt(IV)>Ni(II)-X-Pt(IV). Such an important role of the e-e repulsive energy in mixed-valence complexes has been emphasized in a previous paper.36) For a more concrete discussion, we need information regarding the crystal structures of alternated-metal complexes, which is now under investigation. The optical results will be reported elsewhere.

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