September, 1985] © *1985 The Chemical Society of Japan* **N O T E S** *Bull. Chem. Soc. Jpn., 58, 2697—2698 (1985)* 2697

X-Ray Photoelectron Spectra of Halogen-bridged One-dimensional Pd^{II}-Pd^{IV} Mixed-valence Complexes, $[Pd(en)_2][PdX_2(en)_2](ClO_4)_4$

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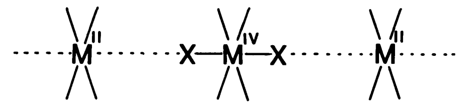
Synopsis. X-Ray photoelectron spectra of $[Pd^{II}(en)_2][Pd^{IV}X_2(en)_2](ClO_4)_4$ (en=ethylenediamine, X=Cl and Br) were measured. The difference in the binding energies of Pd3d between Pd^{II} and Pd^{IV} in the bromo-bridged complex is smaller than that in the chloro-bridged complex. This result is consistent with those of the crystal structures, electrical conductivities, and electronic spectra previously reported.

Recently halogen-bridged one-dimensional M^{II}-M^{IV} mixed-valence complexes of Pt, Pd, and Ni have attracted much interest from the various viewpoints of the chemistry and physics of low-dimensional compounds.[1,2] In these complexes, the four-coordinate M^{II} and six-coordinate M^{IV} are stacked alternately with bridging halogens as shown below.[3–5] In the Pt complexes, it has been pointed out that the ratio between the Pt^{IV}–X and $Pt^{II}\cdots X$ distances increases consecutively and approaches unity on going from the chloro to the iodo homologs, suggesting that the difference between the oxidation states of Pt^{II} and Pt^{IV} decreases in the order of Cl>Br>I. This was clearly verified by the X-ray photoelectron spectra and XANES.[6,7] These results coincide with those of the electrical conductivities, and electronic and emission spectra.[8,9] On the other hand, to our knowledge, X-ray photoelectron spectral studies on the Pd^{II}-Pd^{IV} mixed-valence complexes are few. In this study, the X-ray photoelectron spectra of the Pd^{II}-Pd^{IV} mixed-valence complexes, $[Pd(en)_2][PdX_2(en)_2](ClO_4)_4$ (X=Cl and Br) have been measured in order to evaluate the oxidation states of Pd atoms in the mixed-valence complexes. The results are compared with those of the crystal structures,[10,11] electronic spectra,[9] and electrical conductivities.[8]



Experimental

The Pd^{II}-Pd^{IV} mixed-valence complexes, $[Pd(en)_2][PdX_2(en)_2](ClO_4)_4$ (X=Cl and Br) were prepared by the method previously reported.[12]

The X-ray photoelectron spectra were obtained with a Mg-*Kα* exciting irradiation on a SHIMADZU ESCA 750. The spectrometer was calibrated by using Cls (285.0 eV).

Results and Discussion

Figure 1 shows the X-ray photoelectron spectra of $Pd3d_{5/2}$ and $Pd3d_{3/2}$ for the $[Pd(en)_2][PdX_2(en)_2](ClO_4)_4$. These compounds were very susceptible to X-ray irradiation damage and thereby the spectra changed gradually with time during the measurements as has been experienced in the Ni^{II}-Ni^{IV} mixed-valence complexes.[13,14] Therefore, the spectral measurements were carried out as quick as possible at a lower voltage.

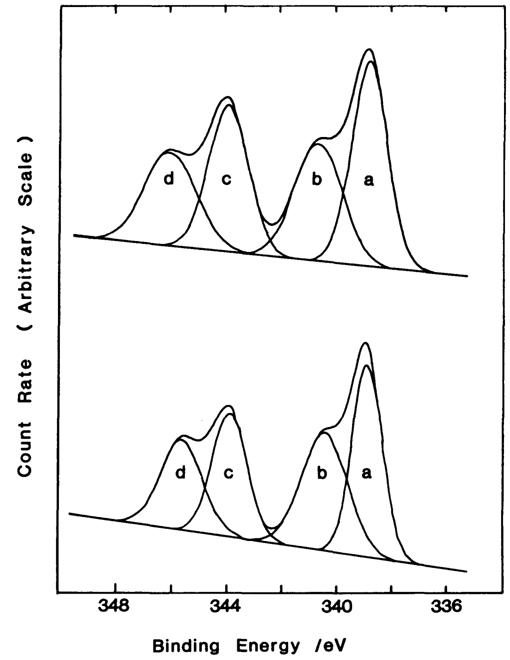


Fig. 1. X-Ray photoelectron spectra of $[Pd(en)_2][PdX_2(en)_2](ClO_4)_4$.
Top and bottom spectra are X=Cl and Br, respectively. Each spectrum is resolved into four components by simulation. a: $Pd^{II}3d_{5/2}$, b: $Pd^{IV}3d_{5/2}$, c: $Pd^{II}3d_{3/2}$, d: $Pd^{IV}3d_{3/2}$.

For the Pd^{II}-Pd^{IV} mixed-valence complexes, the spectra should be interpreted as a superposition of four bands, *i.e.*, $3d_{5/2}$ and $3d_{3/2}$ of Pd^{II} and Pd^{IV}. We have resolved the observed spectra into the Pd^{II} and Pd^{IV} components by the computer simulation. Although the intensities of Pd^{II} and Pd^{IV} components are assumed to be essentially the same as each other, the intensity of Pd^{IV} component is a little smaller than that of the Pd^{II} one. This is probably due to X-ray irradiation damage. Moreover, the intensity of the resolved Pd^{IV} spectra decreased, whereas that of the Pd^{II} spectra increased with time of X-ray irradiation. Since the spectral intensity corresponds to the number of species, it can be said from the observation that the decrease of the Pd^{IV} species were

TABLE 1. RESULTS OF Pd3d BINDING ENERGIES, DISTANCE RATIOS, CONDUCTIVITY MEASUREMENTS, AND PEAK POSITIONS OF ABSORPTION SPECTRA OF $\mathrm{[Pd(en)_2][PdX_2(en)_2](ClO_4)_4}$

X	$3d_{5/2}$		$3d_{3/2}$		R[a)]	$\sigma_{\mathrm{r.t.}}$ [b)]	ΔE [b)]	$h\nu_{\mathrm{max}}$ [c)]
	$\mathrm{Pd^{II}}$	$\mathrm{Pd^{IV}}$	$\mathrm{Pd^{II}}$	$\mathrm{Pd^{IV}}$		$\Omega^{-1}\,\mathrm{cm}^{-1}$	eV	eV
Cl	338.75	340.64	343.94	346.04	0.77	2.0×10^{-12}	0.81	2.05
Br	338.94	340.54	344.09	345.79	0.86	1.2×10^{-8}	0.49	1.22

a) Refs. 10 and 11. b) Ref. 8. c) Ref. 9.

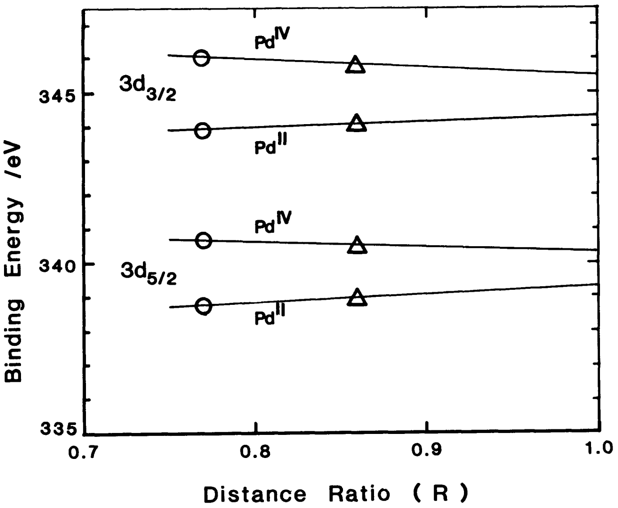


Fig. 2. Correlation between distance ratios and binding energies.
○: $\mathrm{[Pd(en)_2][PdCl_2(en)_2](ClO_4)_4}$, △: $\mathrm{[Pd(en)_2][PdBr_2(en)_2](ClO_4)_4}$.

roughly equal to the increase of the $\mathrm{Pd^{II}}$ species. This indicates that the $\mathrm{Pd^{IV}}$ state is decomposed to produce the $\mathrm{Pd^{II}}$ state. Quite a similar spectral change due to X-ray irradiation has been observed in the $\mathrm{Ni^{II}}$–$\mathrm{Ni^{IV}}$ mixed-valence complexes.[13,14]

As the bridging halogen shifts from Cl to Br, the $\mathrm{Pd^{IV}}$3d binding energies become lower while those of the $\mathrm{Pd^{II}}$ become higher. The difference in the binding energies of $\mathrm{Pd3d_{5/2}}$ between $\mathrm{Pd^{II}}$ and $\mathrm{Pd^{IV}}$ in the bromo-bridged complex (1.6 eV) is smaller than that in the chloro-bridged complex (1.9 eV). This result is essentially consistent with that of the crystal structures, that is, the ratio (R) between the $\mathrm{Pd^{IV}}$–X and $\mathrm{Pd^{II}}\cdots$X distances in the bromo-bridged complex (0.86) is larger than that in the chloro-bridged complex (0.77) as listed in Table 1.[10,11] Therefore, we can estimate roughly the $\mathrm{Pd^{III}}$ binding energy as shown in Fig. 2 by the extrapolation procedure to $R=1$ in the correlation between the binding energies and the distance ratios.

Since the difference between the oxidation states of the $\mathrm{Pd^{II}}$ and $\mathrm{Pd^{IV}}$ in the bromo-bridged complex is smaller than that in the chloro-bridged complex as shown in the X-ray photoelectron spectra, the wave number of the intervalence charge transfer from $\mathrm{Pd^{II}}$ to $\mathrm{Pd^{II}}$ along the chain is lower in the bromo-bridged complex than in the chloro-bridged complex.[9)] In the same way, the activation energy in the electrical conductivity, which is mainly concerned with the oxidation states of $\mathrm{Pd^{II}}$ and $\mathrm{Pd^{IV}}$, is smaller in the bromo-bridged complex than in the chloro-bridged complex.[8)]

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