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EXAFS Study on One-Dimensional Halogen-Bridged Mixed-Metal (Pd, Pt) Mixed-Valence Complexes

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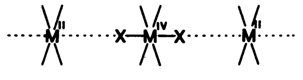
Synopsis. The EXAFS spectra of $[Pd(en)_2X_2Pt(en)_2](ClO_4)_4$ (en=ethylenediamine, X=Cl, Br, and I) were measured for Pd K and Pt L_{III} edges. The Fourier transforms of the Pd K- and Pt L_{III}- edge EXAFS show clearly that the halogen atoms are forming a chemical bond only to Pt(IV) and Pt–Cl, Pt–Br, and Pt-I bond lengths are 2.34, 2.47, and 2.83Å respectively.

Recently halogen-bridged one-dimensional mixed-valence complexes of Pt, Pd, and Ni have attracted much attention from the viewpoint of chemistry and physics of low-dimensional compounds.[1–4]

The compounds with the 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.) show various interesting phenomena such as strong inter-valence charge transfer, progressive resonance Raman spectra, and luminescence with a large Stokes shift. The effects of the metals, bridging halogens, counter anions, and in-plane ligands on the electronic structures of the complexes have been investigated by use of various different kinds of experimental methods.[5–12]

In the crystal structures, the four-coordinated M(II) and six-coordinated M(IV) units are stacked alternately, with bridging halogen atoms, constructing an infinite linear chain. The bridging halogen atom is located not at the middle point between M(II) and M(IV) atoms, but at the point closer to M(IV). In the compound of this type, the ratio of M(IV)–X and M(II)···X distances depends on metals, bridging halogens, counter anions, and in-plane ligands.



Toriumi and Yamashita[13] recently performed preliminary single-crystal X-ray structure analysis on the compounds where M(II)=Pd, M(IV)=Pt, AA= ethylenediamine, Y=ClO_4, and X=Cl, Br, or I, and showed that there is a disorder with regard to the position of bridging halogen atom. The halogen atom occupies two positions equidistant from the midpoint between the two metal atoms, Pt and Pd, with a half occupancy factor. Because of this disorder, it is hard to distinguish Pt and Pd sites, so that the metal sites are represented as(1/2)(Pt+Pd). Thus the state of halogen-metal bonding is not clear in the results of single-crystal X-ray structure analyses of those compounds. In order to establish the bonding of halogens to metals, we studied Pd K- and Pt L_{III}-edge EXAFS of the above-mentioned compounds. The measurements were carried out by use of the EXAFS facility at BL 10B[14] in

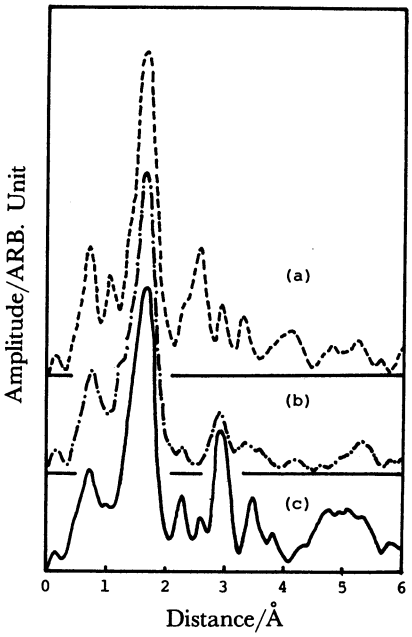


Fig. 1. The Fourier transforms for Pd K edge of (a) X=Cl, (b) X=Br, and (c) X=I.

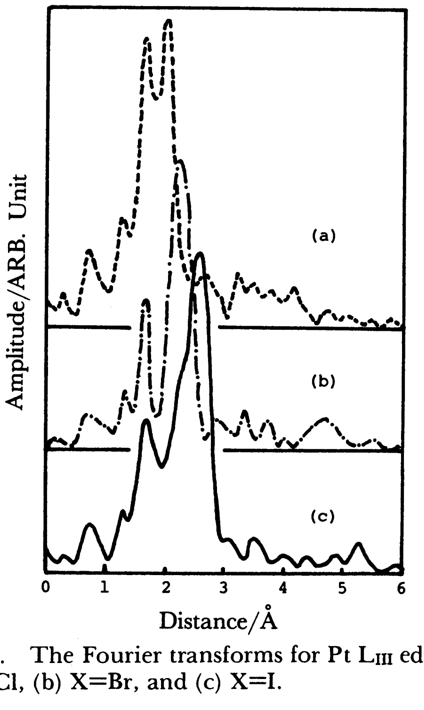


Fig. 2. The Fourier transforms for Pt L_{III} edge of (a) X=Cl, (b) X=Br, and (c) X=I.

Table 1. Bond Lengths/Å Obtained from the Analysis of EXAFS Data

	Pt-X	Pt-N	Pd-N
X=Cl	2.34	1.99	2.05
X=Br	2.47	2.05	2.06
X=I	2.83	2.08	2.05

the Photon Factory, National Laboratory for High Energy Physics (KEK-PF) utilizing a silicon (311) channel-cut monochromator.

The Fourier transform for Pd K edge EXAFS shows only one prominent peak (see Fig. 1). The position of this peak is the same for all the three compounds, therefore, the observed peak is attributable to Pd–N (in-plane ligand). We could not find a peak attributable to Pd-halogen. The Fourier transform for Pt L_{III} edge EXAFS (see Fig. 2) show two prominent peaks. The position of the peak at shorter distance remains the same for the three compounds, whereas the position of other peak shifts to longer distance as the halogen is changed from Cl to Br and to I. Thus we can attribute the former peak to Pt–N (in-plane ligand) and the latter to Pt–X. The results mentioned here clearly indicate that the bridging halogen atoms in the chain are at the position close to Pt(IV), possibly forming a chemical bond with Pt atom. Therefore, these results with XPS results⁶⁾ together indicate that these compounds are formulated as $[Pd(II)(en)_2][Pt(IV)X_2(en)_2](ClO_4)_4$.

Performing the inverse Fourier transformation over the region of the prominent peak of each Fourier transform, we carried out a further analysis for the obtained EXAFS oscillation by means of the nonlinear least square curve fitting method. The results are shown in Table 1. Previously it was reported that M(IV)-X distance is almost independent on the kinds of metals, in-plane ligands, and counter anions, although it is dependent on the kind of halogens. The results obtained in this study are quite consistent with those so far reportd.⁴⁾

The data analyses were carried out on the HITAC M-280H computer system at the Computer Center of the University of Tokyo using the program, EXAFS1.¹⁵⁾

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