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Studies on Mixed-Valence Complexes of Platinum and Palladium.
IV. X-Ray Photoelectron Spectra of Some of the Platinum Complexes

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In the preceding papers of this series [1–3], we have shown that the compounds with the general formula $PtX(A\text{-}A)_2Y_2$ (where A-A) = ethylenediamine(en), trimethylenediamine(tn) or propylenediamine(pn), X = Cl, Br or I, and Y = ClO_4 or BF_4) are composed of chains in which square planar $[Pt(A\text{-}A)_2]^{2+}$ and elongated octahedral $[PtX_2(A\text{-}A)_2]^{2+}$ ions are alternately arranged in line. In these compounds each platinum atom can be readily assigned to Pt(II) or Pt(IV) on the basis of the Pt–X distance. The difference between Pt(II)–X and Pt(IV)–X consecutively decreases in the sequence of Cl > Br > I (*cf.* Table I), suggesting that the oxidation states of platinum atoms approach to the averaged oxidation state, *i.e.*, Pt(III) [4], on going from the chloro- to the iodo-complexes.

In this study, in order to obtain more precise information about the oxidation states of platinum atoms of the mixed-valence compounds, we have measured the X-ray photoelectron spectra of $[Pt(en)_2]Cl_2$, $[PtCl_2(en)_2]Cl_2$, $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$, $[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$, $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$, $[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$ and $[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$.

Experimental

The methods of preparation of the compounds were reported in the preceding paper [1]. For the measurement of XPS the samples were ground and pressed on a nickel mesh. The X-ray photoelectron spectra were measured with an Al-Kα exciting radiation on a VG Scientific ESCA MKII electron spectrometer, the source vacuum being 5 × 10^{-9} Torr. The argon ion bombardment was not applied because the contamination of the surface was very little. The spectrometer was calibrated by using the Au $4f_{7/2}$

TABLE I. Crystal Data.

Complex	Pt^{II}–Pt^{IV} (Å)	Pt^{IV}–X (Å)	Pt^{II}–X (Å)	ρ[a]
$[Pt(pn)_2][PtCl_2(pn)_2](ClO_4)_4$	5.501	2.326	3.069	0.72
$[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$	5.403	2.318	3.095	0.75
$[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$	5.395	2.299	3.096	0.74
$[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$	5.501	2.546	2.955	0.86
$[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$	5.462	2.541	2.921	0.87
$[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$	5.820	2.726	3.093	0.93

[a] $\rho = (Pt^{IV}\text{–}X)/(Pt^{II}\text{–}X)$.

TABLE II. The Binding Energies of Platinum Atoms.[a]

	Pt(II)		Pt(IV)	
	$4f_{7/2}$	$4f_{5/2}$ (eV)	$4f_{7/2}$	$4f_{5/2}$ (eV)
$[Pt(en)_2]Cl_2$	72.6	75.3		
$[PtCl_2(en)_2]Cl_2$			74.9	77.5
$[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$	72.6	75.2	74.6	77.2
$[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$	72.6	75.3	74.6	77.2
$[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$	72.8	75.4	74.2	76.8
$[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$	72.7	75.3	74.2	76.7
$[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$	73.0	75.7	73.9	76.5

[a] These data were obtained after resolving the observed spectra into the Pt(II) and Pt(IV) components.

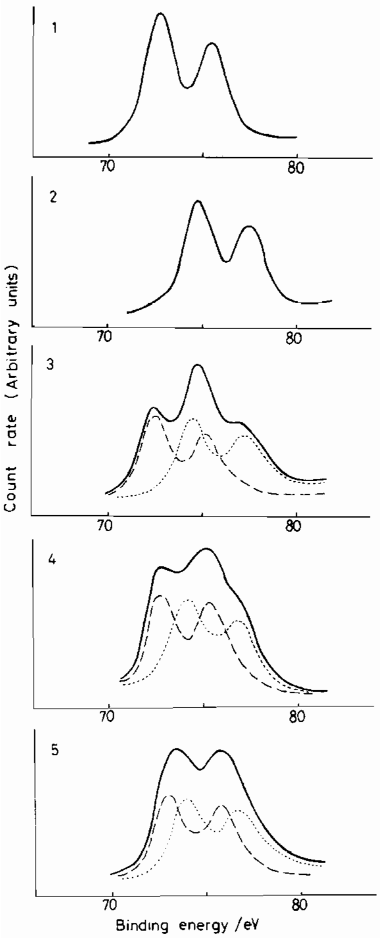

Figure 1. X-ray photoelectron spectra. 1) $[Pt(en)_2]Cl_2$; 2) $[PtCl_2(en)_2]Cl_2$; 3) $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$; 4) $[Pt(en)_2][PtBr_2(en)_2](ClO_4)_4$; 5) $[Pt(en)_2][PtI_2(en)_2]$-$(ClO_4)_4$. Broken lines and dotted lines in 3)–5) are the Pt(II) and the Pt(IV) components, respectively.

reference (83.6 eV). The charging effect was not observed, since these mixed-valence compounds exhibit large electric conductivities ($\approx 10^{-5}$ Ω^{-1} cm^{-1}) [5].

Results and Discussion

The results of X-ray photoelectron spectra are shown in Fig. 1. The binding energy $4f_{7/2}$ and $4f_{5/2}$ of the constituent complexes $[Pt(en)_2]Cl_2$ and $[PtCl_2(en)_2]Cl_2$ are 72.6 eV, 75.3 eV, and 74.9 eV, 77.5 eV respectively. Hence, in mixed-valence complexes, the spectra should be interpreted as a superposition of four bands, *i.e.*, $4f_{7/2}$ and $4f_{5/2}$ of Pt(II) and Pt(IV). Thus, we have resolved the observed spectra into the Pt(II) and Pt(IV) components. This was carried out by a trial-and-error method, premising that each of the resolved components is quite similar to the spectrum of $[Pt(en)_2]Cl_2$ or $[PtCl_2(en)_2]Cl_2$ in contour and in relative intensity. The results are quite satisfactory as seen in Fig. 1. It is obviously seen that each of the $4f_{5/2}$ and $4f_{7/2}$ binding energies of both Pt(II) and Pt(IV) shifts to the corresponding average value of Pt(II) and Pt(IV), when the mixed-valence complexes $[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$ are formed from the component complexes. This tendency is enhanced on going from the chloro- to the iodo-complexes. In the iodo-complex the oxidation states of platinum atoms are almost averaged.

Thus, the present result is quite consistent with the results of the structural studies [2, 3], and gives quantitative information on the oxidation states of platinum atoms in the mixed-valence compounds.

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