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ESCA Study of Pt(III) and Pt(I) Compounds

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A large body of literature exists on the subject of X-ray photoelectron studies of Pt(0), Pt(II), and Pt(IV) compounds (see, for example, refs. [1 - 4]). As far as we know, the X-ray photoelectron spectral data on Pt(I) and Pt(III) are now reported for the first time.

Let us briefly discuss the relationship between binding energy $Pt4f_{7/2}$ and the oxidation number of platinum, for we shall need this relationship during analysis of our results. The data published in refs. [1 - 4] suggest that binding energy $Pt4f_{7/2}$ increases with the oxidation number of Pt, however, the ranges of values for platinum compounds with varying oxidation numbers overlap but insignificantly (see Table I). It is essential, nevertheless, that with the same ligands $Pt4f_{7/2}$ binding energies in Pt(II) and Pt(IV) compounds differ by about 2 eV, *e.g.*, the difference of $Pt4f_{7/2}$ energies is 2.6, 1.8, 2.6 and 2.0 eV, respectively, for the following pairs of compounds: K_2PtCl_6 and K_2PtCl_4, $K_2Pt(NO_2)_6$ and $K_2Pt(NO_2)_4$, K_2PtBr_6 and K_2PtBr_4, $K_2Pt(SCN)_6$ and $K_2Pt(SCN)_4$ (see Table I).

TABLE I. Binding Energies $Pt4f_{7/2}$, HalnI[a], N1s (eV) and Oxidation Number of Pt(II).

Compound	$Pt4f_{7/2}$	HalnI, N1s	N	Reference
Pt(metal)	71.3	-	0	1–3
L_3Pt[b]	71.6	-	0	4
L_2PtPhC_2Ph	72.3	-	0	1
$L_2PtC_2H_4$	72.4	-	0	1
$[(L)Pt(SPPh_2)]_2$	72.0	-	1	present paper
$K_2Pt(NO_2)_4$	74.3	404.9	II	2,3
K_2PtCl_4	73.1	198.9	II	2,3
$K_2Pt(SCN)_4$	72.8	-	II	2,3
K_2PtBr_4	72.8	69.8	II	2,3
$Pt(NH_3)_4Cl_2$	73.6	198.0	II	2,3
$Pt(NH_3)_4Br_2$	73.6	68.6	II	2,3
$Pt(NH_3)_2(NO_2)_2$	73.9	400.5; 404.4	II	2,3
$Pt(NH_3)_2Cl_2$	73.4	400.4; 199.1	II	2,3
K_2PtF_6	77.8	-	IV	2,3
$K_2Pt(NO_2)_6$	76.1	404.9	IV	2,3
K_2PtCl_6	75.7	199.1	IV	2,3
$K_2Pt(SCN)_6$	74.8	-	IV	2,3
K_2PtBr_6	74.8	69.4	IV	2,3
K_2PtI_6	73.6	-	IV	2,3
$[Pt(NH_3)_6]Cl_4$	76.8	198.0	IV	2,3
$(Et_3P)_2PtCl_4$	76.1	199.4	IV	4

[a] HalnI = Cl2p, Br3d. [b] L = PPh_3.

Summarized in this paper are the results of a study of compounds of composition $[Pt(CH_3CONH)_2X]_n$ (Table II). For these compounds, on the basis of their chemical properties similar to those of Rh(II) compounds, there was proposed [5] a binuclear structure of $Pt_2(CH_3CONH)_4X_2$ with a Pt–Pt bond and X groups arranged along this bond. The oxidation number of Pt in these compounds must be III. X-ray photoelectron studies of compounds kindly submitted to us by A. G. Majorova corroborate this structure. Doublet $Pt4f_{5/2,7/2}$ has the usual form, which is indicative of the equivalence of Pt atoms, and hence excludes the possibility of Pt(II) and Pt(IV) being present in 1:1 ratio. Moreover, since the $Pt4f_{7/2}$ energy in $Pt(CH_3CONH)_2 \cdot H_2O$ is equal to 73.8 eV, and the oxidation number being higher by unity must increase this energy by about 1 eV (see above), for Pt(III) compounds of a known composition one should expect a $Pt4f_{7/2}$ value of about 75 eV, which is also confirmed by the experiment (Table II).

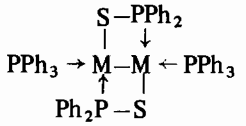
TABLE II. Binding Energies, eV.

Compound	$Pt4f_{7/2}$	N1s[a], HalnI[b]
$Pt_2(CH_3CONH)_4(NO_3)_2$	75.2	407.0
$Pt_2(CH_3CONH)_4(NO_2)_2$	75.2	403.7
$Pt_2(CH_3CONH)_4Cl_2$	75.0	198.2
$Pt_2(CH_3CONH)_4Br_2$	75.1	68.9
$Pt_2(CH_3CONH)_4I_2$	74.8	619.3
$Pt_2(CH_3CH_2OONH)_4Cl_2$	75.0	198.2
$Pt(CH_3CONH)_2 \cdot H_2O$	73.8	

[a] In NO_2^- and NO^3 groups, N1s is equal to 399.6 eV in CH_3CONH^-. [b] HalnI = Cl2p, Br3d, I3d.

Also indicative of the proposed [5] structure are the low values of binding energies N1s and HalnI of ligands X in $[Pt(CH_3CONH)_2X]_n$; these energies are by approximately 0.5 eV lower than in Pt(II) and Pt(IV) compounds where Hal and NO_2 are coordinated by the Pt atom (Tables I and II). The low values of N1s and HalnI demonstrate the relatively ionic nature of the Pt–X bond, which is consistent with the chemical properties [5] – the X groups exchange easily. A more pronounced ionic nature of the Pt–X bond was to be expected [6] as a result of the *trans*-effect of the Pt–Pt bond. Note that a similar phenomenon was observed [7] also for binding energies HalnI, N1s, *etc.* of ligands X in compounds $Rh_2(RCOO)_4X_2$ where a dimeric structure with a X–Rh–Rh–X bond has been revealed by X-ray structure analysis.

We have also examined compounds of the



$$\begin{array}{c} \mathrm{S}-\mathrm{PPh_2} \\ | \quad \downarrow \\ \mathrm{PPh_3} \rightarrow \mathrm{M}-\mathrm{M} \leftarrow \mathrm{PPh_3} \\ \uparrow \quad | \\ \mathrm{Ph_2P}-\mathrm{S} \end{array}$$

(M = Pt, Pd) type, submitted to us by Dr. B. Walther (Martin Lüther Universität in Halle). The results of X-ray structure analysis of a similar compound can be found in ref. [8]. According to the oxidation number of Pt(I), the value of Pt4$f_{7/2}$ (Table I) is lower than in Pt(II) compounds*. However, there are a number of complexes where the formal oxidation number is 0 and the value of Pt4$f_{7/2}$ is higher than in the examined Pt(I) compound.

Thus, the obtained results suggest that the value of Pt4$f_{7/2}$ increases with the formal oxidation number of platinum in a compound, but the ranges of Pt4$f_{7/2}$ values for different oxidation numbers overlap, which is indicative of the essential role of ligands in determining the value of Pt4f. This should be taken into consideration when determining the oxidation number of Pt and other transition elements with the aid of ESCA.

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*The Pd 3$d_{5/2}$ energy in a similar Pd(I) compound is equal to 337.0 eV, which is also lower than the respective values [9] for Pd(II).