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An ESCA Study of Binuclear Platinum Complexes

G. M. BANCROFT, T. CHAN, R. J. PUDDENPHATT

Department of Chemistry, University of Western Ontario, London N6A 5B7, Canada

and M. P. BROWN

Donnan Laboratories, University of Liverpool, Liverpool L69 3BX, U.K.

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Many X-ray photoelectron (or ESCA) spectra of Pt compounds have demonstrated that the Pt 4f binding energies change markedly with the Pt oxidation state [1–9] (Table I). Riggs [2] proposed a Pt 4f binding energy difference of ~1.1 eV per unit of oxidation state. Examination of Table I reveals that Pt(0) compounds such as $Pt(PPh_3)_4$ have a Pt $4f_{7/2}$ binding energy of ~71.5 eV, while Pt(II) and Pt(IV) compounds with halide ligands such as $[PtCl_2L_2]$ and $[PtCl_4L_2]$ (L = phosphine) have Pt $4f_{7/2}$ binding energies of ~73.5 eV and ~76.0 eV respectively. A recent study [7] of Pt(III) compounds shows that the Pt $4f_{7/2}$ binding energies lie between Pt(II) and Pt(IV) at about 75.0 eV. However, it is well known that ligand changes (and sometimes structural changes) markedly alter the binding energy within one oxidation state [6, 7]. For example, replacement of a Cl by CH_3 or C_6H_5 in Pt(II) compounds results in a ~0.5 eV lowering of the Pt $4f_{7/2}$ binding energy (Table 1).

We report our ESCA results on a number of novel Pt dimers of the type $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [dppm = bis(diphenylphosphino)methane] [10], $[Pt_2HL(\mu\text{-dppm})_2][PF_6]$ (L = dppm, CO, PPh_3) [11] and $[Pt_2XY_2(\mu\text{-dppm})_2][PF_6]$ (X, Y = H, CH_3) [12] which have been postulated to contain Pt(I), Pt(I) and Pt(II) respectively. We show that Pt $4f_{7/2}$ binding energy for Pt(I) in $[Pt_2Cl_2(\mu\text{-dppm})_2]$ is midway between Pt(0) and Pt(II) binding energies; and the Pt $4f_{7/2}$ binding energies for the latter two groups of compounds are indeed consistent with previous Pt(I) and Pt(II) formulations.

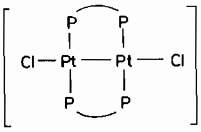
The ESCA results were obtained using a McPherson ESCA 36 spectrometer and a Mg Kα X-ray source (1253.6 eV photons). Powdered samples were ground and pressed onto stainless steel plates. A number of samples were run for each compound, and the binding energies were reproducible to within ±0.1 eV. No

TABLE I. Pt $4f_{7/2}$ Binding Energies (eV).

Compounds	Pt $4f_{7/2}$ Binding Energy	Oxidation number	Ref.
1. $[Pt(PPh_3)_3]$	71.6	0	2
2. $[Pt(PPh_3)_4]$	71.6	0	2
3. $[Pt_2(\mu\text{-}SPPh_2)_2(PPh_3)_2]$	72.0	I	7
4. $[Pt_2H(dppm)(\mu\text{-dppm})_2][PF_6]$	72.3	I	this work
5. $[Pt_2H(CO)(\mu\text{-dppm})_2][PF_6]$	72.4	I	this work
6. $[Pt_2H(PPh_3)(\mu\text{-dppm})_2][PF_6]$	72.5	I	this work
7. $[Pt_2Cl_2(\mu\text{-dppm})_2]$	72.4	I	this work
8. $[PtCl_2(dppm)]$	73.3	II	this work
9. $[PtCl_2(PPh_3)_2]$	73.3	II	this work
			6, 1, 2, 9
10. $[PtCl_2\{P(C_2H_5)_3\}_2]$	72.9	II	7
	73.2	II	1, 9
11. $[PtCl(CH_3)\{P(C_2H_5)_3\}_2]$	72.8	II	1
12. $[Pt(C_6H_5)_2\{P(C_2H_5)_3\}_2]$	72.7	II	1
13. $[Pt(CH_3)_2\{P(C_2H_5)_3\}_2]$	72.4	II	1
14. $[Pt(CH_3)_2(dppm)]$	72.4	II	this work
15. $[Pt_2H_2(\mu\text{-dppm})_2][PF_6]$	72.6	II	this work
16. $[Pt_2(CH_3)_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	72.5	II	this work
17. $[Pt_2(CH_3)_3(\mu\text{-dppm})_2[[SbF_6]$	72.5	II	this work
18. $K_2[PtCl_4]$	73.3	II	8, 2, 6
	73.9	II	5
19. $[Me_4N]_2[PtCl_4]$	73.5	II	5
20. $[Pt_2(CH_3CH_2CONH)_4Cl_2]$	75.0	III	7
21. $[Pt_2(CH_3CONH)_4Cl_2]$	75.0	III	7
22. $[PtCl_4\{P(C_2H_5)_3\}_2]$	76.1	IV	2
	75.5	IV	4
23. $[PtCl_4(Me_2PhP)_2]$	75.8	IV	4

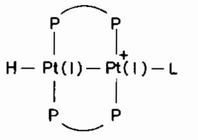
obvious X-ray decomposition was observed. All the spectra were computer fitted to Gauss-Lorentz line shapes using a least squares program [13]. No constraints were used for the final fits. The Pt $4f_{7/2}$ full widths at half maximum were about 2.1 eV. All binding energies were corrected relative to the symmetric C 1s peak at 285.0 eV.

The Pt $4f_{7/2}$ binding energy for the symmetrical Pt(I) dimer $[Pt_2Cl_2(\mu\text{-ddpm})_2]$

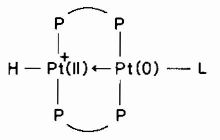


is 72.4 eV. This is ~1 eV lower than the Pt $4f_{7/2}$ binding energies for Pt(II) compounds with two chlorine and two phosphine ligands (Table I, compounds 8–10). This result is entirely consistent with Riggs proposal [2] of a ~1.1 eV binding energy shift per unit of Pt oxidation state.

The complex ions $[Pt_2HL(\mu\text{-ddpm})_2]^+$ can be formulated as either: (A) with a covalent Pt–Pt bond in which both Pt centres are formally Pt(I); or (B) with a coordinate Pt(0) ≈ Pt(II) bond in which both Pt(II) and Pt(0) centres are present.



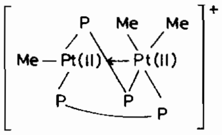
(A)



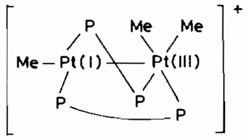
(B)

Formulation (A) is considered more consistent with the molecular structure determined by the X-ray analysis for the L = η'-dppm derivative [11]. It can be considered as a derivative of the symmetrical dichlorodi Pt(I) dimer. The ESCA Pt 4f spectra are entirely consistent with (A) being the dominant resonance form. First, the Pt $4f_{7/2}$ binding energies of 72.3–72.5 eV are very similar to that for the dichloro Pt(I) dimer. Second, only one unbroadened Pt 4f spin orbit doublet is observed. Formulation (B) should show two sets of doublets either due to the ground state or excited state effects [14–16].

The structure of $[Pt_2(CH_3)_3(\mu\text{-dppm})_2]^+$ is unique in platinum chemistry, and either formulation (C) or (D) is consistent with structural and spectroscopic data.



(C)



(D)

The ESCA data is totally consistent with formulation (C) as being the dominant resonance form for this compound. First, the Pt $4f_{7/2}$ binding energies of ~72.5 eV are the same as those for the dimethyl Pt(II) compounds (#13 and 14, Table I). Second, no noticeable broadening of the Pt 4f spinorbit doublet is observed. Again, formulation (D) should show two sets of doublets [14–16].

Both sets of dimers give good illustrations of Paulings electroneutrality principle, since the nature of the Pt–Pt bonding is such as to equalize the charge on each Pt centre.

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