XPS evidence for the photoproduction of tungsten(VI) cyano complexes in charge-transfer photochemistry of $W(CN)_8{}^{3-}$ ion in non-aqueous solvents

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Abstract

The X-ray photoelectron spectra of a series of cyano complexes of tungsten were measured in order to obtain the W4f and N1s binding energies. A correlation between the W4f binding energies and oxidation state of tungsten and N1s core binding energies as a function of chemical environment allowed the identification of three new photoproducts isolated from irradiated octacyanotungstate(V) ion in MeCN. The new species have been found to consist of W(VI) centres and assigned to seven-coordinate mononuclear $W^{VI}(CN)_7{}^-$, dinuclear $(CN)_6-W^{VI}-NC-W^{VI}(CN)_6{}^-$ and trinuclear $(CN)_7-W^{VI}-NC-W^{IV}(CN)_6-CN-W^{VI}(CN)_7{}^{6-}$ complex anions.

Introduction

X-ray photoelectron spectroscopy has proved invaluable in the determination of the oxidation state of the metal centre [1–5], ligand structure and coordination [2, 3, 5, 7–9] and inter- and intramolecular interactions for complexes of transition metals [2–4, 10].

Among the literature on these problems there are a few reports on the XPS study of homoleptic cyanometalates that discussed the trends in charge distribution on the basis of chemical shifts in N1s and C1s binding energies [11–13] as well as changes in valence electron levels [14].

The intriguing photoreactivity of $(TBA)_3W(CN)_8$ (TBA = n-tetrabutylammonium(1 +) cation) in non-aqueous solvents [15] generated our interest in the application of XPS to studies of cyano complexes of tungsten. The main purposes were to use the W4f and N1s spectra of a series of cyanotungstates $(K_4W(CN)_8, (TBA)_3W(CN)_8$ and $(PPh_4)_2W(CN)_6O$ $(PPh_4 = $ tetraphenylphosphonium(1 +) cation)), as a diagnostic tool for identification of the three diamagnetic photoproducts. They were isolated from irradiated $(TBA)_3W(CN)_8$ solution in MeCN [15] and denoted as species I, II and III.

Experimental

All the cyano complexes of tungsten used in this study were synthesized by one of us (B.S.). The preparation methods of these complexes have been published in refs. 15–18.

Species I, II and III were the photoproducts obtained by TLC separation of the reaction mixture of a previously irradiated $(TBA)_3W(CN)_8$ solution in MeCN [15]. The separated photoproducts were characterized by their electronic spectra: species I by the absorption band at 24 160 cm^{-1}, species II and III by the bands at 20 960 and 18 800 cm^{-1}, respectively [15].

XPS spectra were recorded with the ESCA System 100 spectrometer (VSW Scientific Instruments, Manchester). Non-monochromatized Mg $K\alpha$ radiation (1253.6 eV) was used as an excitation source. The samples were deposited on the sample stub from MeCN or MeOH solutions by evaporation of the solvent. The samples were cooled with liquid nitrogen during the measurements in order to reduce irradiation damages. The average temperature of the sample stub was 170 K while the base pressure was 1×10^{-9} Torr or lower. The spectra were calibrated in relation to the C1s binding energy (284.7 eV) which was applied as an internal standard. The raw spectra were smoothed by the Fourier transform method. The background was removed by use of an integral-shape synthetic curve. The W4f and N1s peaks corresponding to the different types of W and

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N atoms, respectively, were obtained by using a Gaussian bandfit program. The relative area under the appropriate curve has been assumed to be proportional to the number of tungsten or nitrogen atoms, respectively.

Results and discussion

The XPS data concerning W4f energies obtained in measurements of the tungsten cyano complexes are given in Table 1. A representative W4f spectrum of $K_4W(CN)_8$ is shown in Fig. 1.

The 2.11 ± 0.06 eV separation between the $W4f_{5/2}$ and $W4f_{7/2}$ peaks with the approximate intensity ratio of 3:4 is characteristic of all the complexes employed. As the electron binding energies show a clear correlation with the oxidation state of metal

TABLE 1. Tungsten 4f spectra parameters for some cyanotungstate complexes (*BE* values related to C1s (284.7 eV))

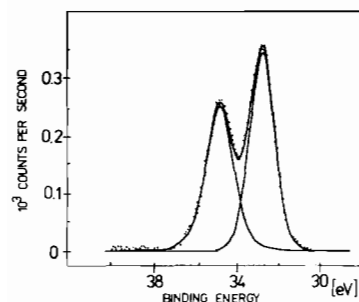| Compound	W4f				Assignment
		BE (eV)	FWHM (eV)	Area	
$K_4W(CN)_8$	7/2	32.8	1.4	0.530	W(IV)
	5/2	34.8	1.6	0.470	
$(TBA)_3W(CN)_8$	7/2	33.6	1.9	0.520	W(V)
	5/2	35.7	1.7	0.480	
$(PPh_4)_2W(CN)_6O$	7/2	34.3	1.7	0.599	W(VI)
	5/2	36.3	1.7	0.401	
Species I	7/2	34.8	2.0	0.589	W(VI)
	5/2	36.9	2.0	0.411	
Species II	7/2	35.1	2.2	0.548	W(VI)
	5/2	37.3	2.2	0.452	
Species III	7/2	35.3	2.4	0.381	W(VI)
	5/2	37.5	2.4	0.287	
	7/2	32.8	2.4	0.190	W(IV)
	5/2	34.9	2.4	0.142	

centre, one may use it as an analytical tool. We have noticed a linear correlation between the binding energy (*BE*) and the oxidation state of reference complexes.

The W4f spectrum of species I exhibits a doublet of binding energies 36.9 and 34.7 eV. Analysis of the data gathered in Table 1 points to the presence of tungsten atom of +6 oxidation state in species I.

The W4f spectrum of species II consists of one doublet of *BE* 37.3 and 35.2 eV. In spite of a small shift of the W4f doublet (about 0.35 eV), the *BE* values obtained for species II indicate also the presence of tungsten(VI).

The W4f spectrum of species III is quite different (Fig. 2); it is deconvoluted as an overlap of two doublets, indicating the presence of non-equivalent tungsten atoms. The *BE* of the first doublet of 37.45 and 35.30 eV and the second one of 34.95 and 32.80 eV, strongly confirmed the presence of W atoms in two oxidation states which are ascribed to W(VI) and W(IV).

A comparison of the doublet intensities shows the presence of two W(VI) atoms and one W(IV) atom. Species III can be therefore assigned to the trinuclear complex, consisting of two equivalent W(VI) centres and one W(IV) centre ([6, 4, 6] notation).

The XPS data for N1s for the tungsten cyano complexes investigated are presented in Table 2. The N1s spectrum of $K_4W(CN)_8$ shows a single peak at 398.1 eV, consistent with the nearly equivalent eight cyano ligands [19] and considerable π-backbonding [11–13].

$(TBA)_3W(CN)_8$ contains two structurally distinguishable types of nitrogen atoms, i.e. tetrabutylammonium and cyano nitrogen atoms in an abundance ratio of 3:8. The N1s spectrum of $(TBA)_3W(CN)_8$ is presented in Fig. 3. The two peaks of *BE* 402.1 and 397.9 eV with the intensity ratio of 3:8.1 correspond to tetrabutylammonium and cyano nitrogen atoms, respectively. The single peak at 397.9 eV is consistent with the practically equivalent eight co-
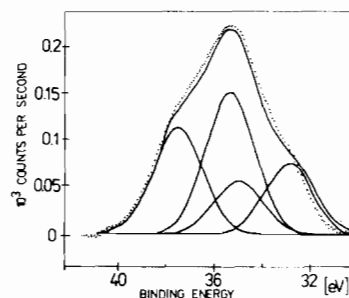

Fig. 1. Tungsten 4f photoelectron spectrum of $K_4W(CN)_8$: ·····, experimental spectrum; ——, fitted peaks.

Fig. 2. Tungsten 4f photoelectron spectrum of species III: ·····, experimental spectrum; ——, fitted peaks.

TABLE 2. Nitrogen 1s spectra parameters for some cyanotungstate complexes (BE values related to C1s (284.7 eV))

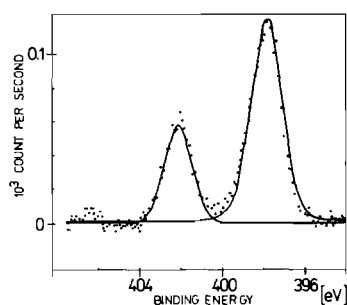| Compound	N1s			Relative intensity
	BE (eV)	FWHM (eV)	Area	
(TBA)Cl	401.4	1.6	1.000	
$K_4W(CN)_8$	398.1	1.7	1.000	
$(TBA)_3W(CN)_8$	397.9	1.7	0.724	8
	402.1	1.5	0.273	3
$(PPh_4)_2W(CN)_6O$	397.2	2.0	0.840	5
	399.3	1.7	0.160	1
Species I	398.2	1.7	0.238	2
	399.9	1.8	0.635	5
	401.6	1.7	0.127	1
Species II	399.5	2.8	0.928	13
	401.9	1.7	0.072	1
Species III	397.9	2.0	0.585	3
	399.7	2.0	0.187	1
	402.1	1.7	0.228	1

Fig. 3. Nitrogen 1s photoelectron spectrum of $(TBA)_3W(CN)_8$: · · · · ·, experimental spectrum, ———, fitted peaks.

ordinated cyano ligands [20]. The BE value of nitrogen cyano ligands of $W(CN)_8{}^{3-}$ is lower compared to $W(CN)_8{}^{4-}$ and can be accounted for by considering the significant interaction of the anion moiety with the cation in the case of $(TBA)_3W(CN)_8$, as demonstrated by the shift of N1s BE of 401.4 eV in (TBA)Cl to a higher value of 402.1 eV in $(TBA)_3W(CN)_8$. The effect of interaction between the anion and the cation can lead to a different charge distribution, overshadowing the decreasing extent of π backbonding and therefore expected increased BE value of N1s of cyano nitrogens on going from $W(CN)_8{}^{4-}$ to $W(CN)_8{}^{3-}$.

The $W(CN)_6O^{2-}$ ion has been characterized [17, 18] as a pentagonal bipyramid with five equatorial CN^- ligands, bent slightly away from the W=O apex due to repulsion by π electrons from the W=O

double bond, and one, more loosely coordinated, axial CN^- ligand reflecting the *trans* influence of the oxo group. The N1s spectrum of $(PPh_4)_2W(CN)_6O$ exhibits two overlapping peaks of BE 397.2 and 399.3 eV with an intensity ratio 5:1, consistent with a 5:1 partition of CN^- ligands. The peak of lower BE has to be assigned to five equatorial cyano nitrogens and is presumably due to the combination of π-repulsion along the axis and large ligand overlap in the equatorial plane, increasing the electron density on the equatorial nitrogens and hence making the equatorial bonds stronger than the axial one.

The N1s spectrum of species I consists of three overlapping peaks corresponding to a binding energy of 401.6, 399.9 and 398.2 with an intensity ratio of 1:5:2. The first peak of highest energy can be assigned to the tetrabutylammonium nitrogen, whereas the lower energy stronger peaks can be attributed to the seven cyano nitrogens. This result and the fact that the oxidation state of W in species I has been assigned as +6 (*vide supra*) suggest the tentative formula of species I as $(TBA)W^{VI}(CN)_7$. The intensity ratio of 5:2 of cyano nitrogens resembles the 5:2 partition of homoleptic ligands of seven-coordinate complexes with pentagonal bipyramid geometry with predicted stronger axial bonds in d^0 systems [21].

The N1s spectrum of species II exhibits the complex band, the components of which have binding energies of 401.9 and 399.5 eV with an intensity ratio 1:13. The peak at 401.9 eV can be attributed to one tetrabutylammonium nitrogen and the lower energy peak can be assigned to cyano nitrogens. On the basis of the above data and the W4f spectrum showing only the +6 oxidation state of W, species II can be formulated as a binuclear compound with a tentative formula $(TBA)W_2(CN)_{13}$. The anionic $W_2(CN)_{13}{}^-$ moiety can be attributed to the cyano-bridged structure $(CN)_6-W^{VI}-CN-W^{VI}-(CN)_6{}^-$, consistent with the equivalency of W(VI) centres.

The N1s spectrum of species III (Fig. 4) consists of the peak of binding energy 402.1 eV and the broad band, which deconvoluted gave two components of binding energies 399.7 and 397.9 eV, and
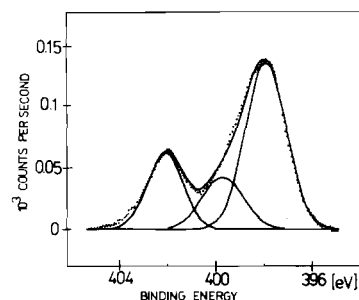

Fig. 4. Nitrogen 1s photoelectron spectrum of species III: · · · · ·, experimental spectrum; ———, fitted peaks.

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the intensity ratio of all three peaks as 1:1:3. The assignment of species III as a trinuclear [6,4,6] complex (*vide supra*) implies the tentative formula $(TBA)_6W_3(CN)_{22}$ and cyano-bridged structure $(CN)_7-W^{VI}-NC-W^{IV}(CN)_6-CN-W^{VI}(CN)_7^{6-}$ for the $W_3(CN)_{22}^{6-}$ moiety. The [6,4,6] notation formally reflects only a localized-valence description of species III, although the equivalency of W(VI) centres can indicate symmetrical trinuclear complexes, having an octacyanotungstate(IV) moiety as the 'bridging ligand'. Such formulation of species III is supported by consideration of the mechanism of the photochemical reaction of the $W(CN)_8^{3-}$ ion [15].

Conclusions

The XPS study of cyano complexes of tungsten proves that

(i) the XPS technique is a reliable tool for identification of various oxidation states of tungsten;

(ii) the N1s spectra provide important information on the structure and coordination of cyanotungstate complexes, particularly of those with n-tetrabutylammonium countercation;

(iii) the three photoproducts of irradiated $(TBA)_3W(CN)_8$ consist of mono-, di- and trinuclear anionic cyanotungstate moieties;

(iv) the mono- and dinuclear species are based on W(VI) as a metal centre and assigned to $W(CN)_7^-$ and $W_2(CN)_{13}^-$ while the trinuclear species consists of W(IV) and W(VI) in a 2:1 ratio and is assigned to $W_3(CN)_{22}^{6-}$.

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