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The X-Ray Photoelectron Spectroscopy of the 5-Hydroxy-6-Methyl-3,4-Pyridinium Dimethanol Hexachloroplatinate(IV)

ALI KATRIB and MOHAMED S. EL-EZABY

Chemistry Department, Faculty of Science, Kuwait University, Kuwait

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The use of X-ray photoelectron spectroscopy as a tool in order to determine the molecular structure of different compounds is well recognized. In the case of platinum complexes having the same ligands, the chemical shift of the platinum ($4f_{7/2,5/2}$) spin–orbit components is approximately 2 eV per oxidation number [1]. As a result, it is possible to determine the oxidation number of the platinum atom in a complex. Recently, Yamashita *et al.* [2] observed the presence of three lines in the energy range of 70–80 eV rather than two lines that are characteristic of the spin–orbit components of a single platinum atom in a complex. These lines were considered as evidence of a binuclear structure of more than one platinum in the complex with different oxidation numbers, namely, Pt(IV) and Pt(II).

We observed a similar effect during the recording of the X-ray photoelectron spectrum of a newly synthesized platinum complex with 5-hydroxy-6-methyl-3,4-pyridine dimethanol hydrochloride (pyridoxol, a vitamin B_6 compound) P, where three lines appeared in the energy range 70–80 eV. However, it was observed that the relative intensity of these lines was dependent on the duration of X-ray irradiation of the sample. Furthermore it was also observed that the relative intensity of these lines was drastically altered by argon ion bombardment. The vacuum effect was also investigated by placing four samples in the sample chamber and recording their spectra at different intervals.

Experimental

A Mcpherson-36 ESCA photoelectron spectrometer with Mg Kα at 1253.6 eV was used; this instrument has a cryogenic pump to provide a pressure in the sample chamber of less than 10^{-9} torr and the temperature is approximately 300 K. The samples were placed on aluminium mesh. The instrument is equipped with an argon ion with acceleration through 10 KV for sample surface treatment. The instrument is calibrated on the Au $4f_{7/2}$ at 84.0 eV. Since the samples studied were non-conductors, the measured binding energies of the compounds were based on the C(1s) at 285.0 eV.

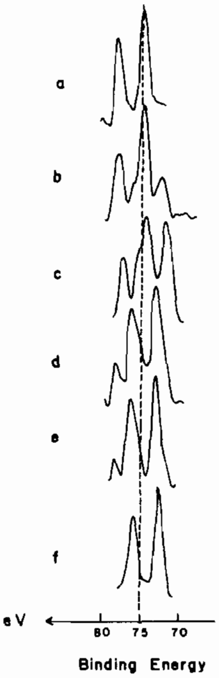
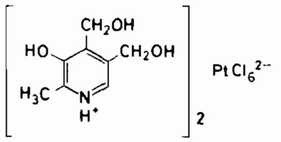


Fig. 1. X-ray photoelectron spectra of the Pt(4f) spin–orbit components in $(PH)_2Pt(IV)Cl_6$ at different intervals of X-ray exposure. 1a) fresh sample; 1b) after 45 minutes; 1c) after one hour and thirty minutes; 1d) after two hours and thirty minutes; 1e) after two hours and forty minutes; 1f) after three hours and forty minutes.

The solid complex of the chloroplatinum acid (H_2PtCl_6) with pyridoxolhydrochloride ($C_8H_{11}O_3NCl$) was isolated from acidic aqueous solutions. The precipitated crystalline orange product was washed by successive portions of water followed by ethanol and dried under reduced pressure. The solid complex was analyzed for C, H, O, N, Cl and Pt content. The analysis was 25.67, 3.19, 12.78, 3.75, 28.38 and 26.16% for C, H, O, N, Cl and Pt respectively. This analysis is compatible with the complex composition of $C_{16}H_{24}O_6N_2Cl_6Pt$ (25.68, 3.23, 12.89, 3.74, 28.43 and 26.08% for C, H, O, N. Cl and Pt respectively). The bulk magnetic susceptibility and ^1H NMR were done in the laboratory of Professor L. M. Venanzi*. These results indicated that the complex is completely diamagnetic with the following possible structure:



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*Eidgenossische Technische Hochschule Zurich, Laboratorium für Anorganische Chemie.

TABLE I. Binding Energies of $(PH)_2Pt(IV)Cl_6$ and $(NH_4)_2$-$Pt(II)Cl_4$ Based on C(1s) at 285 eV.

Compound	Pt		Cl		N 1s
	$4f_{7/2}$	$4f_{5/2}$	$2p_{3/2}$	$2p_{1/2}$	
$(PH)_2Pt(IV)Cl_6$	74.6	78.1	198.3	199.6	400.7
$(NH_4)_2Pt(II)Cl_4$	72.6	75.9	198.4	199.7	400.5

Results and Discussion

Figure 1 shows the X-ray photoelectron spectrum of the platinum complex in the energy range of 70–80 eV at different intervals of X-ray bombardment. Immediate X-ray exposure of the fresh sample showed the presence of two lines at 74.8 and 78.1 eV, Fig. 1a. After ten minutes of continuous X-ray bombardment, two new lines of relatively low intensities appeared at 72.8 and 76.1 eV and they became prominent at 45 minutes of continuous bombardment as shown in Fig. 1b.

This process was accompanied by a relative decrease in the intensity of the original lines (Fig. 1c). The X-ray photoelectron spectrum of the same sample seems to be unchanged when it was left under vacuum for almost twenty four hours and the same trend of relative intensity changes continued after two hours and forty minutes of X-ray bombardment (Fig. 1e). The original lines at 74.8 and 78.1 eV completely disappeared after three hours and forty minutes (Fig. 1f), meanwhile the new lines at 72.8 and 76.1 eV were not affected by further X-ray exposure. The bombardment of a fresh sample by argon ions for less than one minute produced the same effect as the X-ray for three hours and forty minutes. The spectral changes related to the chemical shift of the platinum lines were accompanied by approximately 50 per cent decrease of the Cl(2p) intensity relative to the N(1s) (Fig. 2a and b).

The analysis of the X-ray spectra in the energy range of 70–80 eV reveals that the energy separation between the original and the two new lines is 3.3 eV which is the magnitude of the Pt(4f) spin–orbit components. This also can be observed from the relative intensities of each two lines. The destabilization of the original lines by 2eV is indicative of the reduction of the platinum from the oxidation state (IV) to (II). The binding energies of the two lines are very close to those of Pt(4f) spin–orbit components at 72.6 and 75.9 eV in $(NH_4)_2Pt(II)Cl_4$, Table I.

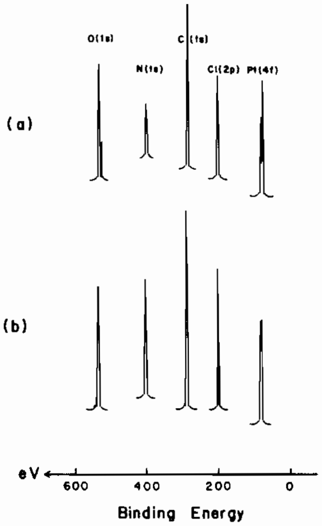

Fig. 2. X-ray photoelectron spectra of the $(PH)_2Pt(IV)Cl_6$. 2a) a fresh sample; 2b) after three hours and forty minutes of X-ray exposure.

As a result, it was possible to predict the molecular structure of the original compound as $(PH)_2$ Pt(IV) Cl_6 which was subsequently reduced to $(PH)_2Pt(II)$-Cl_4 under X-ray or argon ion bombardment. The relative intensity change of the Cl(2p) with respect to the N(1s) is due to the loss of two chlorine atoms in the reduction process. The same effect is observed in the case of $K_2Pt(IV)Cl_6$ when reduced to $K_2Pt(II)Cl_4$ under six hours of X-ray or one minute of argon ion bombardment.

As a result, this effect should be taken into consideration when the octahedral platinum complexes are studied by X-ray diffraction or photoelectron spectroscopy. It is interesting to study the mechanism by which the two chlorine atoms were removed from the original compound. This study will be conducted by changing the ligands in the platinum complex.

References

1 V. 1. Nefedov and Ya. V. Salyn, *Inorg. Chim. Acta, 28,* 135 (1978).

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