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X-Ray Photoelectron Spectroscopic Evidence for Inequivalent Platinum Species in Platinum Oxamate Blue

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The discovery [1] that *cis*-dichlorodiammineplatinum(II) is an effective anti-tumor complex has led to a large research effort aimed at discovering novel platinum drugs with a greater degree of efficacy and lower levels of toxicity. One of the results of this effort was the discovery [2, 3] of a new class of platinum complexes, the so-called platinum pyrimidine blues. These complexes are important because of their anti-tumor activity [2, 3], but are also intriguing chemically because of their intense blue colors. In addition to the reaction with pyrimidines to form blue compounds, platinum 'blues' can also be formed by the reaction of platinum compounds with amides (*e.g.* acetamide), α-pyridone [4], oxamic acid [5], and other compounds [6].

The product of the reaction between K_2PtCl_4 and oxamic acid, the so-called 'platinum oxamate blue', is thought [5] to consist of platinum-containing polyanions with a resultant Pt–Pt interaction along the polymeric or oligomeric chain. It has been suggested [6–9] that all platinum blues essentially consist of mixed-valent, amidate-bridged oligomers with metal–metal interactions. The present report describes the results of X-Ray Photoelectron Spectroscopic (XPS) studies of a sample of platinum oxamate blue. XPS has been used extensively to examine the electronic environment in a large number of platinum complexes [10], and was recently used [11] to study the electronic environment of the platinum atoms in a sample of α-pyridone blue, the only sample of a platinum blue compound to have been fully characterized by X-Ray diffraction [4].

Experimental

The sample of platinum oxamate blue was prepared as previously described [5]. X-Ray Photoelectron Spectroscopic measurements were made with a DuPont Model 650 Electron Spectrometer using Mg K_α radiation (1253.6 eV) as the X-ray source. Samples were diluted with graphite in an approximate 1:1 ratio by weight, then the mixture was made as homogeneous as possible by thorough mixing with a wig-l-bug®. Samples were deposited on the sample probe as an acetone dispersion and the solvent was allowed to evaporate. All spectra were run at a 1 eV per cm abscissa range, at a pressure of approximately 4×10^{-7} torr. The C $1s_{1/2}$ peak from graphite (B.E. = 283.8 eV [12]) was used as a binding energy standard. XPS spectra were deconvoluted according to a previously described procedure [13, 14]. Pt 4f peaks were scanned at the beginning and end of each run. The consistency of the peak shapes and positions suggested that there was no X-ray induced photodecomposition.

TABLE I. Core Electron Binding Energies of Platinum Compounds, eV.[a]

Compound	Pt $4f_{5/2}$	Pt $4f_{7/2}$
Pt oxamate blue	75.6 (2.3)[b]	72.3 (1.9)[b]
	75.7 (1.8)[c]	72.3 (1.7)[c]
	77.3 (2.2)[c]	74.1 (2.2)[c]
K_2PtCl_4	77.9 (1.8)	74.6 (1.7)
cis-$Pt(NH_3)_2Cl_2$	75.4 (1.9)	72.0 (1.8)

[a] Binding energies are reliable to ±0.1 eV; FWHM values are listed in parenthesis. [b] Values for raw data. [c] Obtained by deconvolution of raw data.

Cis-dichlorodiammineplatinum(II) and potassium tetrachloroplatinate(II) were obtained from Engelhard Industries, Inc., and were used without further purification.

Results and Discussion

Binding energies for the $4f_{5/2}$ and $4f_{7/2}$ levels of platinum were determined for the sample of platinum oxamate blue and for K_2PtCl_4 and *cis*-$Pt(NH_3)_2Cl_2$. The results of these measurements are tabulated in Table I. Although the precise structure of the Pt oxamate blue is far from clear, it is thought [5] that the structure consists of a polyanionic platinum-containing chain of square-planar platinum species with chloro and/or hydroxo bridges, stacked above one another perhaps with bridging oxamate ligands with a resultant interaction between platinum ions along the d_{z^2} direction. The ligands directly bound to the platinum would be oxygen (as OH^-), nitrogen as amide or amidate, and chloride. The Pt core-electron binding energies for the platinum oxamate blue are similar to those for *cis*-$Pt(NH_3)_2Cl_2$, indicating that the electronic environment around the platinum ion is similar for the two compounds. The Pt binding energies in the α-pyridone blue sample are also similar to those for *cis*-$Pt(NH_3)_2Cl_2$ [11]. Sometimes XPS is used to provide information about the

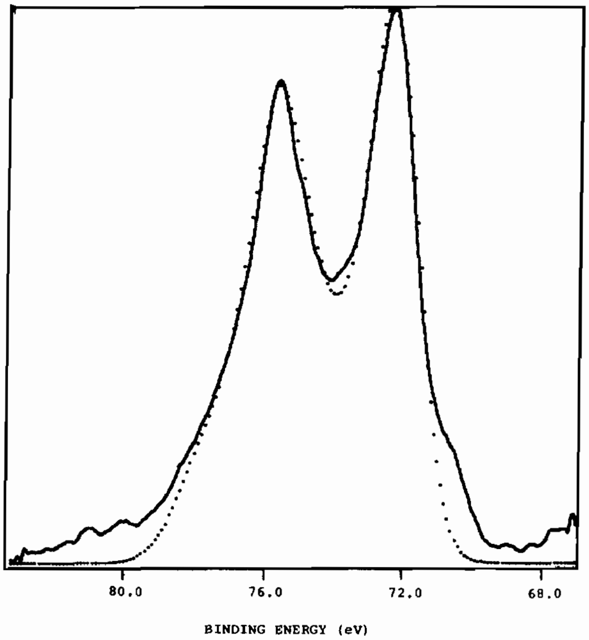

Fig. 1. (———), XPS spectrum of Pt-oxamate blue [19]; (······), calculated peak assuming the presence of two Pt 4f signals.

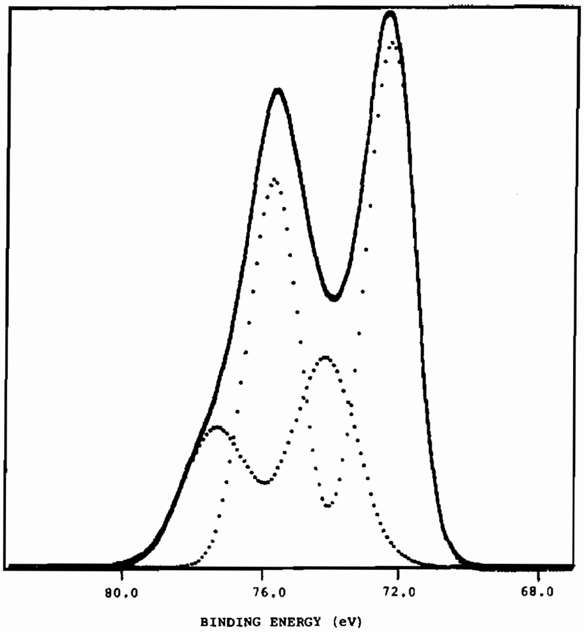

Fig. 2. (······), Deconvoluted peaks which make up the calculated spectrum.

oxidation number of a particular atom in a compound. The correlation between oxidation number and binding energy is only valid for a closely-related series of compounds where the ligands are quite similar [13] and the crystal lattices have similar Madelung potentials [15, 16]. The effect on binding energies when these parameters are changed can be seen in the Pt 4f binding energies for K_2PtCl_4 (Table I). Although the platinum ion has a formal oxidation number of +2 in both *cis*-$Pt(NH_3)_2Cl_2$ and K_2PtCl_4, the core-level binding energies for Pt are approx. 2.5 eV higher for the latter compound. In the absence of these changes, however, it has been shown [10, 17, 18] that Pt binding energies for Pt(IV) compounds are between 2 and 3 eV higher than the Pt(II) analogues.

The data in Table I indicate that the Pt 4f peaks for Pt oxamate blue are somewhat broader than the typical FWHM of 1.7–1.8 eV exhibited by K_2PtCl_4 and *cis*-$Pt(NH_3)_2Cl_2$. The XPS spectrum of the Pt oxamate blue sample is shown in Fig. 1 [19]. Not only are the peaks unusually broad, but the peak-to-valley intensity ratio of the $4f_{5/2}$ and $4f_{7/2}$ peaks is rather small compared to other typical platinum complexes. These results suggested that there was more than one type of electronic environment around the platinum ions in the sample. In order to determine the details of the XPS peaks, the experimental spectrum was deconvoluted. The calculated spectrum, based on the assumption that there were two 'types' of platinum ion, is indicated by the dotted line in Fig. 1. There is good agreement between the experimental and calculated peaks. Agreement at the baseline is poor, but this is usually the case [13] because of the presence of background photoelectrons. The individual sets of peaks which make up the calculated spectrum are shown in Fig. 2. The $4f_{5/2}$–$4f_{7/2}$ separation of approximately 3.3 eV agrees well with the separation in K_2PtCl_4 and *cis*-$Pt(NH_3)_2Cl_2$, as well as a large number of other platinum complexes [10].

The results of the deconvolution indicate that the platinum species giving rise to the more intense set of 4f peaks is electronically quite similar to the platinum ion in *cis*-$Pt(NH_3)_2Cl_2$ (Table I). This would be consistent with the supposition that the Pt oxamate blue sample consists of a Pt(II) ion with chloride and amidate ligands. An important point to note is that the electronic environment around the platinum ion in the blue sample is obviously different from that in the starting material for the synthesis, *i.e.* K_2PtCl_4.

It is evident from Fig. 2 that there is a minor, but significant, amount of a platinum species which is giving rise to a higher binding energy for the $4f_{5/2}$ and $4f_{7/2}$ peaks. In terms of intensities, the XPS (deconvoluted) results indicate that the Pt oxamate blue sample contains 25–30% of the higher binding energy species. The binding energy shift is –0.5 eV relative to K_2PtCl_4. This results shows that it is very unlikely that the platinum blue sample consists of 25–30% of unreacted K_2PtCl_4. Furthermore, visible spectral evidence [5] eliminates this possibility.

The binding energy shift for the less-intense set of peaks is +1.7 eV relative to the more intense doublet. If the ligands are the same as those for the platinum(II) ion giving rise to the signal at lower binding energy, then this result would suggest that there are mixed oxidation state platinum species present in the sample. A large number of platinum blue compounds are thought to consist [6–9] of mixed-valent platinum species. The EPR spectra of the blues, and the fact that broad-line NMR signals are obtained, have been explained [8, 9] on the basis of an interaction between, for example, a paramagnetic Pt(III) ion and a Pt(II) ion coupled along the oligomeric chain. It is interesting that one of the proposed formulations for a platinum pyrimidine blue compound is an oligomeric chain consisting of one Pt(III) ion for every three Pt(II) ions [9]. This formulation agrees with the relative intensities of the two types of 4f signals observed. On the other hand, however, the average oxidation state for Pt in the α-pyridone blue is also 2.25, but only one XPS signal for the platinum 4f levels was observed [11].

Although the results presented herein suggest that there are mixed-valence Pt species in the sample of platinum oxamate blue, the possibility that the compound consists of a mixture of several different platinum(II) species (with different ligands) cannot be ruled out. It is possible that a combination of 'ionic' ligands (Cl^-, OH^-) and bridging ligands could increase the binding energies of a Pt(II) ion by 1.7 eV.

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19 The experimental spectrum has been 'stripped' to normalize the baseline and eliminate a tail at high binding energy attributable to discrete energy loss.