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(16) This investigation was supported by Grant No. CA-12115 awarded by the National Cancer Institute, DHEW.

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Received August 10, 1979

Metal Core Binding Energy and Charge Delocalization in $[Os(NH_3)_4ClN_2Cl(NH_3)_4Os]Cl_3$, a Binuclear Mixed-Valence Osmium Complex: An ESCA Study

Sir:

Recently, there has been some disagreement[1-3] about the interpretation of core level photoelectron spectra[4] of transition metal mixed-valence class II and class III compounds.[5] Citrin[1] reported the presence of two sets of spectral lines from binuclear pyrazine-bridged ruthenium mixed-valence compounds and attributed his results to charge localization in the ground state of the mixed-valence complexes (class II). While it has generally been assumed that the observation of more than one set of lines with the expected intensity ratio and line shapes is proof of the presence of more than one oxidation state for a metal in a given substance, Hush has challenged the uniqueness of this interpretation. For ligand bridged binuclear mixed-valence compounds he has argued that final state relaxation would give rise to two sets of X-ray photoelectron lines with comparable intensities even if valence electron delocalization makes the two metal centers equivalent in the ground state (a class III compound). He thus concluded that the appearance of two metal binding energies was not in itself evidence for electronic ground-state asymmetry in a mixed-valence compounds.

Recently, some investigators[2] claimed to have observed two sets of Os 4f lines in the X-ray photoelectron spectrum of $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$, an Os(II)–Os(III) mixed-valence compound which is considered to be of the valence delocalized type. The two $4f_{7/2}$ lines, of approximately equal intensity, were reported to be separated by 1.2 eV. It was stated that the results support Hush's[3] treatment and provide evidence for the existence of two distinct localized ionized states of the compound.

We have repeated the measurement of the Os 4f spectrum of $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$. In contrast to the results just mentioned, we have seen only one set of Os 4f spin-orbit coupled peaks, with some relatively weak satellites (~13% of the main peak) on the high binding energy side of the spectrum (Table I). This, the first observation of only one set of lines in a well-characterized ligand bridged binuclear transition metal mixed-valence compound is clear confirmation of the fact that here one has a single delocalized initial state. For points of comparison we have also looked at the Os 4f spectra obtained from $[Os(NH_3)_5Cl]Cl_2$, an Os(III) compound, and $[Os(NH_3)_5N_2]Cl_2$, an Os(II) compound.

X-ray photoelectron spectra were obtained on a Varian IEE-15 spectrometer using the 1254-eV Mg ($K\alpha_{1,2}$) radiation. The pass energy of the spherical analyzer was set at 50.0 eV. Pressure in the spectrometer chamber was $\sim 10^{-6}$ Torr. For calibration the 4f lines emitted from a gold foil were employed.

Each sample was brushed onto one side of a double-backed adhesive tape that had been mounted on an aluminum cylinder. This was then attached to the probe and introduced into the spectrometer. The tape gave a flat photoelectron spectrum in the Os 4f region, and thus could not contribute in any way to the Os 4f spectra of the samples. No visible time dependent feature was observed in these spectra. No attempt was made to take account of sample charging. Os compounds were prepared according to literature methods[6,7] and gave satisfactory analysis.

All spectra were computer fitted to a set of combined Gaussian–Lorentzian spectral line functions plus a sloping linear background, using nonlinear least-squares techniques. The linear background was then subtracted both from the data and from the fitted curve before the net spectra (Figure 1) were plotted.

The Os $4f_{5/2,7/2}$ doublet obtained from $[Os(NH_3)_5Cl]Cl_2$ was fitted to two combined Gaussian–Lorentzian spectral functions, with the Gaussian fraction constrained to be equal for both peaks. When the Os 4f spectra obtained from $[Os(NH_3)_5N_2]Cl_2$ and $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$ were treated in the same manner, line widths and areas under the curves turned out to be considerably greater for the $4f_{5/2}$ lines than for the $4f_{7/2}$ lines. Under the assumption that this was the result of the presence of additional satellite peaks buried in the overall envelopes, each spectrum was fitted to four peaks under the following constraint: the separation between the spin-orbit $4f_{7/2}$ and $4f_{5/2}$ peaks was required to be the same as that between their satellites; the relative doublet intensity of the main peaks as well as that of the satellites was fixed at the theoretical value as observed in $[Os(NH_3)_5Cl]Cl_2$; the half-widths of all lines in a given spectrum were constrained to have the same value. The fitted parameters are given in Table I and the spectra are shown in Figure 1.

It is commonly recognized[4] that values of the experimental binding energies are not particularly useful for comparing electronic properties of different nonconducting solids. However, the presence of only one set of Os 4f main spectral lines for the mixed-valence Os compound with some weaker satellite structure is of great significance. An important point is that the resolved main Os 4f line width for the mixed-valence compound is not significantly different from that of the Os 4f of $[Os(NH_3)_5N_2]Cl_2$ or of $[Os(NH_3)_5Cl]Cl_2$. The sample, after having been kept in the refrigerator for 6 months, was rerun with a VG ADES 400 spectrometer at 200-eV pass energy. The Os 4f spectrum thus obtained looks the same as

Table I. XPS Parameter for Some Os Complexes

compd	Os $4f_{7/2}$, eV	S(7/2),[a] eV	*I*,[b] eV	Γ,[c] eV	λ,[d] eV
$\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$	52.62 ± 0.01	55.5 ± 0.1	0.13 ± 0.01	2.25 ± 0.02	2.75 ± 0.02
$[Os(NH_3)_5Cl]Cl_2$	50.75 ± 0.05			2.26 ± 0.15	2.75 ± 0.10
$[Os(NH_3)_5N_2]Cl_2$	49.93 ± 0.05	51.4 ± 0.1	0.34 ± 0.06	1.97 ± 0.10	2.76 ± 0.03

[a] Position of Os $4f_{7/2}$ satellite. [b] Relative intensity of Os $4f_{7/2}$ satellite to the main peak. [c] Full width at half maximum. [d] λ = separation between Os $4f_{7/2}$ and $4f_{5/2}$ main peaks.

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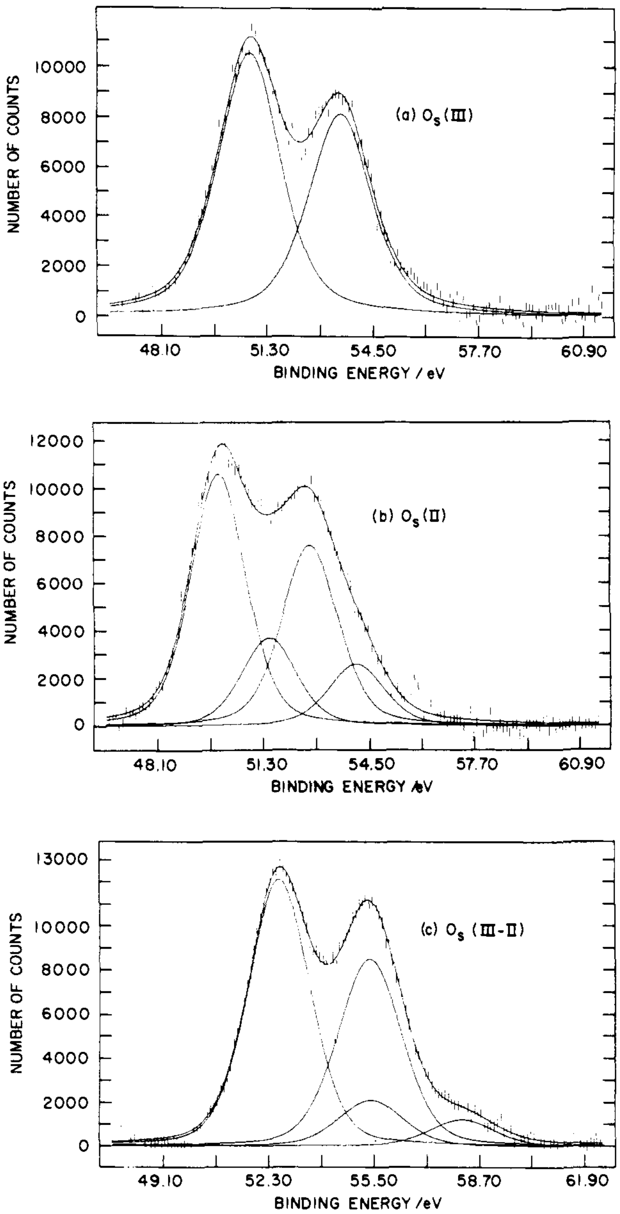

Figure 1. Os 4f spectrum of (a) $[Os(NH_3)_5Cl]Cl_2$, (b) $[Os(NH_3)_5N_2]Cl_2$, and (c) $[Os(NH_3)_4ClN_2Cl(NH_3)_4Os]Cl_3$.

Figure 1c except that the width is now reduced from ~2.3 to 1.8 eV owing to improvement in spectrometer resolution. This strongly suggests that the main peaks observed in the mixed-valence compound do not derive, as Hush proposed,[3] from two distinct final states which would show either two sets of spin orbit coupled peaks having comparable intensities or at least an envelope appearing as two broadened peaks. On the other hand, these results strongly support the view that $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$ is a true class III type of mixed-valence compound,[8] which could not be concluded on the basis of the results previously reported.[2] In that report it was stated also that a shoulder was observed at a binding energy 1.5 eV lower than that of the Os $4f_{7/2}$ peak for $[(NH_3)_4OsCl(pZ)]Cl_2$. Further there was said to be enhancement of the lower binding energy side of the Os $4f_{7/2}$ peak for $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$. These effects were attributed to surface reduction of Os(III) due to radiation damage. It is obvious from Figure 1 that such spectral features[2] are not observable in the mixed-valence compound in our experiment. It is difficult to assess the reasons for these discrepancies as the previous workers did not describe in detail the conditions under which their experiments were conducted, nor did they show figures of their results.

Our work does not contradict the work of Hush,[3] as it is apparent that there must be more than one final state possible for the $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$. However, it is apparent from the spectrum that the higher binding energy states are much less probable than the principal $4f_{7/2}$ final state. In addition, satellite structure was observed in the Os(II) compounds (Figure 1). It is conceivable that in some cases it may be possible for satellites to be probable enough, so that they are mistaken for peaks arising from the presence of more than one oxidation state in a compound.

The presence of satellites in the Os(II) compounds, $[Os(NH_3)_5N_2]Cl_2$ and the mixed-valence compounds, may be associated with the N_2 ligand. In general, satellites are not observed in second- and third-row transition metal core level spectra,[9] with the exception of CO complexes.[10] N_2 is isoelectronic with CO, and, in addition, the π back-bonding effect is very strong in Os(II) analogous to some metal carbonyls.[10] The ground- and excited-state levels arising from N_2 and Os(II) interaction may induce, during photoemission, monopole transitions which give rise to observable satellites.

Acknowledgments. We gratefully acknowledge Dr. J. D. Buhr and Dr. H. Taube for supplying us with the osmium compounds used in this study. We also thank Dr. M. L. Perlman and Dr. C. A. Creutz for their valuable comments. Acknowledgment is made by one of us (M.S.L.) to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Research was performed at BNL under contract with the U.S. Department of Energy and supported by its Division of Basic Energy Sciences.

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Received January 2, 1979

Synthesis of a 4a,5-Epoxy-5-deazaflavin Derivative

Sir:

Oxidized flavins undergo nucleophilic addition reactions with H_2O_2 to form flavin hydroperoxide derivatives which are also observed as intermediates during reaction of reduced flavin with O_2.[1] Compared with the corresponding flavin derivative, 5-deaza analogues I are more susceptible toward nucleophilic attack which typically occurs at position 5 to yield 1,5-dihydro adducts IIa.[2-4] In this communication we report the formation of a novel 4a,5-epoxy derivative (III) by reaction of 5-deazaisoalloxazine (I) with H_2O_2, *tert*-butyl hydroperoxide, or *m*-chloroperoxybenzoic acid. This epoxide is isoelectronic with the N-5 oxide formed by reaction of the isoalloxazine analogue

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