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ESCA Spectra of Some N-Bonded Osmium Complexes

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ESCA spectra provide a valuable investigation tool for the characterization of effective oxidation states of metals in coordination compounds, and are expected to be of particular importance in the elucidation of the electronic structure of polynuclear bridged complexes, especially of those containing two or more atoms of the same metal in different formal oxidation states [1, 2], although Hush has recently shown [3, 4] that mixed-valence complexes, *e.g.* containing M(II) and M(III), should exhibit ESCA peaks close to the superposition of the peaks of the corresponding single-valence M(II) and M(III) complexes, both in the case of localized different valences, and of delocalized ground-state, the difference between the two cases consisting of smaller second-order shifts which would scarcely be detected at the present stage of instrumental resolution of most common ESCA spectrometers.

We have measured the ESCA spectra of osmium in some nitrogen-bonded complexes investigated by Taube and coworkers [5, 6], including the bridged complex $[Cl(NH_3)_4Os(N_2)Os(NH_3)_4Cl]Cl_3$, an example of mixed-valence Os(II)–Os(III) species which, according to Taube [7] is valence-delocalised in the ground state; we attempted also measurements on some related Ru species, but experimental difficulties proved here more severe, and the results are less conclusive.

The measured binding energies of Ru $3d_{5/2,3/2}$ and Os $4f_{7/2,5/2}$ (solid samples measured in a Vacuum Generator ESCA–3 spectrometer with $AlK_{\alpha_{1,2}}$ radiation; calibration against the Au $4f_{7/2}$ peak at 84.0 eV) are reported in the Table. The mononuclear osmium reference compounds $[Os^{II}(NH_3)_4(N_2)_2]Cl_2$ and $[Os^{III}(NH_3)_4Cl(pz)Cl_2$ (pz = pyrazine) have nearly equal $4f_{7/2}$ b.e. at 52.6–52.7 eV$_1$ hence do not show the usual b.e. variation with the formal oxidation state (which is small but not negligible for Os compounds [8], *e.g.* 50.7 eV for *trans*-$[OsCl_2(PMe_2Ph)_4]$ [9], and 51.8 eV for *mer*-$[OsCl_3(PMe_2Ph)_3]$ and represent instead a striking example of the influence of π-acceptor ligands, such as dinitrogen, which effectively lower the charge density of the central atom. Taube [7] points out that π-backbonding effects are particularly strong with Os(II), and stronger than with Ru(II), so *e.g.* pK values for pzH^+, $[A_5RupzH]^{3+}$ and $[A_5OspzH]^{3+}$ are 0.6, 2.5 and ~ 7.0 respectively. In addition, $[Os^{III}A_4Cl(pz)]Cl_2$ shows smaller shoulders at 51.2 eV, probably due to Os(II) formed by surface reduction by radiation damage, as often observed in ESCA.

TABLE I. ESCA b.e.'s of Ru ($3d_{5/2}$) and Osmium ($4f_{7/2}$) in Some Complexes.

Compound	b.e. (eV)	Notes
$[(NH_3)_4Os(N_2)_2]Cl_2$	52.7	$4f_{5/2}$ at 55.3
$[(NH_3)_4OsCl(pz)]Cl_2$	52.6	small 7/2 shoulder at 51.2 $4f_{5/2}$ at 55.4
$[Cl(NH_3)_4Os(N_2)Os(NH_3)_4Cl]Cl_3$	51.6 52.8	$4f_{5/2}$ at 54.1 and 54.9
$[(NH_3)_5(CH_3CN)Ru]Br_2$	281.0	
$[(NH_3)_5(CH_3CN)Ru]Br_3$	283.1	smaller peak (Ru(II)?) at 280.6

The binuclear compound $[Cl(NH_3)_4Os^{II}(N_2)Os^{III}(NH_3)_4Cl]Cl_3$ is a mixed valence (II, III) species, whose ground state has been clearly characterized as valence-delocalised [7]. The experimental ESCA spectrum has two 4f doublets separated by about 1 eV, clearly attributable to Os(III) (52.8–54.9 eV) and Os(II) (51.6–54.1 eV). The two doublets have essentially equal intensities, apart from the effect of radiation damage which tends to increase the Os(II) signal. The appearance of separate signals close to those of the single (II) and (III) valences in a case of valence-delocalised ground state, where previous models [2] predicted a single, averaged b.e. value, lends support to the recent treatment by Hush [3] and gives evidence for lack of delocalization in the ionized state. The (II)–(III) separation is expected, according to Hush's model [3], to be only slightly larger in the ground state-delocalized systems, and no conclusion can be drawn to this regard in the present case because of both the smallness of the predicted effect (~ 0.1 eV) [3], which compared unfavorably with the instrumental accuracy of ESCA measurements, and of the uncertainty on the exact value of the (II)–(III) difference for osmium species [8, 9].

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We attempted an analogous investigation on Ru complexes, however with less conclusive results. The mononuclear reference compounds $[(NH_3)_5(CH_3CN)Ru]Br_n$ (n = 2, 3) are clearly much better examples of b.e. variation with oxidation state, having the same coordination environment around Ru, and Ru $3d_{5/2}$ shows in fact a (II–III) difference of about 2.1 eV, a value in good agreement with literature reports for similar cases [2, 9], which should reflect only intrinsic effects of electronic structure of ruthenium, apart from lattice Madelung effects. The ruthenium $3d_{5/2}$ peaks fall close to the large C 1s peak, but can anyway be detected clearly [2], We attempted also measurements on binuclear samples of $[(NH_3)_5Ru(NCCN)Ru(NH_3)_5]^{n+}$ (n = 4, 5, 6), but they underwent rapid decomposition under irradiation, showing at most broad and unresolved signals [10]. Of the substances reported here, binuclear compounds of Os proved therefore more stable and amenable to ESCA investigation than those of ruthenium.

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