Inorganica Chimica Acta, 146 (1988) 119–121

The Solid State Chemistry of Uranium.
Part V. X-ray Photoelectron Studies of some Nitrato Complexes of Uranium(IV) and Dioxouranium(VI)

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(Received December 15, 1987)

Studies of the electronic structure of uranium compounds are normally concerned with a detailed description of the valence electrons of the uranium. Thibaut and co-workers investigated a number of uranium halides and oxyhalides and used the results to make an assessment of the ionicity in the solid state [1]. An increasingly larger shift towards lower binding energy of the core level as well as the valence electron peaks were observed for the more covalent compounds.

Except for a single reference to the U($4f_{7/2}$) peak of 'uranyl nitrate' [2], experimental data on the electronic structure of uranium(IV) and dioxouranium(VI) nitrato complexes are non-existent. This motivated a study of the electronic structure of some uranium(IV) and dioxouranium(VI) nitrato complexes. The compounds investigated were $U(NO_3)_4L_2$ and $UO_2(NO_3)_2L_2$ (where L = tppo (triphenylphosphine oxide), tdpo (tris-(dimethylamino)-phosphine oxide) and tpyrp (tris-(*N*,*N*-tetramethylene)phosphoric acid triamide)).

Experimental

The uranium(IV) compounds $U(NO_3)_4L_2$ were prepared as described previously [3].

The uranyl compounds were prepared by mixing methylene chloride solutions of the appropriate ligand (2 mmol) with an acetone solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1 mmol). Yellow crystals were obtained upon standing at room temperature.

X-ray photoelectron spectra were obtained with the samples cooled to liquid nitrogen temperatures on a VG ESCALAB MK II instrument, using Al Kα (hν = 1486.6 eV) radiation. In order to prevent decomposition of the nitrates, an X-ray beam of only 25 W was used. In addition to this, a 25-mm distance between sample and source was maintained during measurements. This resulted in a reduced count rate, but no significant decomposition of the compounds was observed. An average of 30 scans per sample were used for data collection.

Results and Discussions

Table I (with some spectra illustrated in Figs. 1 and 2) summarises the core and valence binding energies of the compounds studied.

Valence Band Energy Region: 0 to 40 eV

Thibaut *et al.* [1] reported an ionization energy of 2.8 eV for the U(5f) level in UF_4, while Dyke *et al.* [4] obtained a value of 3.2 eV for the same level. Ionization from the U–F(2p) level was observed at 7.0 eV by Thibaut and at 8.5 eV by Dyke. A broad peak with maximum at approximately 9 to 10 eV was observed for all the $U(NO_3)_4L_2$ complexes. This peak seems to be due to ionization from an energy level having mainly U–O(2p) character. Each of the peaks showed a shoulder at approximately 6 eV. The peaks which were observed for the

TABLE I. Experimental Binding Energies (eV)

Compound	U($4f_{7/2}$)	U($4f_{5/2}$)	U–O(2p)	U($6p_{3/2}$)	U($6p_{1/2}$)	P(2p)	C(1s)
tppo						134.4	286.9
tdpo						134.5	291.7
$U(NO_3)_4(tppo)_2$	384.8	396.1	9.6; 5.7(sh)[a]	(17.7)[b]	30.1	136.5	288.2
$U(NO_3)_4(tpyrp)_2$	384.7	396.5	9.9; 6.4(sh)	17.4	28.4	137.3	288.5
$U(NO_3)_4(tdpo)_2$	385.9	397.8	10.3; 6.2(sh)	(19.0)	28.8	138.8	290.7
$UO_2(NO_3)_2(tppo)_2$	385.9	397.5	9.3; –	(20.5)	30.2	136.2	288.3
$UO_2(NO_3)_2(tpyrp)_2$	387.9	399.4	10.4; 6.6(sh)	20.1	29.9	138.1	290.4
$UO_2(NO_3)_2(tdpo)_2$	387.8	399.5	11.7; –	(20.3)	30.2	138.8	291.1

[a] sh = shoulder to main peak. [b] Parentheses denote less-certain data.

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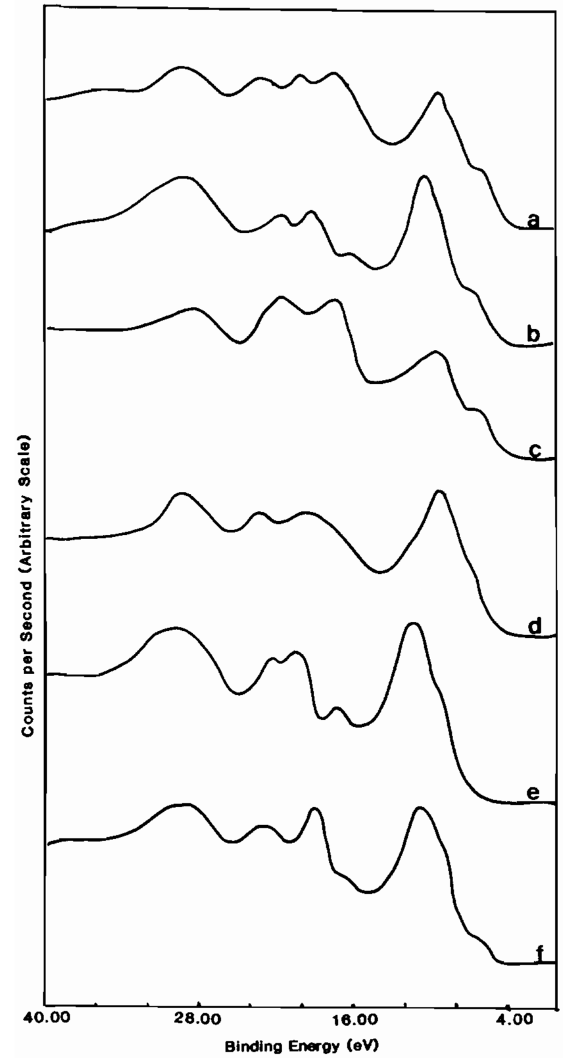

Fig. 1. Valence band spectra: (a) $U(NO_3)_4(tppo)_2$; (b) $U(NO_3)_4(tdpo)_2$; (c) $U(NO_3)_4(tpyrp)_2$; (d) $UO_2(NO_3)_2(tppo)_2$; (e) $UO_2(NO_3)_2(tdpo)_2$; (f) $UO_2(NO_3)_2(tpyrp)_2$.

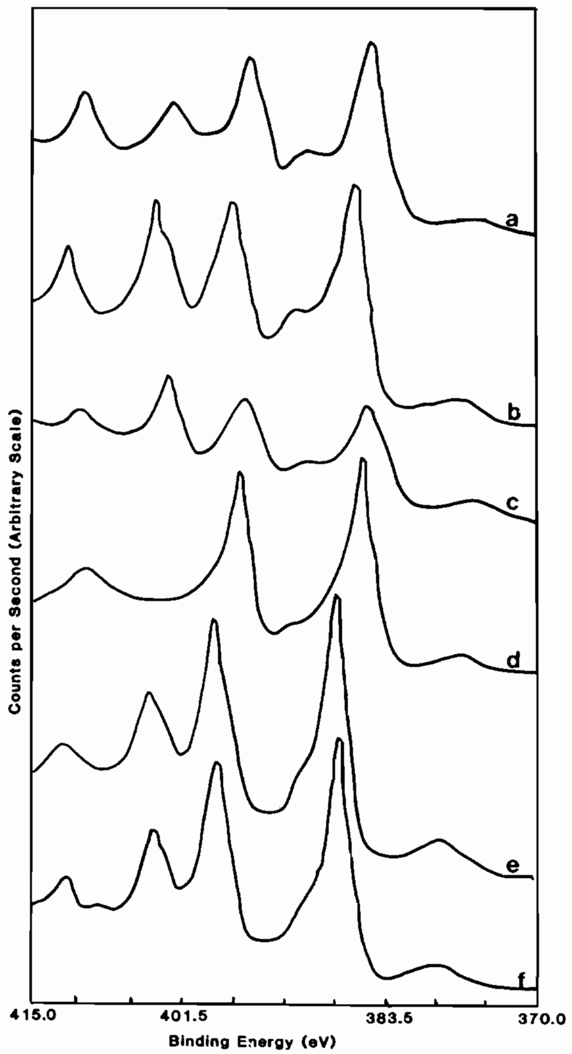

Fig. 2. Core level spectra: (a) $U(NO_3)_4(tppo)_2$; (b) $U(NO_3)_4(tdpo)_2$; (c) $U(NO_3)_4(tpyrp)_2$; (d) $UO_2(NO_3)_2(tppo)_2$; (e) $UO_2(NO_3)_2(tdpo)_2$; (f) $UO_2(NO_3)_2(tpyrp)_2$.

$UO_2(NO_3)_2L_2$ complexes differ from that of the uranium(IV) in so far as they occur at a slightly higher binding energy and, with the exception of the tpyrp complex, no shoulders to the main peak were observed. The shoulders which were observed could perhaps be interpreted as being due to ionization from the U(5f) level. The high binding energy, 5 to 6 eV (*cf.* 2.8 eV for UF_4), as well as the fact that the U(5f) level in the uranyl complex should not be occupied, seems to overrule this possibility.

The broad peak centred at approximately 18 and 20 eV in the uranium(IV) and uranyl complexes, respectively, consists of at least three peaks: the $U(6p_{3/2})$ and peaks due to ionization from the O(2s) level. Ionization from the $U(6p_{1/2})$ level in the various uranium(IV) complexes was observed at lower binding energies than in the corresponding uranyl complexes.

A detailed interpretation of the spectra should take into account the local symmetry of the uranium ion. The fact that more peaks were observed than could be accounted for originates perhaps from different symmetry combinations of the ligand valence orbitals in the symmetry, centred on the uranium ion.

Core Level Energy Region: 370 to 417 eV

The $U(4f_{7/2})$ and $U(4f_{5/2})$ peaks were observed at higher binding energies in the uranyl than in the uranium(IV) compounds, suggesting a more ionic nature in the uranyl complexes. It is, however, noticeable that they occur at binding energies significantly higher than in UF_4 ($4f_{5/2}$ at 392.8 eV and $4f_{7/2}$ at 382.0 eV) or UO_2F_2 ($4f_{5/2}$ at 393.7 eV and $4f_{7/2}$ at 382.8 eV). It seems, therefore, that the nitrate complexes are more ionic than the uranium halides and oxyhalides. Satellite structures were observed for the $U(4f_{7/2})$ peaks in all the complexes studied. The $U(4f_{5/2})$ satellite structures were, however, concealed by the nearby N(1s) peak.

Peaks due to ionization from orbitals having mainly P(2p) character were observed at 134.4 eV for tppo and at 134.5 eV for tdpo. These peaks were observed at significantly higher binding energies for the complexes (Table I), which is a direct result of coordination of the neutral ligand to the uranium ion.

Acknowledgements

The authors thank the University of Pretoria and the Council for Scientific and Industrial Research (FRD) for financial support.

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