

X-Ray Photoelectron Spectra of Uranium(VI) Complexes of 8-Hydroxyquinoline

By D. B. ADAMS and D. T. CLARK*

(Department of Chemistry, University of Durham, South Road, Durham)

and A. D. BAKER and M. THOMPSON*†

(Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP)

Summary Molecular core binding energies have been measured for $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$, $\text{C}_9\text{H}_7\text{NO}$, $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$, and $\text{C}_9\text{H}_8\text{NO}^+\text{Cl}^-$; the results show the potential of X-ray photoelectron spectroscopy for the study of the binding of extra molecules of ligands in compounds of a similar composition to the 1:3 uranium(VI) complex and of other metal chelates in general.

THERE has been considerable interest in the nature of the binding of the "additional" 8-hydroxyquinoline molecule in $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$.¹ An X-ray structure determination² showed that the extra molecule is co-ordinated through its oxygen atom as a monodentate zwitterion, and that the zwitterionic proton is involved in a hydrogen bond between the unco-ordinated nitrogen atom of the extra

ligand molecule and the oxygen atom of the neighbouring bidentate ligand. The i.r. spectrum of the 1:3 complex confirmed this suggestion and located the zwitterionic proton on the nitrogen atom of the monodentate ligand.³

Since the structure of the 1:3 complex is now well established, it serves as a model for X-ray photoelectron spectroscopic studies of similar compounds such as $\text{Y}(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$,⁴ $\text{SbO}(\text{C}_9\text{H}_6\text{NO}) \cdot 2\text{C}_9\text{H}_7\text{NO}$,⁵ and $\text{Na}(\text{C}_9\text{H}_6\text{NO}) \cdot \text{C}_9\text{H}_7\text{NO}$ ⁶ where the binding of additional 8-hydroxyquinoline has not been examined. Therefore, we now report the molecular core binding energies of $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$, $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$ (prepared thermally from the 1:3 complex⁷), 8-hydroxyquinoline, and its hydrochloride salt. The samples were studied as thin films on a conducting backing, using Mg- K_α radiation. Binding energies are given in the Table.

TABLE

		Binding energies (eV) ^a				
		C(1s) ^b	N(1s)	U(4f _{7/2})	Cl(2p _{3/2})	O(1s)
$\text{C}_9\text{H}_7\text{NO}$	285.7	400.3			534.6
$\text{C}_9\text{H}_8\text{NO}^+\text{Cl}^-$	285.7	402.1		197.7	534.7
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$	285.7	400.6	383.2		533.2 ^b
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$	285.7	402.1 (1) 400.5 (2)	383.1		533.1 ^b

^a All levels were calibrated with respect to Au(4f_{7/2}) - 84 eV binding energy. ^b Centroid of relatively broad peak of half-width *ca.* 1.8 and 2.3 eV for C(1s) and O(1s), respectively.

† Present address: Department of Chemistry, University of Technology, Loughborough, Leicestershire LE11 3TU.

The N(1s) spectrum of the 1:3 complex exhibits two peaks centred at 402.1 and 400.5 eV of intensity ratio 1:2, respectively. The peak at higher energy corresponds to the binding energy of the N(1s) level in $C_9H_8NO^+Cl^-$ (402.1 eV). That these two values are identical is probably fortuitous since the chelate has an $\overset{+}{N}-H \cdots O$ hydrogen bond whereas with the salt an $\overset{+}{N}-H \cdots Cl$ system is involved. Indeed, Jack and Hercules⁸ found a slight variation of N(1s) binding energies with counterion and Madelung constant in a series of tetra-alkylammonium salts. However, our results do confirm the i.r. studies which located the zwitterionic proton on the nitrogen atom of the monodentate ligand. The N(1s) binding energy of the two indistinguishable nitrogen atoms (400.5 eV) of the bidentate ligands in the 1:3 complex is close to that for the 1:2 complex (400.6 eV) and for free 8-hydroxyquinoline (400.3 eV). The slightly lower value for the latter reflects transfer of

some electron density from ligand nitrogen atoms to metal in the complexes.

As expected the O(1s) binding energies of the complexes are significantly lower than in the free or protonated ligand. This result suggests higher electron density (*i.e.* greater anionic character) on the oxygen atoms of the former than the latter. Charge migration to and from the quinoline ring system has little effect on any individual carbon atom, since it is spread over so many centres and the C(1s) levels therefore consist of a broad peak centred at 284.7 eV. The U($4f_{7/2}$) levels of the chelates are almost identical as their co-ordination spheres are similar. (It has been suggested that co-ordinative unsaturation of uranium in the 1:2 complex is at least partially satisfied by polymerization through bridging oxygen atoms.⁹)

Thanks are due to S.R.C. for the provision of equipment.

(Received, September 29th, 1971; Com. 1701.)

¹ T. Moeller and M. V. Ramaniah, *J. Amer. Chem. Soc.*, 1954, **76**, 5251; J. H. Van Tassel and W. W. Wendlandt, *ibid.*, 1959, **81**, 813; E. P. Bullwinkel and P. Noble, *ibid.*, 1958, **80**, 2955; J. E. Tackett and D. T. Sawyer, *Inorg. Chem.*, 1964, **3**, 692.

² D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, 1967, **22**, 258.

³ A. Corsini, J. Abraham, and M. Thompson, *Chem. Comm.*, 1967, 1101; *Talanta*, 1971, **18**, 481.

⁴ T. J. Cardwell and R. J. Magee, *Analyt. Chim. Acta*, 1968, **43**, 321.

⁵ T. J. Cardwell, F. G. Nasouri, H. H. McConnell, and R. J. Magee, *Austral. J. Chem.*, 1968, **21**, 359.

⁶ A. K. Banerjee, A. J. Layton, R. S. Nyholm, and M. R. Truter, *J. Chem. Soc. (A)*, 1969, 2536.

⁷ A. Corsini and J. Abraham, *Talanta*, 1968, **15**, 562.

⁸ J. J. Jack and D. M. Hercules, *Analyt. Chem.*, 1971, **43**, 729.

⁹ A. Corsini and J. Abraham, *Canad. J. Chem.*, 1970, **48**, 2360.