

## Di-iodotetrakis(triphenylarsine oxide)uranium(IV) Hexaiodouranate(IV). A New Type of Actinoid Co-ordination Compound

Jan G. H. du Preez\* and B. Zeelie

Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, Republic of South Africa

A new type of co-ordination compound having  $UX_4L_2$  stoichiometry consisting of both cationic and anionic six co-ordinated metal species has been isolated (M = uranium, X = iodide, and L = neutral donor ligand).

*trans* Octahedral species of the type  $UX_4L_2$  where X =  $Cl^-$ ,  $Br^-$  and L = a bulky oxygen donor ligand are commonly found,<sup>1-3</sup> although a small number of *cis* species like  $UCl_4(tppo)_2$ <sup>4</sup> (tppo = triphenylphosphine oxide) are also known. Very insoluble *trans* octahedral  $UX_4L_2$  species are formed upon treating the tetra-chloride or -bromide with two

equivalents of triphenylarsine oxide (tpao) in acetone or acetonitrile solution. No such solid could be isolated when  $UI_4$  and tpao were allowed to react in these solvents. If, however, solid  $UI_4(MeCN)_4$  (0.8 g) is suspended in dry  $CH_2Cl_2$  and a 0.4 M solution, containing two equivalents of tpao in the same solvent, is added, a red solution is obtained. A red solid is

precipitated from this solution upon addition of either light petroleum or ethyl acetate. Microanalysis of the dried solid complex proved it to have  $\text{UI}_4(\text{tpao})_2$  stoichiometry. The red colour is uncommon for  $\text{UI}_4\text{L}_2$  species where L = neutral oxygen donor ligands since all the other complexes of this type recently isolated by us are yellow-green solids, e.g. L =  $\text{tpo}$ ,<sup>5</sup>  $\text{tmu}$ ,<sup>5,6</sup> and a variety of other C=O amide and phosphine oxide ligands.<sup>7</sup> ( $\text{tmu} = N,N,N',N'$ -tetramethylurea.) The structure of  $\text{UI}_4(\text{tmu})_2$  was recently proved to be *trans* octahedral.<sup>6</sup>

The solid reflectance electronic spectrum of  $\text{UI}_4(\text{tpao})_2$  indicated it to be di-iodotetrakis(triphenylarsine oxide)-uranium(IV) hexaiodouranate(IV) since both the peaks corresponding to  $\text{UI}_2(\text{tpao})_4^{2+}$ , as it appears in  $\text{UI}_4(\text{tpao})_4$ ,<sup>7</sup> and  $\text{UI}_6^{2-}$ , as seen in the tetraphenyl phosphonium salt, are present. This electronic spectrum is also significantly different from that of *trans* octahedral  $\text{UI}_4(\text{tmu})_2$ <sup>6</sup> and other similar complexes mentioned above. Its red colour is also typical of  $\text{UI}_6^{2-}$  salts.<sup>8</sup> The i.r. spectra of  $\text{UI}_4(\text{tpao})_2$  and  $\text{UI}_4(\text{tpao})_4$  are virtually identical and no indication of a uranyl peak at ca. 900  $\text{cm}^{-1}$  is present.

This autoionising behaviour is very surprising since it is normally expected only when the donor strength of the anion and the neutral ligand are similar.<sup>9</sup> In this case the arsine oxide ligand is a very much stronger donor ligand than iodide for uranium(IV). The strong ion pairing and good matching of the two bulky counter ions must play a very important role in stabilising this complex.

This work thus indicated that arsine oxide ligands cannot readily be used to stabilise tetravalent actinoid iodides of the

heavier metals, in the same way as the tetra-chlorides and -bromides are used, because of the possibility of  $\text{MI}_6^{2-}$  formation through solid state autoionisation. These will be much more unstable than their *trans* octahedral  $\text{MI}_4\text{L}_2$  analogues, where tetragonal distortion can occur with M-I bond lengthening.

We thank the Council for Scientific and Industrial Research and the University of Port Elizabeth for financial assistance.

Received, 13th November 1986; Com. 1626

## References

- 1 K. W. Bagnall, *Coord. Chem. Rev.*, 1967, 2, 145; 'Halogen Chemistry' ed. V. Gutmann, vol. 3, p. 303 Academic Press, London, 1969.
- 2 D. Brown, J. Hill, and C. E. F. Rickard, *J. Chem. Soc. A*, 1970, 497.
- 3 J. G. H. du Preez, B. J. Gellatly, G. Jackson, L. R. Nassimbeni, and A. L. Rodgers, *Inorg. Chim. Acta*, 1978, 27, 181.
- 4 G. Bombieri, D. Brown, and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1975, 1873.
- 5 J. G. H. du Preez, and B. Zeelie, *J. Chem. Soc., Chem. Commun.*, 1986, 743.
- 6 U. Casellato, J. G. H. du Preez, R. Graziani, and B. Zeelie, *Inorg. Chim. Acta*, 1987, 129.
- 7 B. Zeelie, M.Sc. dissertation, University of Port Elizabeth, 1986.
- 8 K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, 1965, 350.
- 9 V. Gutmann, 'Coordination Chemistry in Non-aqueous Solutions,' Springer-Verlag, Vienna, New York, 1968.