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

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A new type of co-ordination compound having UX_4L_2 stoicheiometry 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,[1—3] although a small number of *cis* species like $UCl_4(tppo)_2$[4] (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 $UI_4(tpao)_2$ stoicheiometry. The red colour is uncommon for UI_4L_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 = tppo,[5] tmu,[5,6] and a variety of other C=O amide and phosphine oxide ligands.[7] (tmu = *N,N,N′,N′*-tetramethylurea.) The structure of $UI_4(tmu)_2$ was recently proved to be *trans* octahedral.[6]

The solid reflectance electronic spectrum of $UI_4(tpao)_2$ indicated it to be di-iodotetrakis(triphenylarsine oxide)-uranium(IV) hexaiodouranate(IV) since both the peaks corresponding to $UI_2(tpao)_4{}^{2+}$, as its appears in $UI_4(tpao)_4$,[7] and $UI_6{}^{2-}$, as seen in the tetraphenyl phosphonium salt, are present. This electronic spectrum is also significantly different from that of *trans* octahedral $UI_4(tmu)_2$[6] and other similar complexes mentioned above. Its red colour is also typical of $UI_6{}^{2-}$ salts.[8] The i.r. spectra of $UI_4(tpao)_2$ and $UI_4(tpao)_4$ are virtually identical and no indication of a uranyl peak at *ca.* 900 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.[9] 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 $MI_6{}^{2-}$ formation through solid state autoionisation. These will be much more unstable than their *trans* octahedral MI_4L_2 analogues, where tetragonal distortion can occur with M–I bond lengthening.

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