New Uranium Tetraiodide Complexes

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A new type of uranium tetraiodide complex, *viz.* UI_4L_2 (where L = a bulky amide or phosphine oxide ligand) and new suitable starting materials for the preparation of uranium(IV) iodo-complexes have been prepared.

The method[1] generally used for the preparation of UI_4[2,3] is laborious and tedious. Efforts to prepare a starting material for the preparation of iodo-complexes of uranium(IV) from the reaction of uranium metal with an iodine solution have thus far been unsuccessful.[4] A thermally stable UI_4 starting material which can readily be prepared in high yield in the pure solid form and which contains weakly co-ordinated donor molecules is therefore required.

We now report the preparation of $UI_4(dpk)_2$ and $UI_4(mecn)_4$, where dpk = diphenyl ketone and mecn = methyl cyanide. $UI_4(dpk)_2$ could be prepared by the room temperature reaction of uranium metal turnings (3 g) with iodine (6.39 g, 4 equiv.) and dpk (4.59 g, 2 equiv.) in dry, oxygen free, CH_2Cl_2 solution (150 cm^3) in a closed Schlenk vessel filled with high purity nitrogen while stirring for six hours. The resulting dark brown solution was filtered, vacuum concentrated to 30 cm^3 and cooled to −18 °C. The black, hygroscopic solid product was subsequently filtered, quickly dried *in vacuo*, and analysed (yield 60%). The complex is very soluble in CH_2Cl_2, methyl cyanide, acetone, and tetrahydrofuran. Crystals of pure hygroscopic orange-red $UI_4(mecn)_4$ in >60% yield could readily be prepared from $UI_4(dpk)_2$ by dissolving the latter in the minimum volume of dry oxygen-free methyl cyanide and cooling the red solution to −18 °C.

Both $UI_4(dpk)_2$ and $UI_4(mecn)_4$ could readily be used to prepare other iodo-complexes according to equation (1). The

$$UI_4(dpk)_2 \text{ or } UI_4(mecn)_4 \xrightarrow[\text{MeCN}]{\text{2L in}} UI_4L_2\,(s) \qquad (1)$$

stable yellow–green six co-ordinate complexes for L = tmu and tppo (tmu = *N,N,N′,N′*-tetramethylurea and tppo = triphenylphosphine oxide) have larger C=O (116 cm^{-1}) and P=O (173 cm^{-1}) shifts in stretching frequencies than those of their bromo analogues, *i.e.* 113 and 150 cm^{-1}, respectively.

Neither $UI_4(dpk)_2$ nor $UI_4(mecn)_4$ could be desolvated *in vacuo* without loss of iodine.

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