

New Uranium Tetraiodide Complexes

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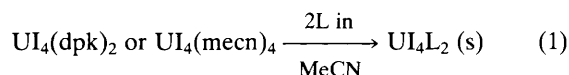
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A new type of uranium tetraiodide complex, viz. UI_4L_2 (where L = a bulky amide or phosphine oxide ligand) and new suitable starting materials for the preparation of uranium(IV) iodo-complexes have been prepared.

The method¹ 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 cm³) 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 cm³ 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



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.

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

Received, 26th November 1985; Com. 1671

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