

## Preparation of the 1 : 2 Uranyl Nitrate–Methyl Diphenyl Phosphate Solid Complex

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**Summary** The anhydrous solid complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{mdpp})$  (mdpp = methyl diphenyl phosphate) (m.p.  $92^\circ$ ) is soluble in  $\text{CHCl}_3$ , dioxan, MeOH,  $\text{C}_6\text{H}_6$ , and  $\text{Bu}^1\text{COMe}$ , but almost insoluble in  $\text{H}_2\text{O}$ , dilute mineral acids,  $\text{Pr}_2\text{O}$ , and hydrocarbons.

ORGANIC phosphates, especially tributyl phosphate (tbp) are frequently used as extractants for separation of uranium from other elements. Usually complexes formed in the organic phase are not isolated as solids; therefore their composition and properties have to be determined by indirect methods. In the present work a solid complex was prepared by equilibrating methyl diphenyl phosphate (mdpp) with a saturated solution of uranyl nitrate. After separation yellow crystals (m.p.  $92 \pm 0.5^\circ$ ) appeared gradually in the mdpp phase. The crystals were washed with  $\text{Pr}_2\text{O}$  and dried. The ether is miscible with (mdpp) but dissolves the uranyl complex only slightly. The solid obtained was soluble in  $\text{CCl}_4$ , dioxan, MeOH,  $\text{C}_6\text{H}_6$ ,  $\text{Bu}^1\text{COMe}$ , and to some extent in  $\text{CCl}_4$  but almost insoluble in  $\text{H}_2\text{O}$ , dilute mineral acids, dodecane, and cyclohexane. The uranyl complex was analysed for uranium(VI), nitrate, phosphorus, and water. The complex was dissolved in  $\text{CHCl}_3$  and uranyl nitrate was extracted into water. The aqueous phase was analysed for uranium and nitrate.

Uranium(VI) was determined spectrophotometrically by the modified thiocyanate method.<sup>1</sup> Nitrate was determined gravimetrically with nitron.<sup>2</sup> Phosphorus was determined directly as phosphovanadomolybdate complex<sup>3</sup> after wet combustion of the solid with a mixture of nitric and perchloric acids. The molecular weight was determined by vapour pressure osmometry using  $\text{CCl}_4$  as solvent and (tbp) as standard.<sup>4</sup> The measured molecular weight,  $915 \pm 20$ , and the results of chemical analysis are consistent with formation of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{mdpp})$  (formula weight 922.5). In all the preparations, the solid was anhydrous (with one exception where 2.8% of water was found). Probably in this last case some water was not removed from the crystals. Water was determined with Karl Fisher reagent after dissolution of the solid in methanol. It is possible that hydrated complexes can also be prepared.

The solid complex has the same composition as the  $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{tbp})$  complex, which plays such an important role in the production of nuclear fuel. Therefore, the crystal structure and other properties of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{mdpp})$  are of considerable interest.

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