Another interesting fact emerges from the spectrophotometric study of Cu(II)-chromotrope 2B, viz. the possible colorimetric estimation of Cu(II) with the help of this reagent. Preliminary results have revealed that estimation of copper is possible in the concentration range $2 \times 10^{-4}$–$1 \times 10^{-6}$ M and over a wide pH range 7·0–11·5.

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## Complexes of uranium (VI), uranium (IV) and vanadium (IV) with triphenylphosphine

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COMPLEXES of uranium (VI) with substituted phosphines are unknown. ALLISON and MANN,(1) however, have prepared a few trialkyl phosphine complexes with uranium (IV). The present note describes the isolation of stable complexes of uranium (VI), uranium (IV) and vanadium (IV) with triphenylphosphine as a monoligand.

The diamagnetic uranium (VI) complexes are of the type $UO_2X_2.2(C_6H_5)_3P$, where X = Cl, Br, I and $NO_3$.

Bis(triphenylphosphine) uranylchloride, $UO_2Cl_2.2(C_6H_5)_3P$, was prepared by boiling uranylchloride with an excess of triphenylphosphine in n–butanol for about 30 min, the deposited yellow crystals, after crystallization from ethanol, melt at 288°C (Found P, 7·20% U, 27·44%; $UO_2Cl_2.2(C_6H_5)_3P$ requires P, 7·16% and U, 27·52%. It is soluble in methanol, ethanol, nitrobenzene and dioxane and insoluble in chloroform and benzene.

Yellow crystals of bis(triphenylphosphine) uranylbromide, $UO_2Br_2.2(C_6H_5)_3P$, of m.p. 300°C was obtained in a similar way from uranylbromide using cyclohexanol as the solvent (Found P, 6·45%, U, 24·90%; $UO_2Br_2.2(C_6H_5)_3P$ requires P, 6·50% and U, 24·96%. It is insoluble in benzene and ether, slightly soluble in nitrobenzene but highly soluble in methanol and ethanol.

Bis(triphenylphosphine) uranyliodide, $UO_2I_2.2(C_6H_5)_3P$, of m.p. 262°C was prepared as orange red crystals on refluxing an ether solution of uranyliodide with an excess of triphenylphosphine. (Found P, 6·42%, U, 22·9%; $UO_2I_2.2(C_6H_5)_3P$ requires P, 6·21% and U, 22·7%.

Bis(triphenylphosphine) uranylnitrate, $UO_2(NO_3)_2.2(C_6H_5)_3P$, of m.p. 274°C was obtained as yellow crystals following exactly the same procedure as described above for the bromo-derivative. (Found P, 6·72% U, 26·28%; $UO_2(NO_3)_2.2(C_6H_5)_3P$ requires P, 6·75% and U, 25·9%. It is moderately soluble in ethanol, methanol and hot dioxane, but insoluble in benzene, ether, carbon tetrachloride and nitrobenzene.

Bis(triphenylphosphine) uranium (IV) tetrachloride, $UCl_4.2(C_6H_5)_3P.C_6H_{12}O$, of m.p. 168°C was prepared as follows. A solution of uranylchloride, $UO_2Cl_2$ (4 g), in cyclohexanol was saturated with dry hydrogen chloride and reduced with zinc. To the clear green filtrate was added, with stirring, a warm solution of triphenylphosphine (7 g) in cyclohexanol when pale blue crystals immediately separated. These were filtered and washed with petroleum ether (Found C, 50·5%; H, 4·3%; Cl, 13·81%: P, 6·21%; U, 23·2%, $UCl_4.2(C_6H_5)_3P.C_6H_{12}O$ requires C, 50·2%; H, 4·18%; Cl, 14·0%; P, 6·17%; and U, 23·7%). This compound was always found to be associated with one mole of cyclohexanol. Attempts to remove the cyclohexanol by refluxing in various solvents met with no success. Prolonged dry heating at 120°C decomposes the complex. The thermogravimetric curve, as obtained in a Chevenard's thermobalance, type 3, indicates that the complex begins to lose cyclohexanol at 123°C, and thereafter with the rise of temperature it decomposes slowly to $U_3O_8$. It is insoluble in benzene, petroleum ether, chloroform, carbon tetrachloride and ether, but highly soluble in methanol, ethanol and acetone, forming deep green solutions. The compound, however, cannot be crystallized from these solutions, as it decomposes with the liberation of hexanol and triphenylphosphine. The absorption spectrum of the compound is, therefore, identical to that of uranium (IV) tetrachloride in methanol. Detailed study of the spectra in other solvents is in progress. Its magnetic moment was found to be 1·73 B. M.

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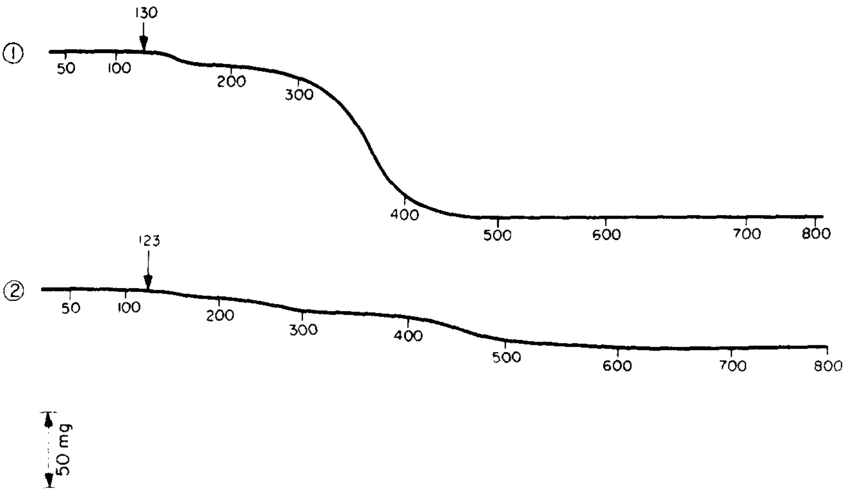
(1) J. A. C. ALLISON and F. G. MANN, *J. Chem. Soc.* 2915 (1949).



1. Vanadium complex.
2. Uranium complex.

Diaquobis(triphenylphosphine) vanadyl (IV) chloride, $VOCl_2.2(C_6H_5)_3P.2H_2O$, of m.p. 128°C was prepared by treating a cyclohexanol solution of vanadyl(IV) chloride, $VOCl_2.2H_2O$, with triphenylphosphine and concentrating the mixture to a viscous mass, which was then extracted with diethyl ether and filtered. The blue filtrate on concentration and cooling deposited greenish blue crystals of magnetic moment 1·61 B.M. (Found Cl, 9·73 %, P, 8·80 %, V, 7·41 %; $VOCl_2.2H_2O.2(C_6H_5)_3P$ requires Cl, 10·1 %; P, 8·88 %; V, 7·44 %). The compound gives a blue coloured solution in ether and alcohol and is decomposed by water with the liberation of triphenylphosphine. On thermogravimetric analysis the compound was found to lose two molecules of water at 130°C.

Further work in this line is in progress, the details of which will be published in due course.

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# On the use of auxiliary ligands in Job's method in equimolar solutions

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BABKO *et al.*⁽¹⁾ obtained a composition of 1:2 for the complex between titanium$^{IV}$ and salicylic acid at pH 4·0, by a modified Bent and French method and a 1:1 complex by Job's method in equimolar solutions using a constant amount of oxalic acid (auxiliary ligand). While discussing our findings on the titanium-sulphosalicylic acid (SSA) system, we⁽²⁾ expressed our doubt regarding the 1:1 composition reported by BABKO *et al.*⁽¹⁾ This note describes a reinvestigation of the titanium-salicylic acid system at pH $\simeq$ 4·0 by Job's method in equimolar solutions using EDTA, oxalic and malonic acids as auxiliary ligands.

Reagents and apparatus: described earlier.⁽²⁾

Salicylic acid: BDH AnalaR grade was dissolved in ammonium acetate because of its low solubility in water.

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(1) A. K. BABKO, A. I. VOLKOVA and T. E. GETMAN, *Russ. J. Inorg. Chem.*, Eng. Trans., Chem. Soc., London **6,** 529 (1961).

(2) N. MAHADEVAN, R. M. SATHE and CH. VENKATESWARLU, *J. Inorg. Nucl. Chem.*, **25,** 1005 (1963).