

### 801. Phosphonium Salts and Phosphine Oxide Addition Compounds of Uranium(IV) and Uranium(VI).

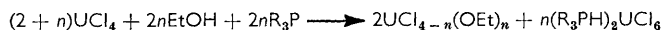
By P. GANS and B. C. SMITH.

Tertiary phosphines react with uranium tetrachloride in ethanol to give crystalline diphosphonium hexachlorouranates(IV). Oxidation of these by air gives diphosphonium tetrachlorodioxouranates(VI), but oxidation by chlorine gives uranium tetrachloride-bis(phosphine oxide) addition compounds. Further oxidation by hydrogen peroxide gives uranyl chloride-bis(phosphine oxide) addition compounds. Features of the infrared spectra are reported. Uranium tetrachloride-phosphine and uranium tetrachloride-phosphine sulphide addition compounds have not been obtained.

URANIUM TETRACHLORIDE is insoluble in hydrocarbons and non-polar solvents, and dissolves only in polar liquids that are electron-donors. Crystalline molecular addition compounds are formed between uranium tetrachloride and the lower alcohols,<sup>1</sup> but solvolysis occurs on heating, or in the presence of a suitable base. Reaction occurs when a solution of uranium tetrachloride in ethanol is added slowly to an excess of tertiary phosphine in ethanol. The colour darkens, but the products are soluble in ethanol, and no precipitate is formed.



A different situation occurs when a tertiary phosphine solution is added to a uranium tetrachloride solution, and an excess of uranium tetrachloride reacts with the phosphonium chloride to form sparingly soluble hexachlorouranate(IV) salts.<sup>2</sup> Addition of the first few drops of the phosphine solution causes a darkening in colour of the uranium tetrachloride solution, then the diphosphonium hexachlorouranate(IV) separates from the solution, and the colour does not darken on further addition of the phosphine.



Triethyl-, diethylphenyl-, ethyldiphenyl-, triphenyl-, diphenyl-, tri-*n*-propyl-, and tri-*n*-butyl-phosphine react in this way. Almost quantitative yields of the diphosphonium hexachlorouranates(IV) are obtained on addition of gaseous hydrogen chloride or concentrated hydrochloric acid. Diquaternary phosphonium salts,  $(\text{R}_4\text{P})_2\text{UCl}_6$ , are prepared by addition of stoichiometric quantities of quaternary phosphonium iodide to a solution containing uranium tetrachloride and a little concentrated hydrochloric acid in ethanol. Diphosphonium hexachlorouranates(IV) form green non-hygroscopic crystals which are stable in air for reasonable periods. They are slightly soluble in ethanol, and can be

<sup>1</sup> Bradley, Kapoor, and Smith, *J. Inorg. Nuclear Chem.*, 1962, **24**, 863.

<sup>2</sup> Gans and Smith, *Chem. and Ind.*, 1963, 911.

[1964] *Addition Compounds of Uranium(IV) and Uranium(VI)*. 4173

recrystallised also from solvents such as nitromethane or acetonitrile. Attempted recrystallisation from dimethylformamide–benzene gives bis(uranium tetrachloride)–pentakis(dimethylformamide).<sup>3</sup> A similar reaction between dicesium hexachlorouranate(IV) and dimethylacetamide gave the compound  $\text{UCl}_4 \cdot 2 \cdot 5 \text{MeCO} \cdot \text{NMe}_2$ .<sup>4</sup> No product was obtained from attempted reaction between uranium tetrachloride, hydrochloric acid, and bis(diphenylphosphino)methane in ethanol or tetrahydrofuran. Reaction with 1,2-bis(diphenylphosphino)ethane gave an unstable phosphonium salt, but the diphosphine was recovered on attempted recrystallisation.

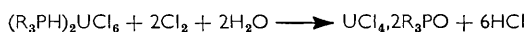
Diphosphonium hexachlorouranates(IV) in boiling ethanol are oxidised by air or a little hydrogen peroxide to tetrachlorodioxouranates(VI).



Oxidation occurs particularly easily with the lower trialkylphosphonium salts but bis(tri-*n*-butylphosphonium) hexachlorouranate(IV) is more stable and crystallises unchanged even after prolonged boiling. The ease of oxidation of diquaternary phosphonium hexachlorouranates(IV) also depends on the cation; the dimethyldiphenylphosphonium salt is oxidised much more rapidly than the triethylphenylphosphonium salt under apparently similar conditions. Diphosphonium tetrachlorodioxouranates(VI) form yellow non-hygroscopic crystals which are stable indefinitely in air, but repeated recrystallisation of the tertiary phosphonium salts may cause partial oxidation to phosphine oxide addition compounds and give products with low melting points.

No evidence has been obtained for the formation of uranium tetrachloride–tertiary phosphine addition compounds in ethanol, tetrahydrofuran, or acetonitrile. It seems possible that the compounds reported as  $\text{UCl}_4 \cdot 2\text{Et}_3\text{P}$ , m. p. 253–256° (decomp.), and  $\text{UCl}_4 \cdot 2\text{Pr}^n_3\text{P}$ , m. p. 208–210° (decomp.),<sup>5</sup> may be identical with the tetrachlorodioxouranates(VI),  $(\text{Et}_3\text{PH})_2\text{UO}_2\text{Cl}_4$ , m. p. 265–267° (decomp.), falling to 255–257° (decomp.) on recrystallisation, and  $(\text{Pr}^n_3\text{PH})_2\text{UO}_2\text{Cl}_4$ , m. p. 204–206° (decomp.), described here. The only other reported phosphine addition compound of uranium(IV) is an insoluble tan solid,<sup>6</sup> whose analysis suggests that it may also be a tetrachlorodioxouranate(VI).

Ditertiary phosphonium hexachlorouranates(IV) or solutions of the phosphine and uranium tetrachloride in ethanol are oxidised by chlorine or bromine to uranium tetrachloride–bis(phosphine oxide) addition compounds. This method of preparation is useful when the phosphine oxide is not readily available, and the formation of hydrogen chloride as a by-product prevents solvolysis.



The compounds  $(\text{Pr}^n_3\text{PH})_2\text{UCl}_6$  and  $(\text{Bu}^n_3\text{PH})_2\text{UCl}_6$  both appear to be oxidised by chlorine, but crystalline addition compounds were not obtained. Uranium tetrachloride–bis(phosphine oxide) addition compounds can be prepared also by direct precipitation from ethanol or tetrahydrofuran, but reaction with tri-*n*-propylphosphine oxide gave an uncharacterised oil from both solvents. The compound  $\text{UCl}_4 \cdot 3\text{Me}_3\text{PO}$  is formed by direct reaction with an excess of trimethylphosphine oxide in tetrahydrofuran, but attempts to make the tetrakis(trimethylphosphine oxide) and other tris(phosphine oxide) addition compounds were unsuccessful. Both addition compounds of trimethylphosphine oxide are hygroscopic but the other crystalline addition compounds are stable in air. Uranium tetrachloride forms 1 : 1 addition compounds with the diphosphine dioxides  $\text{Ph}_2\text{PO} \cdot \text{CH}_2 \cdot \text{PO} \cdot \text{Ph}_2$  and  $\text{Ph}_2\text{PO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{PO} \cdot \text{Ph}_2$ . Attempts to make addition compounds with the corresponding diphosphine disulphides and with triphenylphosphine sulphide were unsuccessful.

Solutions of ditertiary phosphonium tetrachlorodioxouranates(VI) and uranium tetrachloride–bis(phosphine oxide) addition compounds are oxidised by air or hydrogen peroxide

<sup>3</sup> Gans and Smith, following Paper.

<sup>4</sup> Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

<sup>5</sup> Allison and Mann, *J.*, 1949, 2915.

<sup>6</sup> Mannerskantz, Parshall, and Wilkinson, *J.*, 1963, 3163.

4174 *Gans and Smith: Phosphonium Salts and Phosphine Oxide*

to uranyl chloride-bis(phosphine oxide) addition compounds which form yellow non-hygroscopic crystals. The ease of oxidation appears to increase with the number of phenyl groups. Addition compounds of uranyl chloride, uranyl bromide, and uranyl nitrate with phosphine oxides are prepared also by precipitation from acetone.

The infrared spectra of the compounds investigated are an important guide to identification. The phosphonium salts show a band associated with the P-H stretching mode at *ca.* 2430  $\text{cm}^{-1}$ . The intensity is greatest in arylphosphonium salts and least in trialkylphosphonium salts. A weak second band occurs sometimes on the low-frequency side of the main band, and in the diphenylphosphonium salt  $(\text{Ph}_2\text{PH}_2)_2\text{UCl}_6$  two bands are seen clearly at 2430 and 2350  $\text{cm}^{-1}$ .

The U=O stretching band in salts containing the  $[\text{UO}_2\text{Cl}_4]^{2-}$  anion or in phosphine oxide addition compounds,  $\text{UO}_2\text{X}_2 \cdot 2\text{R}_3\text{PO}$ , occurs in the region 930—920  $\text{cm}^{-1}$ , and the intensity is comparable to that of C=O or P=O stretching bands. The absence of this band provides valuable information about the purity of quadrivalent uranium compounds.

The P=O stretching frequency in free phosphine oxides occurs in the region 1200—1150  $\text{cm}^{-1}$ . When the phosphine oxides are involved in co-ordinate-bond formation the frequency decreases because of a decrease in the P=O bond order.<sup>7</sup> In phosphine oxide addition compounds with uranium tetrachloride or uranyl salts there is a shift of *ca.* 100  $\text{cm}^{-1}$  which is greater than that found with transition metals. The P=O stretching frequency occurs at 1175  $\text{cm}^{-1}$  in trimethylphosphine oxide and at 1050  $\text{cm}^{-1}$  in the addition compounds  $\text{UCl}_4 \cdot 2\text{Me}_3\text{PO}$  and  $\text{UCl}_4 \cdot 3\text{Me}_3\text{PO}$  which have identical spectra. No absorption occurs at 1175  $\text{cm}^{-1}$ , and all other bands are found also in the spectrum of the free ligand. The P=O stretching frequencies of the addition compounds  $\text{UCl}_4 \cdot (\text{Ph}_2\text{PO})_2\text{CH}_2$  and  $\text{UCl}_4 \cdot (\text{Ph}_2\text{PO} \cdot \text{CH}_2)_2$  occur at 1085 and 1045  $\text{cm}^{-1}$ , respectively, and there are no bands at 1190  $\text{cm}^{-1}$  where the P=O stretching frequency occurs in the free phosphine oxides. Hence, the phosphine oxides donate electrons from both oxygen atoms, and the addition compounds may contain chelate rings. The P=O band occurs at 1295  $\text{cm}^{-1}$  in phosphorus oxychloride and at 1240  $\text{cm}^{-1}$  in the addition compound<sup>8</sup>  $\text{UCl}_4 \cdot 4\text{POCl}_3$ . Bonding occurs through oxygen, and the small value of the shift (55  $\text{cm}^{-1}$ ) may depend on the presence of four ligands or on the high electronegativity of chlorine. The P=O stretching frequencies of a number of compounds are recorded in Table I. For a particular acceptor, shifts

TABLE I.

Compound	P=O stretching frequency ( $\text{cm}^{-1}$ ).						
	$\text{Me}_3\text{PO}$	$\text{Et}_3\text{PO}$	$\text{Ph}_3\text{PO}$	Compound	$\text{Me}_3\text{PO}$	$\text{Et}_3\text{PO}$	$\text{Ph}_3\text{PO}$
$\text{R}_3\text{PO}$ .....	1175	1160	1195	$\text{UO}_2\text{Br}_2 \cdot 2\text{R}_3\text{PO}$ .....	1060	1065	1060
$\text{UCl}_4 \cdot 2\text{R}_3\text{PO}$ .....	1050	1055	1070	$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{R}_3\text{PO}$ ...	1090	1080	1080
$\text{UO}_2\text{Cl}_2 \cdot 2\text{R}_3\text{PO}$ .....	1070	1065	1070				

increase in the order  $\text{Et}_3\text{PO} < \text{Me}_3\text{PO} < \text{Ph}_3\text{PO}$ , and for each phosphine oxide shifts increase in the order  $\text{UO}_2(\text{NO}_3)_2 < \text{UO}_2\text{Cl}_2 < \text{UO}_2\text{Br}_2 < \text{UCl}_4$ , although the compound  $\text{UO}_2\text{Br}_2 \cdot 2\text{Ph}_3\text{PO}$  appears to be anomalous.

## EXPERIMENTAL

Uranium tetrachloride was prepared from uranium trioxide and hexachloropropene.<sup>9</sup> Organic solvents were dried rigorously and purified by conventional methods, and were stored in molecular-sieve columns. Reactions were carried out in an atmosphere of dry nitrogen when necessary. Spectra were recorded on an Infracord spectrophotometer equipped with sodium chloride optics.

*Phosphines*.—Triphenylphosphine, m. p. 80—81°, was recrystallised from ethanol. Triethylphosphine, b. p. 127—130°/760 mm., and tri-*n*-propylphosphine, b. p. 60°/0.1 mm., were

<sup>7</sup> Cotton, Barnes, and Bannister, *J.*, 1960, 2199.

<sup>8</sup> Panzer and Suttle, *J. Inorg. Nuclear Chem.*, 1960, 15, 67.

<sup>9</sup> Hermann and Suttle, *Inorg. Synth.*, 1957, 5, 143.

prepared from phosphorus trichloride and Grignard reagents. The authors thank Dr. N. Johnstone for a gift of tri-*n*-butylphosphine, and Dr. W. Gee for a gift of diphenylphosphine. Diethylphenylphosphine was prepared from phenyldichlorophosphine and ethylmagnesium iodide. Reactions of diphenylphosphinosodium in liquid ammonia<sup>10</sup> with ethyl iodide gave ethyldiphenylphosphine, b. p. 98°/0.1 mm., with methylene chloride gave bis(diphenylphosphino)methane, m. p. 120°, and with 1,2-dichloroethane gave 1,2-bis(diphenylphosphino)ethane, m. p. 141—142°.

*Quaternary Phosphonium Iodides.*—The phosphonium iodides Et<sub>4</sub>PI, m. p. 314—315°, Et<sub>3</sub>PhI, m. p. 140—141°, Me<sub>2</sub>Ph<sub>2</sub>PI, m. p. 204—205°, and MePh<sub>3</sub>PI, were prepared by reaction between the appropriate phosphine and an excess of alkyl iodide.

*Phosphine Oxides.*—Trimethylphosphine oxide, triethylphosphine oxide, and tri-*n*-propylphosphine oxide were prepared from Grignard reagents and phosphorus oxychloride, and were purified by sublimation at 100°/0.1 mm. Triphenylphosphine oxide, m. p. 153°, bis(diphenylphosphinyl)methane, m. p. 156—158°, and 1,2-bis(diphenylphosphinyl)ethane, m. p. 275—276°, were prepared by oxidation of the appropriate phosphine with potassium permanganate in acetone.

*Phosphine Sulphides.*—Triphenylphosphine sulphide, m. p. 161°, bis(diphenylsulphophosphino)methane, m. p. 233—235°, and 1,2-bis(diphenylsulphophosphino)ethane, m. p. 175—177°, were prepared by reaction of sulphur with the appropriate phosphine in benzene, and were recrystallised from ethanol. Solutions of uranium tetrachloride and phosphine sulphides in tetrahydrofuran were boiled under reflux. The phosphine sulphides crystallised on cooling.

*Diphosphonium Hexachlorouranates(IV).*—Ethanol solutions of the phosphines Et<sub>3</sub>P, Et<sub>2</sub>PhP, EtPh<sub>2</sub>P, Ph<sub>3</sub>P, Ph<sub>2</sub>PH, Pr<sup>n</sup><sub>3</sub>P, and Bu<sup>n</sup><sub>3</sub>P (2 moles) reacted with uranium tetrachloride (1 mole) in ethanol to give green crystalline *diphosphonium hexachlorouranates(IV)*. Addition of concentrated hydrochloric acid to the filtrates caused almost complete precipitation. Addition of quaternary phosphonium iodides (2 moles) to uranium tetrachloride (1 mole) in ethanol gave hygroscopic precipitates, and, in the presence of a little concentrated hydrochloric acid, *di-quaternary phosphonium hexachlorouranates(IV)* were formed. The compounds were recrystallised from ethanol, acetonitrile, or nitromethane, and analytical data are recorded in Table 2.

TABLE 2.

## Diphosphonium hexachlorouranates(IV).

Compound	M. p. (decomp.)	Found (%)				Formula	Required (%)			
		C	H	Cl	P		C	H	Cl	P
(Et <sub>3</sub> PH) <sub>2</sub> UCl <sub>6</sub>	220—223°	20.9	4.5	31.4	—	C <sub>12</sub> H <sub>32</sub> Cl <sub>6</sub> P <sub>2</sub> U	20.9	4.7	30.9	9.0
(Pr <sup>n</sup> <sub>3</sub> PH) <sub>2</sub> UCl <sub>6</sub>	185—186	27.8	4.5	—	—	C <sub>18</sub> H <sub>44</sub> Cl <sub>6</sub> P <sub>2</sub> U	27.9	5.7	27.5	8.0
(Bu <sup>n</sup> <sub>3</sub> PH) <sub>2</sub> UCl <sub>6</sub>	147—150	33.6	6.0	25.2	7.8	C <sub>24</sub> H <sub>56</sub> Cl <sub>6</sub> P <sub>2</sub> U	33.6	6.6	24.8	7.2
(Et <sub>2</sub> PhPH) <sub>2</sub> UCl <sub>6</sub>	176—178	30.9	4.0	—	8.6	C <sub>20</sub> H <sub>32</sub> Cl <sub>6</sub> P <sub>2</sub> U	30.6	4.1	27.1	7.9
(EtPh <sub>2</sub> PH) <sub>2</sub> UCl <sub>6</sub>	—	38.8	3.5	—	—	C <sub>28</sub> H <sub>32</sub> Cl <sub>6</sub> P <sub>2</sub> U	38.1	3.7	24.2	7.0
(Ph <sub>2</sub> PH) <sub>2</sub> UCl <sub>6</sub>	> 170	34.4	3.1	—	—	C <sub>24</sub> H <sub>24</sub> Cl <sub>6</sub> P <sub>2</sub> U	34.9	2.9	25.8	7.5
(Ph <sub>3</sub> PH) <sub>2</sub> UCl <sub>6</sub>	> 180	44.0	3.3	22.5	6.9	C <sub>36</sub> H <sub>32</sub> Cl <sub>6</sub> P <sub>2</sub> U	44.2	3.3	21.8	6.3
(Et <sub>4</sub> P) <sub>2</sub> UCl <sub>6</sub>	> 300	26.6	5.3	28.3	8.1	C <sub>16</sub> H <sub>40</sub> Cl <sub>6</sub> P <sub>2</sub> U	25.8	5.4	28.6	8.3
(Et <sub>3</sub> PhP) <sub>2</sub> UCl <sub>6</sub>	151—152	34.3	4.5	25.1	7.5	C <sub>24</sub> H <sub>40</sub> Cl <sub>6</sub> P <sub>2</sub> U	34.2	4.8	25.3	7.4
(Me <sub>2</sub> Ph <sub>2</sub> P) <sub>2</sub> UCl <sub>6</sub>	177—178	38.7	3.4	24.4	6.75	C <sub>28</sub> H <sub>32</sub> Cl <sub>6</sub> P <sub>2</sub> U	38.1	3.65	24.2	7.0
(MePh <sub>3</sub> P) <sub>2</sub> UCl <sub>6</sub>	268—269	46.2	3.6	—	6.4	C <sub>38</sub> H <sub>36</sub> Cl <sub>6</sub> P <sub>2</sub> U	45.4	3.6	21.2	6.2

*Diphosphonium Tetrachlorodioxouranates(VI).*—Attempted recrystallisation of bis(triethylphosphonium) hexachlorouranate(IV) from ethanol in air gave a mixture of yellow and green crystals, and eventually *bis(triethylphosphonium) tetrachlorodioxouranate(VI)*. Other yellow crystalline *diphosphonium tetrachlorodioxouranates(VI)* were prepared similarly, or by oxidation with a little hydrogen peroxide, and were recrystallised from ethanol. Analytical data are recorded in Table 3.

*Uranium Tetrachloride-Phosphine Oxide Addition Compounds.*—Addition of uranium tetrachloride to a hot stirred solution containing an excess of trimethylphosphine oxide in tetrahydrofuran gave green crystalline *uranium tetrachloride-tris(trimethylphosphine oxide)*. Similar reactions of triethyl- and triphenylphosphine oxide gave only *uranium tetrachloride-bis(phosphine oxides)*. Uranium tetrachloride-bis(phosphine oxides) were prepared also by bubbling chlorine

<sup>10</sup> Hewertson and Watson, *J.*, 1962, 1490.

TABLE 3.  
 Diphosphonium tetrachlorodioxouranates(vi).

Compound	M. p. (decomp.)	Found (%)				Formula	Required (%)			
		C	H	Cl	P		C	H	Cl	P
(Et <sub>3</sub> PH) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	265—267°	22.1	4.8	22.6	10.1	C <sub>12</sub> H <sub>32</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	22.1	5.0	21.8	9.5
(Pr <sup>n</sup> <sub>3</sub> PH) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	204—206	29.0	4.8	—	—	C <sub>18</sub> H <sub>44</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	29.4	6.0	19.3	8.4
(Et <sub>2</sub> PhPH) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	166—167	32.0	4.0	19.4	9.0	C <sub>20</sub> H <sub>32</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	32.2	4.3	19.0	8.3
(EtPh <sub>2</sub> PH) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	—	39.5	3.9	—	—	C <sub>28</sub> H <sub>32</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	39.9	3.8	16.85	7.35
(Ph <sub>3</sub> PH) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	—	46.4	3.3	—	—	C <sub>36</sub> H <sub>32</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	46.1	3.4	15.1	6.6
(Et <sub>4</sub> P) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	>360	28.4	5.5	20.4	8.8	C <sub>16</sub> H <sub>40</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	27.2	5.7	20.1	8.8
(Me <sub>2</sub> Ph <sub>2</sub> P) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	255—256	38.8	3.2	—	7.7	C <sub>28</sub> H <sub>32</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	39.9	3.8	16.85	7.35
(MePh <sub>3</sub> P) <sub>2</sub> UO <sub>2</sub> Cl <sub>4</sub>	316—317	47.4	3.5	—	6.25	C <sub>38</sub> H <sub>36</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	47.2	3.75	14.7	6.4

gas through hot ethanol solutions of the compounds (Ph<sub>3</sub>PH)<sub>2</sub>UCl<sub>6</sub> and (Et<sub>2</sub>PH)<sub>2</sub>UCl<sub>6</sub>, and a mixture of uranium tetrachloride (1 mole) and ethyldiphenylphosphine (2 moles). The compounds were recrystallised from acetonitrile-ethanol or nitromethane. Reaction in ethanol between uranium tetrachloride and the diphosphine dioxides Ph<sub>2</sub>PO·CH<sub>2</sub>·PO·Ph<sub>2</sub> and Ph<sub>2</sub>PO·CH<sub>2</sub>·CH<sub>2</sub>·PO·Ph<sub>2</sub> gave green crystalline 1 : 1 addition compounds which are insoluble in acetonitrile, nitromethane, and nitrobenzene. The addition compound UCl<sub>4</sub>·Ph<sub>2</sub>PO·CH<sub>2</sub>·PO·Ph<sub>2</sub> is slightly soluble in ethanol, but poor analyses were obtained. Analytical data are recorded in Table 4. Uranium tetrachloride-tetrakis(phosphorus oxychloride) was prepared by the method of Panzer and Suttle<sup>8</sup> (Found: Cl, 56.5; U, 24.6. Calc. for Cl<sub>16</sub>O<sub>4</sub>P<sub>4</sub>U: Cl, 57.3; U, 24.0%).

 TABLE 4.  
 Uranium tetrachloride-phosphine oxide addition compounds.

Compound	M. p.	Found (%)			Formula	Required (%)		
		C	H	P		C	H	P
UCl <sub>4</sub> ·3Me <sub>3</sub> PO	ca. 95° *	16.6	3.8	13.7	C <sub>9</sub> H <sub>27</sub> Cl <sub>4</sub> O <sub>3</sub> P <sub>3</sub> U	16.5	4.2	14.2
UCl <sub>4</sub> ·2Me <sub>3</sub> PO	*	12.95	3.0	—	C <sub>6</sub> H <sub>15</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	12.8	3.2	11.0
UCl <sub>4</sub> ·2Et <sub>3</sub> PO	202—206	22.7	4.9	9.9	C <sub>12</sub> H <sub>30</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	22.2	4.7	9.6
UCl <sub>4</sub> ·2Et <sub>2</sub> PhPO	199—200 *	32.0	3.7	8.8	C <sub>20</sub> H <sub>30</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	32.3	4.0	8.3
UCl <sub>4</sub> ·2EtPh <sub>2</sub> PO	—	40.1	3.2	7.4	C <sub>28</sub> H <sub>30</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	40.0	3.6	7.4
UCl <sub>4</sub> ·2Ph <sub>3</sub> PO	> 300	46.3	3.4	6.8	C <sub>36</sub> H <sub>30</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	46.2	3.2	6.6
UCl <sub>4</sub> ·(Ph <sub>2</sub> PO) <sub>2</sub> CH <sub>2</sub>	156—158	38.9	3.3	6.65	C <sub>25</sub> H <sub>22</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	37.7	2.8	7.8
UCl <sub>4</sub> ·(Ph <sub>2</sub> POCH <sub>2</sub> ) <sub>2</sub>	275—276	38.2	3.4	6.65	C <sub>26</sub> H <sub>24</sub> Cl <sub>4</sub> O <sub>2</sub> P <sub>2</sub> U	38.5	3.0	7.65

\* Decomp.

*Uranyl Salt-Phosphine Oxide Addition Compounds.*—Oxidation of uranium tetrachloride-bis(phosphine oxides) by the minimum quantity of 100 volume hydrogen peroxide gave yellow *uranyl chloride-bis(phosphine oxides)*. Other *uranyl salt-bis(phosphine oxides)* were prepared from their components by precipitation from methanol or acetone. The compounds were recrystallised from methanol, ethanol, or acetone. Analytical data are recorded in Table 5.

 TABLE 5.  
 Uranyl salt-phosphine oxide addition compounds.

Compound	M. p. (decomp.)	Found (%)				Formula	Required (%)			
		C	H	Hal	P		C	H	Hal	P
UO <sub>2</sub> Cl <sub>2</sub> ·2Me <sub>3</sub> PO	172—173°	13.5	3.1	13.5	11.1	C <sub>6</sub> H <sub>15</sub> Cl <sub>2</sub> O <sub>4</sub> P <sub>3</sub> U	13.7	3.4	13.5	11.8
UO <sub>2</sub> Cl <sub>2</sub> ·2Et <sub>3</sub> PO	199—200	24.2	4.4	12.3	11.5	C <sub>12</sub> H <sub>30</sub> Cl <sub>2</sub> O <sub>4</sub> P <sub>2</sub> U	23.6	5.0	11.7	10.2
UO <sub>2</sub> Cl <sub>2</sub> ·2Ph <sub>3</sub> PO	298	48.0	3.4	8.2	7.2	C <sub>36</sub> H <sub>30</sub> Cl <sub>2</sub> O <sub>4</sub> P <sub>2</sub> U	48.2	3.4	7.9	6.9
UO <sub>2</sub> Br <sub>2</sub> ·2Me <sub>3</sub> PO	>250	12.2	2.6	—	—	C <sub>6</sub> H <sub>15</sub> Br <sub>2</sub> O <sub>4</sub> P <sub>3</sub> U	11.7	2.95	26.0	10.1
UO <sub>2</sub> Br <sub>2</sub> ·2Et <sub>3</sub> PO	235—236	21.4	4.3	—	—	C <sub>12</sub> H <sub>30</sub> Br <sub>2</sub> O <sub>4</sub> P <sub>2</sub> U	20.6	4.3	22.9	8.9
UO <sub>2</sub> Br <sub>2</sub> ·2Ph <sub>3</sub> PO	318—320	43.6	3.1	—	—	C <sub>36</sub> H <sub>30</sub> Br <sub>2</sub> O <sub>4</sub> P <sub>2</sub> U	43.8	3.1	16.2	6.3
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2Me <sub>3</sub> PO	>220	13.5	3.0	—	—	C <sub>6</sub> H <sub>15</sub> N <sub>2</sub> O <sub>10</sub> P <sub>2</sub> U	12.5	3.1	—	10.7
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2Ph <sub>3</sub> PO	300—304	44.5	3.2	—	6.5	C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>10</sub> P <sub>2</sub> U	44.9	3.2	—	6.5

This work was supported by the Atomic Energy Research Establishment, Harwell, and the authors thank Mr. F. Hudswell for his interest and encouragement.

DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE (UNIVERSITY OF LONDON),

MALET STREET, LONDON W.C.1.

[Received, January 2nd, 1964.]