970. *The Preparation and Spectra of Uranium Pentachloride Complexes*

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Stable uranium pentachloride complexes with phosphine oxides, UCl_5,Ph_3PO and $UCl_5,(C_8H_{17})_3PO$, have been prepared from $CsUCl_6$. Magnetic data for UCl_5,Ph_3PO, and the absorption spectra of both complexes and of other stable uranium(v) solutions over the range 0·4—2·0 μ, are reported. The complexes show an unusually large P=O vibrational frequency shift. Other oxygen donor ligands have been treated with $CsUCl_6$ but complexes could not be isolated.

COMPLEXES of uranium pentachloride with thionyl chloride,[1] $UCl_5,SOCl_2$, and phosphorus pentachloride,[2,3] UCl_5,PCl_5, have been characterised previously, and an unusual complex with trichloroacryloyl chloride, $5UCl_5,CCl_2{:}CCl{\cdot}COCl$, has been claimed.[4] Few reliable spectral data are available for uranium(v) chloride solutions, apart from those obtained using thionyl chloride,[5] carbon tetrachloride,[6] or phosphorus oxytrichloride [3] as solvent, owing to the rapid disproportionation observed [7] in all except anhydrous or complexing solvents. The absorption spectra of uranium(v) fluoro-complexes, from mulls in Fluorolube [8] and solutions in aqueous hydrofluoric acid,[9] have also been reported. We recently described [5] the preparation of stable hexachloro- and octachloro-uranates(v), amongst them cæsium hexachlorouranate(v), $CsUCl_6$. This work has been extended, and the reaction of $CsUCl_6$ or $UCl_5,SOCl_2$ with various oxygen-containing ligands $R_xM=O$ ($R =$ alkyl or aryl; $M =$ N, P, As, C, or S) has been investigated. Stable complexes have been isolated only for ligands containing the phosphine oxide group, for example, the complexes with triphenylphosphine oxide and tri-n-octylphosphine oxide, UCl_5,Ph_3PO and $UCl_5,(C_8H_{17})_3PO$, respectively. Originally it was intended to investigate the preparation of similar quinquevalent tungsten complexes but these are being investigated by Professor Y. Tyree, jun., and his associates.[10]

Methylene dichloride was the most satisfactory solvent for the preparation of the above complexes since it was easily obtained perfectly anhydrous and no disproportionation of uranium(v), readily detected from the absorption spectra (see later), was observed. Methyl cyanide was less satisfactory. Treatment of $CsUCl_6$, suspended in methylene chloride, with trialkyl- or triaryl-phosphine oxides results in the formation of an intensely red solution of the uranium pentachloride complex and precipitation of cæsium chloride. The yellow-orange crystalline triphenylphosphine oxide complex, UCl_5,Ph_3PO, is isolated by vacuum-evaporation of the solvent or by precipitation with isopentane. The tri-n-octylphosphine oxide complex, $UCl_5,(C_8H_{17})_3PO$, an orange-red oil, is isolated by the former method. The complexes are sensitive to moisture but appear to be indefinitely stable in a dry argon atmosphere or in methylene dichloride solution. Similar reactions occur between $CsUCl_6$ and benzyldiphenylphosphine oxide and octyldiphenylphosphine oxide; these complexes have not been isolated from the stable red solutions but undoubtedly they will be analogous to those described above. Hexamethylphosphoramide, $(NMe_2)_3PO$, initially yields a red solution of the uranium(v) complex but disproportionation takes place within a few minutes.

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The triphenylphosphine oxide complex, which melts with decomposition at ~120°, exhibits similar magnetic properties to those [5] of the hexachlorouranates(V). Curie–Weiss dependence is observed (Table 1) between 305 and 160°K below which temperature marked deviation occurs. The magnetic moment calculated at the higher temperatures, 2·13 B.M., probably has little significance owing to the large value (−270°) of θ, the Weiss constant. Molar susceptibilities shown in Table 1 are corrected for the diamagnetism of uranium(V),[11] chloride,[12] and the ligand.[12]

TABLE 1

Magnetic susceptibilities of UCl_5,Ph_3PO

Temp. (°K)	305	266	230	191	169	153	125	100	89
$10^6\chi_m$ (c.g.s. units)	982·6	1056	1130	1213	1268	1342	1489	1861	1995

The P=O vibrational frequency in the infrared spectra of UCl_5,Ph_3PO and $UCl_5,(C_8H_{17})_3PO$ has shifted from the free-ligand frequencies by −217 and −161 cm.$^{-1}$, respectively. The uranium–chlorine stretching vibrations occur at 285 and 304 cm.$^{-1}$ compared with values [5] between 303 and 310 cm.$^{-1}$ for the hexachlorouranates(V) (Table 2). Part of the spectrum of UCl_5,Ph_3PO, illustrating the large P=O vibration shift, is shown in Figure 1. Our value for the position of this vibration in Ph_3PO, 1192 cm.$^{-1}$, is in good agreement with those obtained by others; [13,14] the infrared spectrum of tri-n-octylphosphine oxide (P=O at 1144 cm.$^{-1}$) does not appear to have been reported previously. The vibrations at 1441, 1120, and 995 cm.$^{-1}$ are characteristic of *P*-phenyl compounds [13,15] although there is still doubt as to their true origin; at least the latter two are probably activated C–H or ring

TABLE 2

Infrared vibrations (cm.$^{-1}$)

	Ph_3PO	UCl_5,Ph_3PO	$(C_8H_{17})_3PO$	$UCl_5,(C_8H_{17})_3PO$
P=O	1192	973	1144	983
$\Delta_{P=O}$	—	219	—	161
U–Cl	—	285	—	304

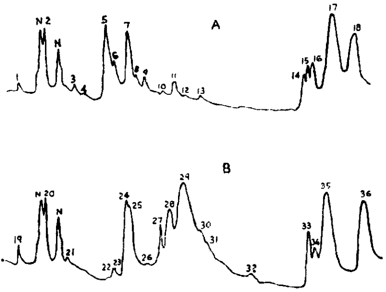

FIGURE 1. Infrared spectra of (A) Ph_3PO, and (B) UCl_5,Ph_3PO

1, 1590; 2, 1441; 3, 1309; 4, 1277; 5, 1192 (P=O str.); 6, 1163; 7, 1120; 8, 1094; 9, 1071; 10, 1025; 11, 995; 12, 938; 13, 860; 14, 758; 15, 752; 16, 745; 17, 719; 18, 693 cm.$^{-1}$.

19, 1587; 20, 1438; 21, 1337; 22, 1168; 23, 1161; 24, 1121; 25, 1112; 26, 1066; 27, 1027; 28, 1004; 29, 973 (P=O str.); 30, 936; 31, 921; 32, 840; 33, 751; 34, 742; 35, 725; 36, 682 cm.$^{-1}$.

N, Nujol mulling agent.

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vibrations.[16,17] The shift in the P=O vibration on complex formation, reflecting an overall decrease in the bond order of the P=O probably due to a large decrease in p_π–d_π bonding because of the great affinity of uranium(V) for oxygen, is much larger than that observed for phosphine oxide–transition-metal complexes [14,18,19] but is of the same order as the shift [20,21] in the uranium(IV) and thorium(IV) complexes $MCl_4,2(NMe_2)_3PO$ and $MCl_4,2Ph_3PO$.

A uranium pentachloride–phosphorus oxytrichloride complex appears to be formed on the addition of anhydrous $POCl_3$ to a thionyl chloride solution of uranium pentachloride, the absorption spectrum of the mixture showing slight differences from that of $UCl_5,SOCl_2$ alone (Table 3). Vacuum-evaporation of the mixture, however did not yield a pure complex; the absorption spectrum of a thionyl chloride solution of the yellow solid so obtained indicated that much disproportionation of the uranium(V) had occurred. Since our analytical method, oxidation to uranium(VI) with dichromate, did not distinguish pure uranium(V) from an equimolar mixture of uranium(IV) and uranium(VI), formed on disproportionation of the former, we used absorption spectra as the criterion of purity of the uranium(V) complexes and solutions. In the range 16,600—11,000 cm.$^{-1}$ uranium(V) solutions show only one characteristic peak (11,500—11,850 cm.$^{-1}$ for various solutions). The presence of small amounts of uranium(IV) is therefore readily detected by the appearance of peaks around 1500 cm.$^{-1}$ which are little affected by change of solvent. For solutions in phosphorus oxytrichloride these occur at 1555 and 1488 cm.$^{-1}$. This is illustrated in Figure 2 which shows the spectrum of $CsUCl_6$ and $UCl_5,SOCl_2$ in phosphorus oxytrichloride; disproportionation accounts for the presence of the uranium(IV) peaks. Uranyl chloride shows no absorption in this region under these conditions.

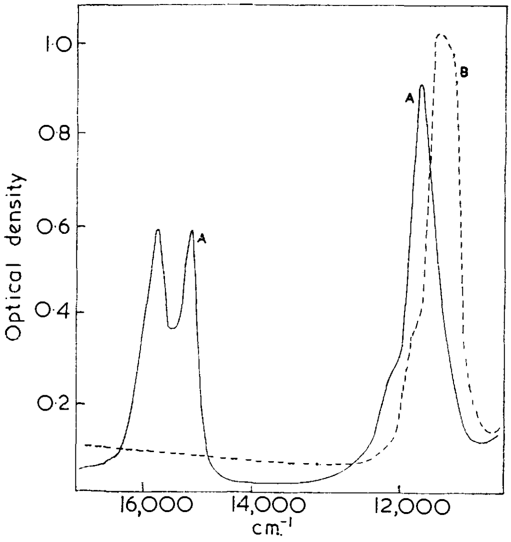

FIGURE 2. Absorption spectra, in phosphorus oxytrichloride, of 0·2M-solutions of (A) $UCl_5,SOCl_2$, and (B) $CsUCl_6$

It is apparent from our results that the spectrum reported [3] for UCl_5,PCl_5 is of a genuine uranium(V) solution but that of the trichloro-acryloyl complex [4] is of a solution containing an appreciable quantity of uranium(IV). Details of the spectra of several uranium(V) solutions which are perfectly stable in stoppered cells and which contain only quinquevalent uranium are listed in Table 3. An example of such a spectrum between 13,000 and

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TABLE 3

Absorption spectra of 0·2M-uranium(V) solutions

Compound	Solvent	Colour of soln.*	Maxima (cm.$^{-1}$)
UCl_5,Ph_3PO	CH_2Cl_2	R–O	11,846, 10,693, 10,126, 7108, 6878, 6801, 6708
$UCl_5(C_8H_{17})_3PO$	CH_2Cl_2	R–O	11,846, 10,671, 10,098, 7107, 6858, 6775, 6665
UCl_5,Ph_3PO	CH_2Cl_2–MeCN	O–Y	11,776, 10,608, 10,086, 7092, 6862, 6763, 6665
$UCl_5,SOCl_2$ (ref. 5)	$SOCl_2$	R	11,710, 10,360, 9325, 7220, 6850, 6765, 6675
$CsUCl_6$	MeCN	O–Y	11,831, 10,684, 10,123, 7015, 6862, 6776, 6684
$CsUCl_6$	$MeNO_2$	O–Y	11,585, 10,459, 9939, 7079, 6838, 6751, 6659
$CsUCl_6$	$POCl_3$	O–Y	11,508, 10,461, 9931, 7100, 6814, 6748, 6649
$CsUCl_6$	5M-Ph_2CO–CH_2Cl_2	R–O	11,587, 10,477, 9954, 7015, 6834, 6751, 6677

* R = Red, O = orange, Y = yellow.

5000 cm.$^{-1}$ is shown in Figure 3. The peak at about 7000 cm.$^{-1}$ is extremely weak and was previously overlooked [5] in the spectrum of $UCl_5,SOCl_2$ in thionyl chloride. All the spectra are characterised by a group of three very sharp, intense peaks between 6700 and 6900 cm.$^{-1}$ similar to those reported [8,9] for certain of the hexafluorouranates, between 7200 and 7500 cm.$^{-1}$. The relative intensities of these three peaks vary slightly from solution to solution.

Although cæsium hexachlorouranate(V) is virtually insoluble in methylene dichloride, it dissolves readily in mixtures of this solvent with acetophenone or benzophenone, the resulting solutions containing only uranium(V). No reaction analogous to that with R_3PO ligands, where cæsium chloride precipitates, is observed, although complex formation obviously occurs and differences in the absorption spectra of such solutions and those containing pentachloride complexes are apparent (Table 3). Attempts to isolate UCl_5,nPh_2CO by reaction of $UCl_5,SOCl_2$ with benzophenone in methylene dichloride were unsuccessful; some disproportionation was observed in each instance. Thus, the UCl_6^- species, as $CsUCl_6$, is more stable in methylene dichloride–ketone mixtures than $UCl_5,SOCl_2$. Cæsium hexachlorouranate(V) is also soluble in phosphorous oxytrichloride, methyl cyanide, and nitromethane. A small quantity of uranium(IV) was formed in the last two solvents, presumably owing to the presence of traces of water, and precipitated as Cs_2UCl_6.

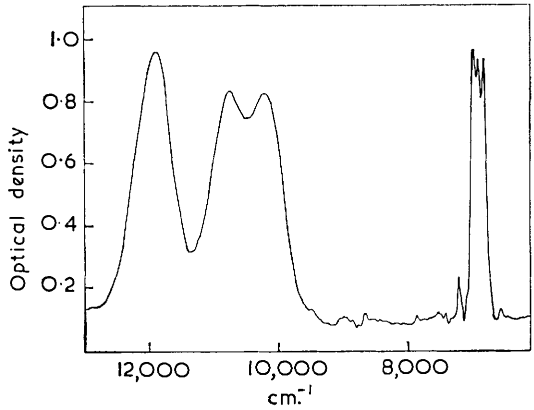

FIGURE 3. Absorption spectrum, in methylene dichloride, of a 0·2M-solution of UCl_5,Ph_3PO

Attempts to prepare uranium pentachloride complexes with other classes of oxygen-containing ligands were unsuccessful; disproportionation occurred to a greater or lesser extent when $CsUCl_6,CH_2Cl_2$ was treated with triphenylarsine oxide, pyridine *N*-oxide, dimethylacetamide (in each case CsCl was precipitated), dimethyl sulphone, diphenyl sulphone, ethyl acetoacetate, and acetylacetone ($CsUCl_6$ dissolved to some extent in these solvents). The reaction with dimethyl sulphoxide gave an insoluble yellow product which did not dissolve in methylene dichloride containing benzophenone, indicating that reaction had occurred. Owing to reaction between dimethyl sulphoxide and thionyl chloride, its reaction with $UCl_5,SOCl_2$ could not be attempted. Notable amongst the ligands which failed to furnish a stable complex is Ph_3AsO which, with molybdenum(V), forms[22] the complex $MoCl_5,Ph_3AsO$ whereas Ph_3PO gives only $MoOCl_3,2Ph_3PO$. Although repeated attempts were made to purify both the purchased ligand and material prepared as described in the literature[23] by repeated recrystallisation and even by heating at 160° in a vacuum, the authors still feel that it should be possible to prepare UCl_5,Ph_3AsO since hydroxyl stretching vibrations were detected in the infrared spectrum of the purified ligand.

EXPERIMENTAL

Materials.—Cæsium hexachlorouranate(V) was prepared as described previously;[5] benzyldiphenylphosphine oxide and octyldiphenylphosphine oxide were prepared by Dr. E. Lane (Chemistry Division, A.E.R.E., Harwell), and triphenylarsine oxide was obtained from Chemical Procurements Ltd. or made by an established method.[23] The remaining ligands were commercially available and were dried either under a vacuum or by contact with molecular sieves. Methylene dichloride (b. p. 39—41°) and phosphorus oxytrichloride (b. p. 105—106°) were dried by repeated distillation from phosphorus pentoxide in a nitrogen atmosphere. The former, and the remaining solvents, which were dried as described previously,[24] were stored on molecular sieves. Water determinations by the Karl Fischer method[25] indicated that the solvents contained less than 0·01% of water. Reactions were carried out in a dry argon atmosphere in a glove-box in which the moisture-sensitive products were prepared for analysis, infrared, magnetic susceptibility, *X*-ray diffraction, and spectral studies.

Preparations.—*Uranium pentachloride–triphenylphosphine oxide complex.* Excess of cæsium hexachlorouranate(V) (1·9 g.) was stirred with triphenylphosphine oxide (0·7 g.) in methylene dichloride (7 ml.) for about 30 min. The precipitated cæsium chloride and unreacted hexachlorouranate(V) were filtered or centrifuged off and the clear red solution either evaporated to dryness in a vacuum or added to isopentane. In the latter instance the resulting *complex* was vacuum-dried at room temperature (Found: U, 34·0; Cl^-, 25·35. UCl_5,Ph_3PO requires U, 34·32; Cl^-, 25·56%).

Uranium pentachloride–tri-n-octylphosphine oxide complex. This was prepared in the same way. After removal of excess of hexachlorouranate(V) and cæsium chloride the dark red solution was evaporated to dryness in a vacuum and the resulting orange-red oil was maintained at $40°/10^{-4}$ mm. for several hours [Found: U, 30·0; Cl, 21·7. $UCl_5(C_8H_{17})_3PO$ requires U, 29·7; Cl, 22·11%).

Analysis.—Uranium(V) and chloride were determined as described previously;[5] the precipitated uranium hydroxide was washed thoroughly with acetone to remove the ligand (L) and so prevent the formation of complexes, such as $UCl_4,2L$, on dissolving the hydroxide in hydrochloric acid prior to reduction on the lead column.

Physical Properties.—Magnetic susceptibilities were measured by the Gouy method, over the temperature range 89—305°K, on a balance described elsewhere.[26] Previously calibrated quartz tubes were filled in a dry-box and stoppered with Polythene bungs to exclude moisture during measurements. Visible spectra were measured, using 0·2M-uranium(V) solutions in 1-cm. stoppered cells, with an Optika CF 4 DR double-beam recording spectrometer (0·4—1 μ) and with a Unicam S.P. 700 spectrophotometer (0·7—2 μ). Infrared spectra were taken, for mulls in Nujol, on a Hilger H800 spectrometer; samples for spectra in the ranges 2—15 and 25—34 μ were mounted between potassium bromide and Polythene plates, respectively. Spectra below 34 μ were obtained using a vacuum grating instrument, the samples being mounted in wax discs.

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