$(C_6H_5)_4P[UOCl_5]$: a New Type of Uranium(VI) Oxochloro-complex

By KENNETH W. BAGNALL* and JAN G. H. DU PREEZ
(*Chemistry Department, The University of Manchester, Manchester* M13 9PL)

Summary The tetraphenylphosphonium salt, $Ph_4P[UOCl_5]$ has been obtained by reaction of $SOCl_2$ with either hydrated UO_2Cl_2 in the presence of Ph_4PCl or with $[Ph_4P]_2[UO_2Cl_4]$.

THE only known oxide chloride of U^{VI} is UO_2Cl_2, from which the complex anion $[UO_2Cl_4]^{2-}$ is derived. A trioxo-species, $M^I_2UO_3Cl_2$, is also known, but neither $UOCl_4$ nor anions derived from it have been recorded, although the corresponding fluoride, UOF_4, has recently been reported.[1]

In the reductive chlorination of hydrated UO_2Cl_2 with $SOCl_2$ in the presence of aryl phosphonium (or arsonium) chloride, which ultimately yields salts of the UCl_6^- anion, the $SOCl_2$ solution slowly becomes dark red at room temperature and, when Ph_4PCl is present, deep brick-red crystals of $Ph_4P[UOCl_5]$ separate slowly. Because of the low solubility of UO_2Cl_2 in $SOCl_2$, the compound is better prepared by allowing a concentrated solution of $[Ph_4P]_2[UO_2Cl_4]$ in $SOCl_2$ to stand at room temperature. A dark red solution is also formed initially when Ph_3PHCl, Ph_4AsCl, or Ph_3PhCH_2PCl are used instead of Ph_4PCl, but no solid product has yet been isolated. These red solutions become orange-yellow on standing; the electronic spectrum shows an increasing concentration of U^V with time, but no U^{IV}. Analysis of the solids precipitated from the orange-yellow solutions by 2-methylbutane confirmed that only U^V was present. Reduction to U^V is much faster at room temperature in the presence of Et_4NCl, Et_2NH_2Cl, or Bu^n_4NCl, and in these three instances no intermediate red colouration developed.

$Ph_4P[UOCl_5]$ was characterised by chemical analysis and it was shown by titration against $K_2Cr_2O_7$ in aqueous HCl that oxidation states lower than U^{VI} were absent. In the i.r. spectrum there is a strong feature at 838 cm^{-1} and a weak one at 928 cm^{-1} (*cf.* 940 cm^{-1} in the i.r. spectrum[2] of UOF_4) neither of which appear in the i.r. spectrum of $[Ph_4P]_2[UO_2Cl_4]$; the very strong asymmetric O–U–O stretching mode, which appears at 903 cm^{-1} in the spectrum of the latter, is absent in that of the former. In the corresponding green U^V compound,[2] $[Et_4N]_2[UOCl_5]$, the U–O stretching modes appear at 813 and 913 cm^{-1}, and it is reasonable to conclude that the 838 and 928 cm^{-1} features in the spectrum of the U^{VI} analogue arise from U–O vibrations. The U–Cl stretching mode in the new compound appears as a strong feature at 290 cm^{-1}, with shoulders at 280 and 300 cm^{-1}, as compared with 253 cm^{-1} (indications of shoulders at 245 and 265 cm^{-1}) in $[Ph_4P]_2$-$[UO_2Cl_4]$ and[2] 253 cm^{-1} (with side bands at 296 and 197 cm^{-1}) in $[Et_4N]_2[UOCl_5]$. The electronic spectrum of 0·1 M $Ph_4P[UOCl_5]$ in CH_2Cl_2 is featureless between 600 and 2000 nm.

$Ph_4P[UOCl_5]$ is hygroscopic and dissolves in water with immediate hydrolysis to UO_2^{2+}; it is soluble in most polar organic solvents and melts, with some decomposition, at 224° to a dark red liquid, in contrast to light yellow $[Ph_4P]_2$-$[UO_2Cl_4]$, which melts at 296—298° with charring.

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[1] P. W. Wilson, *J.C.S., Chem. Comm.*, 1972, **1241**.

[2] J. L. Ryan, *J. Inorg. Nuclear Chem.*, 1971, **33**, 153.