Novel Complexes of Uranium(V)

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Summary Several new complexes of formally quinquevalent uranium, all but one of which have the general formula UCl_5L_x, have been synthesized (the donor atoms in the organic ligands being N, P, As, S, Se, and Te) for which there is e.s.r. evidence suggesting that the lone U^V electron is strongly delocalized on to the unsaturated organic moiety, perhaps into π-antibonding MO's.

URANIUM(V) chemistry has been confined to a very limited number and type of compounds because of the extreme instability of this oxidation state relative to the four and six states.[1] Apart from UX_6^- (X = F or Cl), there were only seven examples of complexes of the UX_5L type known until now, the only donor atoms in these compounds being halogen and oxygen. We have extended the chemistry of uranium(v) to compounds containing ligands in which N, P, As, S, Se, and Te act as the donor atoms. The new compounds, listed in the Table, were characterized by elemental analyses (which support the stoicheiometries given), differential thermal analyses, magnetic susceptibilities (in cases where sufficient quantities were available for Gouy determinations), i.r., visible–u.v., and e.s.r. spectra.

The general preparative procedure for all of the new compounds is based upon the use as a starting material of UCl_5(tcac) the preparation of which we reported recently.[2] The ligand tcac, trichloroacrylyl chloride, $Cl_2C:CCl{\cdot}COCl$, co-ordinates to the U^V through the oxygen atom, but apparently so weakly that this ligand can be readily replaced by almost any other ligand, provided the latter does not react either with the tcac or with the U^V in a redox manner.

The UCl_5 tcac is dissolved in benzene, the solution is filtered, and then a benzene solution containing the ligand (in a 3 : 1 ligand : UCl_5 tcac mole ratio) is added with stirring. Immediate reaction occurs, the red colour of the UCl_5 tcac solution fading as a coloured precipitate deposits. Stirring is continued for several hours, followed by filtration and washing with benzene and CCl_4 or hexane. No recrystallization has been possible so far with any of the products since they are either insoluble in common organic solvents or dissolve with decomposition. They are dried *in vacuo* and stored under dry argon or nitrogen. All the preparative work and subsequent manipulations of these compounds must be carried out with rigorous exclusion of both oxygen and moisture.

TABLE

New uranium(v) *Compounds*[a]

Compound	Colour	M.p.	corr μ_{eff}	$<g>$[b]
UCl$_5$(pyrazine)$_2$	Yellow	133dec.	2·04	2·000
UCl$_5$(phthalazine)$_2$	Orange	230dec.	2·28	2·006
UCl$_5$ phenazine	Red-brown	215dec.	—	2·006
UCl$_5$ bipy . .	Gray	—	—	2·054
UCl$_5$Ph$_3$P	Med. green	>300[c]	—	2·008
UCl$_5$ diphos	Pale green	>300[d]	2·70	2·022
UCl$_5$Ph$_3$As[e]	Green	—	—	—
[UCl$_4$(PhS)]$_2$[f]	Gray	104dec.	—	1·990
UCl$_5$PhSeSePh	Yellow	57dec.	3·1	2·005
UCl$_5$PhTeTePh	Violet-black	151dec.	2·84	2·007
Pr$_4$NUCl$_6$[g]	Golden yellow	—	—	1·063
UCl$_5$ tcac[g]	Orange-red	147—149[h]	1·54	1·090
UCl$_5$SOCl$_2$[g]	Red-orange	—	—	1·106

[a] Abbreviations are: bipy = 2,2′-bipyridyl; diphos = ethylenebis(diphenylphosphine).

[b] All e.s.r. spectra had to be run on powdered samples.

[c] Starts to darken at 140°, becomes very dark at 242°.

[d] Darkens above 200°.

[e] Analyses indicate there are impurities in this compound, but it forms in the same way, has the same appearance as, and gives an optical spectrum like that of the analogous Ph$_3$P compound.

[f] Presumed to be a dimer due to its insolubility and the double signal found in the e.s.r. spectrum.

[g] Ref. 2. The SOCl$_2$ compound was reported earlier by H. Hecht, G. Jander, and H. Schlopmann, *Z. anorg. Chem.*, 1947, **254**, 255.

[h] Sealed-tube values.

The structures are not yet known for any of these new complexes, but presumably the U^V retains six-co-ordination in most of them although seven-co-ordination cannot be ruled out in certain cases, such as UCl$_5$ diphos, UCl$_5$ bipy, and the pyrazine and phthalazine compounds. In both the diphos and Ph$_3$P compounds, i.r. spectra rule out P–H bonds (no bands in the 2400 cm.$^{-1}$ region) and P=O bonds (no strong bands in the 1050—1100 cm.$^{-1}$ region not present in the free non-oxy-ligand). Thus we believe U–P bonds are indeed formed here, and not phosphonium salts or phosphine oxide compounds.

The most interesting results to be obtained so far for these compounds are from their e.s.r. spectra. We have already reported[2] the first e.s.r. spectra for U^V compounds (all as powders) three of which are listed last in the Table, and found the average *g* values to be *ca.* 1·1 (with sign undetermined). The signals were extremely broad (*ca.* 1200 Gauss). Yet for all of our new compounds, which have ligands containing aromatic systems, we find the average *g* values very close to the free-electron value, and furthermore the line-widths are quite narrow, ranging from 4—60 Gauss. The extreme broadness of the signal in the complexes which have ligands with no low-lying empty antibonding MO's suggests that the lone electron is very much confined to a highly localized 5*f*-orbital. The narrow signal in the case of the new complexes, plus the free-electron *g* value, suggests that the lone 5*f*-electron of the free U^V has been heavily delocalized on to the ligands and may spend (on the average) a great deal of time in the delocalized antibonding MO's of these molecules. The optical spectral data, to be reported later in a full paper and to be compared there with the previously obtained spectral data on U^V complexes,[2] support the idea that such delocalization is taking place. Indeed, there is a striking correlation between the clarity and detail of the optical spectra and the width of the e.s.r. signal. The smaller this width, the less clear and fewer in number are the optical bands. The optical spectra rule out all but trace amounts of U^{IV} compounds, and the analytical data and e.s.r. spectra, as well as mode of formation, support the formulation of these products as U^V compounds despite some seemingly incongruous magnetic susceptibility data. These matters will be dealt with in more detail in the full paper.

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[1] J. Selbin and J. D. Ortego, *Chem. Rev.*, 1969, **69**, in the press.

[2] J. Selbin, J. D. Ortego, and G. Gritzner, *Inorg. Chem.*, 1968, **7**, 966.