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Chemistry of the Trivalent Actinoids. Part 6 [1]. Uranium(III) Complexes with a Variety of Neutral, Oxygen-donor Ligands and Hexacyanoferrate(II)

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Few solid complexes of Uranium(III) with organic ligands have been isolated in a pure state; all are readily oxidised by atmospheric oxygen. The types of compound were summarised recently ([2] and referenced therein) and were (i) tetrakis-complexes with bidentate amides, (ii) the cyclopentadienyl $U(C_5H_5)_3$ and its adducts, (iii) an acetonitrile complex $UCl_3 \cdot MeCN$ and (iv) complexes with phenazones. Since then two complexes with a crown ether, $U(18\text{-crown-}6)Cl_3$ and $U(18\text{-crown-}6)_{3/4}[BH_4]_3$, have been reported. The present paper describes several new types of uranium(III) complexes and in particular shows that the phosphonates complex readily.

As before [2], the new complexes (Types 1–6, Table I) were prepared by dissolving the red [4] double chloride $NH_4UCl_4 \cdot 5H_2O$ in an ethanolic solution of the ligand and, where appropriate, adding to this an ethanolic solution of sodium tetraphenylborate or ammonium hexafluorophosphate. For some ligands, only hexafluorophosphate gave an analytically pure complex. With the crown ethers and cryptand-222, chlorides were sometimes precipitated before the addition of $Na[BPh_4]$ or $[NH_4][PF_6]$ and occasionally complexes containing chloride in addition to $[BPh_4]^-$ or $[PF_6]^-$ were obtained. These results are in agreement with our previous observations [1] for bi- and uni-dentate amides where difficulties in replacing co-ordinated chloride from $NH_4UCl_4 \cdot 5H_2O$ were experienced and with those of Moody, Penneman, and Salazar [3]. The complex $HU[Fe(CN)_6] \cdot 9\text{–}10H_2O$ was obtained by the addition of $K_4[Fe(CN)_6] \cdot 3H_2O$ in water to a solution of U^{III} in 0.3 *M* sulphuric acid prepared [5] by electrochemical reduction of U^{VI} at a mercury cathode.

TABLE I. New Complexes of Uranium(III).

1.	*Phosphonates*		
	(a) Tetraethylethylenediphosphonate (teep)		
	$[U(teep)_4][X]_3$	$[X] = [PF_6]$	red-mauve
		$[X] = [BPh_4]$	lilac-mauve
	(b) Tetraethyltrimethylenediphosphonate (temp)		
	$[U(temp)_3][PF_6]_3$		red
2.	*Octamethylpyrophosphoramide (ompa)*		
	$[U(ompa)_4][X]_3$	$[X] = [PF_6]$	red-brown
		$[X] = [BPh_4]$	pink
3.	*Diethyl N,N-dimethylcarbamoylmethylenephosphonate (cmp)*		
	$[U(cmp)_4][X]_3$	$[X] = [PF_6]$	red
		$[X] = [BPh_4]$	mauve
4.	*1,1′-methylenebis(pyrrolid-2-one) (mbpo)*		
	$[U(mbpo)_4][PF_6]_3$		red-purple
5.	*Crown Ethers*		
	$U(18\text{-crown-}6)Cl_3$		orange-brown
	$U(18\text{-crown-}6)_2[PF_6]_3$		orange-brown
	$U(\text{dicyclohexyl-}18\text{-crown-}6)Cl_2[BPh_4]$		pink
	$U(15\text{-crown-}5)Cl_3 \cdot H_2O$		red
6.	*Cryptand-222* $(C_{18}H_{36}N_2O_2)$		
	$U(\text{cryptate-}222)Cl_3$		black
	$U(\text{cryptate-}222)Cl_2[PF_6]$		mauve
7.	*Hexacyanoferrate(II)*		
	$HU[Fe(CN)_6] \cdot 9\text{–}10\ H_2O$		dark-green

Satisfactory analytical figures for the complexes listed in Table I were obtained except for U(cryptate-222)Cl$_3$ where low results were obtained but the C:N atomic ratio was 9:1 as expected. The complex precipitated before [NH$_4$]UCl$_4$·5H$_2$O had dissolved completely but a satisfactory product with [PF$_6$]$^-$ was obtained from the filtrate. All operations were performed in a nitrogen atmosphere and the complexes are readily oxidised by atmospheric oxygen.

There was no evidence for co-ordinated [PF$_6$]$^-$ (i.r. spectroscopy) but falls in the C=O ($\approx$35 cm^{-1}) and/or P=O ($\approx$30–60 cm^{-1}) stretching frequencies were observed on comparing the spectra of appropriate complexes with those of the free ligands. The complexes contained little or no uranium(IV) (no significant [4] absorption at 1475 nm) except for HU[Fe(CN)$_6$]·9–10H$_2$O for which a small degree of oxidation was apparent.

There were some interesting variations in stoichiometry with bidentate oxygen-donor ligands. 4,4′-Methylenebis[1,5-dimethyl-2-phenylpyrazol-3(2-*H*)-one] (mbp) yielded [1] [U(mbp)$_3$][X]$_3$ and 1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one (mppo) gave [4] [U(mppo)$_6$][BPh$_4$]$_3$ which are apparently six-co-ordinate with large f–f nephelauxetic shifts whereas the bidentate amides, *e.g.*, NNN′N′-tetramethylmalonamide (tmma) gave [U(tmma)$_4$][X]$_3$ and the 4-dimethyl amino-derivate of mppo gave a tetrakis complex with [BPh$_4$]$^-$ as counter-anion [4]. These differences are explainable in terms of steric hindrance by the 2-phenyl groups in mbp and mppo which would not be important with the 4-dimethylamino derivative. This conclusion is confirmed here for teep, ompa, cmp, and mbpo, which has no bulky substituent in the position corresponding to 2-phenyl in mbp and mppo, all yielded tetrakis-complexes. However, temp gave a 3:1 complex which was very much more hygroscopic than those derived from teep which would support the suggestion of a six-co-ordinate complex. For the bidentate amides [2] no such change in stoichiometry was observed on increasing the separation between the carbonyl groups but related changes are observed [6] in tmma complexes of the lanthanoid(III) ions so that size ratios are important.

With the crown ethers, satisfactory results were obtained for the 1:1 ligand to metal ion mol ratio but with the non-complexing [PF$_6$]$^-$ the previously unknown 2:1 ratio was found. Alkali metal cations give [7] this stoichiometry with dibenzo-18-crown-6. Dicyclohexyl-18-crown-6 gave a complex (not included in Table I) corresponding closely to [U(C$_{20}$H$_{36}$O$_6$)$_{3/4}$Cl$_3$] which is in tentative agreement with the report [3] of [U(18-crown-6)$_{3/4}$][BH$_4$]$_3$. With 15-crown-5 a monohydrate was precipitated but the 18-crown-6 complexes are anhydrous; a similar variation in composition has been reported [8] for lanthanoid(III) thiocyanate complexes of benzo-15-crown-5. Dicyclohexyl-24-crown-8 gave a red gum with U^{III} and [BPh$_4$]$^-$.

Cryptand-222 gave the usual 1:1 stoichiometry (Table I) and both complexes contain chloride.

The dark-green hexacyanoferrate(II), HU-[Fe(CN$_6$]·9–10H$_2$O is formulated from C, H, N and thermogravimetric analysis in a similar manner [9] to complexes reported for Pu^{III} and Am^{III}. The ultraviolet, visible, and near-i.r. electronic spectra were consistent for U^{III} and Fe^{II}. Over several months the compound decomposes *in vacuo* with the evolution of hydrogen to a yellow-green substance which has the same spectra as a compound prepared from U^{IV} and [Fe(CN)$_6$]$^{4-}$. On exposure to air over eight days, the dark-green complex gives a brown product which contains U^{IV} and Fe^{III}.

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