Protactinium(V) and Uranium(V) Tropolonates

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Penta(tropolonato)-protactinium(V) and -uranium(V), [Pa(trop)$_5$] and [U(trop)$_5$], have been prepared by reactions involving tropolone and the appropriate pentaethoxide in anhydrous benzene. Reactions between uranium pentachloride and an excess of tropolone in non-aqueous solvents have yielded chlorotetra(tropolonato)uranium(V), [U(trop)$_4$Cl]. Some physical and chemical properties of these complexes are reported and the UCl$_5$–tropolone reaction is discussed.

PROTACTINIUM(V) tropolonato-complexes of the type [Pa(trop)$_4$X] (X = Cl, Br, ClO$_4$, and OEt; Htrop = 2-hydroxycyclohepta-2,4,6-trien-1-one, tropolone) and [Pa(trop)$_4$Cl]·dmso (dmso = dimethyl sulphoxide) have been characterised previously [1] but the only uranium(V) tropolonate reported to date [2] is [UCl$_4$(trop)]·4Htrop. In view of the unusual composition of this uranium(V) complex and the paucity of data on uranium(V) tropolonates, the U(OEt)$_5$– and UCl$_5$–tropolone reactions have been investigated in an attempt to characterise [U(trop)$_5$] and new chlorouranium(V) tropolonates. During the course of these studies it became apparent that the previously reported [Pa(trop)$_4$(OEt)] had been incorrectly characterised and further work on the protactinium(V)–tropolone system was undertaken to clarify the situation.

RESULTS AND DISCUSSION

Pentakis(tropolonato)-protactinium(V) *and -uranium*(V).—The reaction between tropolone (Htrop) and U(OEt)$_5$ in anhydrous, oxygen-free benzene (>5 : 1 mol ratio of reactants) at room temperature yielded an immediate black precipitate of pentakis(tropolonato)uranium(V), [U(trop)$_5$], which is completely insoluble in this solvent. Attempts to convert [U(trop)$_4$] to [U(trop)$_5$] or [U(trop)$_4$Br] by bromine oxidation in chloroform containing Htrop were unsuccessful. The complex [U(trop)$_5$] is stable in contact with refluxing benzene (5 h) provided the solvent is perfectly anhydrous and oxygen free. Traces of water result in decomposition to a reddish brown, unidentified product and Htrop. In wet acetone the decomposition occurs much faster. Pentakis(tropolonato)uranium(V) does not dissolve in or react with carbon disulphide; the addition of chloroform, however, results in formation of a brown solution, the spectrum of which is identical with that of [U(trop)$_4$] in the same solvent. Similar decomposition appears to occur on addition of methylene dichloride, nitromethane, methyl cyanide, and *NN*-dimethylformamide.

The *X*-ray powder pattern of [U(trop)$_5$] was found to be identical with that previously recorded [1] for [Pa(trop)$_4$(OEt)] and, since the analytical results for the former complex were reproducibly close to theoretical, it was necessary to reinvestigate the protactinium(V) complex which had been obtained during attempts to prepare [Pa(trop)$_5$] from relatively small-scale reactions involving [Pa(trop)$_4$Cl] and Li(trop) in ethanol. With larger-scale preparations using an improved micro-analytical technique for the determination of carbon in radioactive compounds, together with a gravimetric method to determine protactinium rather than compound dissolution followed by α spectrometry, we have now shown that the complex previously believed to be [Pa(trop)$_4$(OEt)] is in fact [Pa(trop)$_5$]. It was obtained when Pa(OEt)$_5$ was treated with Htrop in anhydrous benzene, and when [Pa(trop)$_4$] and an alcoholic solution of Htrop were exposed to the atmosphere to induce oxidation of the protactinium(IV) complex.

It now appears that the extra bands in the i.r. spectra of both [Pa(trop)$_5$] and [U(trop)$_5$] relative to the spectra of actinoid(IV) tropolonates (*viz.* 1 100, 1 055, 915, 905, and 860 cm^{-1}; see Table 1) are not, as previously believed,[1] associated with an ethoxo-group but are probably due to the presence of one uniquely bonded Htrop molecule. This inference is substantiated to some extent by the chemical behaviour of [Pa(trop)$_5$]. Thus reactions previously attributed to [Pa(trop)$_4$(OEt)]

TABLE 1

I.r. spectral results (4 000—700 cm^{-1})

[Pa(trop)$_5$]	Tentative assignment *	[U(trop)$_4$]
1 593s	C=O stretch	1 596s
1 518s	C=C stretch	1 518s
1 465m		1 472m
1 435s	C–C stretch	1 432s
1 410s		
1 340s		1 355s
1 249w	C–H in-plane def.	1 252w
1 232(sh)		1 236(sh)
		1 230m
1 222m		1 221(sh)
1 100m	C–C–C def., comb. mode	1 078vw
1 055m		
		1 020vw
970w		974m
924w		925w
915w		
905w		
875m	C–C–C ring def., overtone	878m
860w		
765(sh)	C–H out-of-plane def., C–C stretch	776(sh)
750(sh)		755(sh)
736m		734m
729m		
706m		710m

* Based on previous i.r. and Raman results; [3] s = strong sh = shoulder, m = medium, w = weak, and vw = very weak.

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[1] D. Brown and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 3373.

[2] J. Selbin, N. Ahmad, and M. J. Pribble, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3249.

[3] Y. Ikegami, *Bull. Chem. Soc. Japan*, 1961, **34**, 94.

include those with aqueous HCl– and aqueous $HClO_4$–acetone mixtures which yield [Pa(trop)$_4$Cl] and [Pa(trop)$_4$-(ClO_4)], respectively. The i.r. spectra of these products do not contain the extra bands mentioned above. The complex [Pa(trop)$_5$] is appreciably more stable than its uranium analogue, being unaffected by cold water and 1M-HCl. It is insoluble in benzene, carbon tetrachloride, diethyl ether, and 2-methylbutane and has only a very limited solubility in methyl cyanide and nitromethane. It is decomposed by hot 8M-HNO_3.

Chlorouranium(V) *Tropolonates*.—Uranium pentachloride reacted exothermically with Htrop in oxygen-free, anhydrous benzene or carbon tetrachloride to yield insoluble dark brown to black products. Our first set of investigations were quite irreproducible, yielding apparently different products under identical conditions; in addition, many of these products had non-integral Cl : U ratios. Furthermore, with a large excess of Htrop over UCl_5 (10 or 12 : 1 mol ratios) it appeared that fewer chlorine atoms were replaced than in reactions involving 4 or 5 : 1 mol ratios of reactants and in one instance (10 : 1 mol ratio) the product had a composition close to [UCl_4(trop)]·4Htrop, *i.e.* the same as the compound reported by Selbin *et al.*[2] Such observations are at variance with results obtained[1] for the $PaCl_5$–Htrop reaction which, with an excess of Htrop, resulted in formation of [Pa(trop)$_4$Cl] initially contaminated by unidentified impurities. The latter could be removed by washing the product with acetone, ethanol, or water, a procedure which could not be employed in the case of the uranium(V) products because of their ready decomposition.

The apparent differences between the UCl_5– and $PaCl_5$–Htrop reactions and the irreproducibility in the former system have been traced to the formation of tropolone hydrochloride from the reaction between the liberated hydrogen chloride and some of the added Htrop. Reactions between Htrop and HCl gas in benzene or carbon tetrachloride gave an immediate precipitate of white tropolone hydrochloride which is almost totally insoluble in these solvents. Thus, the irreproducible analytical results obtained in our initial experiments were due in part to this insolubility and to the time for which the products had been vacuum dried, since the hydrochloride has a sufficiently high vapour pressure for it to be removed at *ca.* 17 mg h^{-1} on continuous pumping at 10^{-4} Torr, partly as unchanged hydrochloride and as Htrop and HCl gas.*

Following these observations it was shown that the reaction between Htrop and UCl_5 (10 : 1 mol ratio) in oxygen-free, anhydrous benzene or carbon tetrachloride followed by vacuum drying of the product to constant weight (*ca.* 50 h) yields pure [U(trop)$_4$Cl] which is isostructural with the protactinium(V) analogue. It was also shown in control reactions that the 'molecular-weight' changes (based on uranium assays) and the changes in Cl : U ratios during this vacuum treatment were consistent with the removal of between 2·3 and 2·6 molecules of tropolone hydrochloride from the initial product, *i.e.* [U(trop)$_4$Cl]·2·3—2·6(Htrop·HCl).

The amount of tropolone hydrochloride formed in a given reaction will obviously vary with factors such as volume of solvent, rate of addition, temperature, stirring, *etc.* and the observation that one of our earlier products not vacuum 'dried' to constant weight had a composition close to [U(trop)Cl_4]·4(Htrop) was probably fortuitous. However, using UCl_5 in place of [UCl_5]·tcac (tcac = trichloroacryl chloride) we repeated the experiment of Selbin *et al.*[2] (5 : 1 ratio Htrop : UCl_5 in benzene) and obtained initial products (vacuum dried for only 2 h) of 'composition' [U(trop)Cl_4]·4(Htrop) (*e.g.* Found: U, 23·7; Cl, 13·7. Calc.: U, 24·05; Cl, 14·35%). These products, however, lost weight on prolonged vacuum 'drying'; the composition of the final material at constant weight was variable suggesting that the initial products were mixtures of chlorouranium(V) tropolonates and tropolone hydrochloride rather than [U(trop)Cl_4]·4(Htrop). This was confirmed by *X*-ray powder-diffraction analysis of the initial products, the films containing lines due to tropolone hydrochloride which were not present after drying to constant weight.

Physical Properties.—The complexes [U(trop)$_5$] and [U(trop)$_4$Cl] are isostructural with [Pa(trop)$_5$] and [Pa(trop)$_4$Cl], respectively, for which *X*-ray powder-diffraction data were published previously.[1] The i.r. spectra of [Pa(trop)$_5$] and [U(trop)$_5$] were virtually identical; details for the former (4 000—700 cm^{-1}) are given in Table 1 together with tentative assignments. Comparison with the i.r. results for [U(trop)$_4$] (Table 1) identifies those bands previously believed to be due to the presence of an ethoxide group in the supposed [Pa(trop)$_4$(OEt)]. The C=O (1 588—1 593 cm^{-1}) and C=C (1 518—1 523 cm^{-1}) vibrations for the actinoid(V) tropolonates occur close to those recorded previously for tetra- and penta-(tropolonates) of the types [M(trop)$_4$] and Li[M(trop)$_5$], respectively (M = actinoid element), the positions being appreciably different from those observed for Htrop itself (1 613 and 1 548, respectively) but at only slightly lower frequencies than observed for Li(trop) and Na(trop).

The i.r. spectra of the penta(tropolonato) complexes and the tetra(tropolonato) chlorides were quite different from that of Htrop in the region 525—100 cm^{-1} as illustrated in the Figure where the spectra of [U(trop)$_5$] and Htrop are compared. The features at *ca.* 200 cm^{-1} are very similar to those observed[4] in the spectra of actinoid(IV) tetra(pentane-2,4-dionates) and are tentatively assigned to M–O vibrations. In the absence of a full co-ordinate analysis it is not possible to decide whether there is any M–O vibration contribution to the apparently new band at 500 cm^{-1} in the spectra of the metal(V) tropolonates. A similar band appears in the spectra of actinoid(IV) tetra- and penta-(tropolonato) complexes (490—498 cm^{-1}) and in the spectrum of

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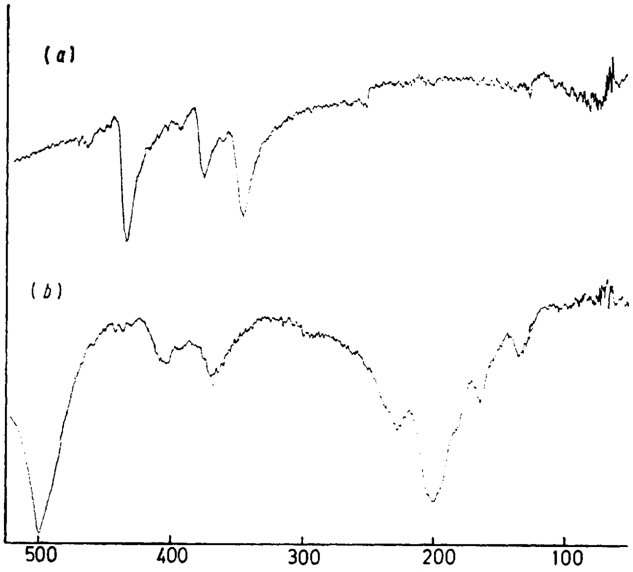
* 1 Torr = (101 325/760) Pa, 1 mmHg ≈ 13·6 × 9·8 Pa.

[4] D. Brown, B. Whittaker, and J. Tacon, *J.C.S. Dalton*, 1975, 34.

$[Nd(trop)_3]$ (481 cm^{-1}) but not in that of Na(trop).[1] The positions of bands in the spectra of $[U(trop)_5]$ and $[U(trop)_4Cl]$ are shown in Table 2 together with the results for $[U(trop)_4]$ and Htrop.

Due to ready decomposition of $[U(trop)_5]$ in most common organic solvents, we were unable to obtain visible–near-i.r. solution spectra. The solid-state transmission and reflectance spectra of $[U(trop)_4Cl]$ and $[U(trop)_5]$ both contained only three bands in the region 4 760—13 000 cm^{-1} with no features attributable to uranium(IV) species. The strongest band in each instance occurred at *ca.* 6 500 cm^{-1} (Table 3), a position close to those reported[5] for bands characteristic of a wide range of uranium(V) complexes of varying stereochemistries and assigned in the case of octahedral species to the Γ_7–Γ_7' transition. No bands could be observed above *ca.* 11 000 cm^{-1} for the uranium(V) tropolonates due to very strong absorption which started at approximately this wavelength and it is not possible to make any deduction regarding the stereochemistry of the complex from our spectral results.



I.r. spectrum of (*a*) tropolone and (*b*) $[U(trop)_5]$

TABLE 2

I.r. spectral results [a] in the region 525—50 cm^{-1}

$[U(trop)_5]$	$[U(trop)_4Cl]$ [b]	$[U(trop)_4]$	Htrop
498s	502s	500s	434s
405w,b	405w,b	404m	375w
367w,b		390(sh)	345m
228w [c]			
200s [c]	212s [c]	212s [c]	
182(sh) [c]	190(sh),b	185(sh),b [c]	
165w [c]			
135w [c]	145w,b [c]	135w [c]	
		112w,b	

[a] b = Broad. [b] A medium broad feature was also observed at 300 cm^{-1}. [c] Tentatively assigned to M–O vibrations.

TABLE 3

Electronic spectra ($\bar{\nu}$/cm^{-1})

$[U(trop)_5]$	$[U(trop)_4Cl]$
6 451s,b	6 518s,(sh)
	6 622s,(sh)
7 812m,b	7 418m,b
9 389m,b	8 474m,b

sh = Sharp.

EXPERIMENTAL

All preparative work was done in inert-atmosphere glove-boxes (oxygen and water content each <20 p.p.m.) because of the radioactive hazards associated with weighable amounts of protactinium-231 and the sensitivity of the uranium(V) complexes to moisture and oxygen. Samples were dispensed for analysis and for the various chemical and physical studies in such boxes.

Materials.—Uranium pentaethoxide,[6] uranium pentachloride,[7] and protactinium pentachloride[8] were prepared by the published methods. In addition, $U(OEt)_5$ was prepared by reactions between $Cs[UCl_6]$ and Na(OEt) in refluxing benzene, the product being isolated by distillation (140 °C) under reduced pressure (0·06 mmHg) [Found: C, 23·4; H, 5·3; U, 50·0. Calc. for $U(OEt)_5$: C, 25·9; H, 5·4; U, 51·4%], yield 63%. Commercially available tropolone (Aldrich Chemicals) was recrystallised several times from 2-methylbutane (m.p. 48—50 °C). Ethanol was purified and dried by heating under reflux over freshly ignited quicklime, followed by distillation, a further distillation from sodium ethoxide, and finally azeotropic distillation from benzene. Benzene was contacted with sodium wire for 2 d, heated under reflux over sodium metal, distilled, and dried azeotropically with ethanol. Methyl cyanide was purified as described previously.[9] All solvents were deoxygenated by flushing with high-purity nitrogen and stored in contact with degassed molecular sieves (type 5A) in inert-atmosphere glove-boxes.

Analysis.—Complexes were hydrolysed by treatment with aqueous ammonia–acetone mixtures, chloride being precipitated as the silver(I) salt after acidification of the supernatant with dilute HNO_3. It was shown in separate experiments that tropolone (Htrop) did not interfere under these conditions. However, if the uranium(V) complex was first dissolved in 8M-HNO_3 an orange precipitate formed together with AgCl on the addition of $AgNO_3$. Uranium and protactinium were determined by ignition to U_3O_8 and Pa_2O_5, respectively, after the destruction of weighed samples by repeated treatment with hot concentrated HNO_3. Carbon and hydrogen were determined by microanalytical techniques; in the case of $[Pa(trop)_5]$, 10 mg samples were used. The analytical results are summarised in Table 4.

TABLE 4

Analytical results (%)

	Found				Calc.			
Complex	M	C	H	Cl	M	C	H	Cl
$[U(trop)_5]$	27·8	49·6	3·5		28·2	49·8	3·0	
$[Pa(trop)_5]$	27·5	50·1			27·6	50·2		
$[U(trop)_4Cl]$	30·9	43·2		4·6	31·4	44·3		4·7

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[5] J. Selbin and J. D. Ortego, *Chem. Rev.*, 1969, **69**, 657.

[6] R. G. Jones, E. Bindschadler, G. Karmas, F. A. Yoeman, and H. Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 4287.

[7] D. Brown, P. Lidster, S. P. Stocks, and B. Whittaker, unpublished work.

[8] D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 874.

[9] D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 247.

Penta(tropolonato)uranium(V).—The complex $U(OEt)_5$ in anhydrous, oxygen-free benzene (0·63 g; 5 cm^3) was added dropwise to a benzene solution (5 cm^3) of Htrop (0·82 g) and the mixture was stirred and allowed to stand for *ca.* 1 h. The fine, black *product* was isolated by filtration, washed with anhydrous, oxygen-free benzene (5 × 1 cm^3), and vacuum dried (10^{-4} Torr) at room temperature, yield >95%.

Penta(tropolonato)protactinium(V).—Sodium ethoxide (0·022 g) in ethanol (1·3 cm^3) was added to $PaCl_5$ (0·07 g) and the mixture allowed to stand for *ca.* 1 h. The ethanol was removed by vacuum evaporation and the penta-ethoxoprotactinium(V) [10] extracted from sodium chloride into benzene (1 cm^3). Addition of an excess of Htrop (0·125 g) caused an immediate red colouration in the benzene following which the yellow *product* precipitated rapidly. The mixture was allowed to stand overnight and the product was then isolated by centrifugation, washed with benzene, and vacuum dried at room temperature, yield >95%.

Chlorotetra(tropolonato)uranium(V).—An excess of Htrop (10 : 1 mol ratio; 1·8 g) dissolved in either oxygen-free, anhydrous benzene or carbon tetrachloride (5 cm^3) was added to UCl_5 (0·620 g) in the same solvent (5 cm^3). The mixture was stirred well and allowed to stand overnight, following which the dark brown *product* was isolated by centrifugation and washed with benzene to remove excess of Htrop. Tropolone hydrochloride in the product was removed by prolonged pumping at 10^{-4} Torr (*ca.* 50 h), yield 90%. The loss of weight on pumping and the analytical results before and after pumping indicated that between two and three molecules of tropolone hydrochloride were present in the initial product.

Physical Measurements.—I.r. spectra, electronic spectra, and *X*-ray powder-diffraction photographs were recorded as described previously.[11]

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