Nature of the Dioxobis(tropolonato)uranium(VI) System and its Complexes with Neutral Ligands. Crystal and Molecular Structure of Dioxo(pyridine)bis(tropolonato)uranium(VI)

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Uranyl tropolonato-complexes, of general formula UO_2t_2 and $UO_2t_2.xH_2O$ (Ht = tropolone) have been prepared. Physical properties are discussed and structures suggested. Their reactivities were tested by preparing adducts with a series of neutral ligands L (L = methanol, water, dimethyl sulphoxide, pyridine *N*-oxide, triphenylphosphine oxide, cyclohexanone, pyridine, and aniline). The crystal structure of the pyridine (py) adduct UO_2t_2(py) has been determined by *X*-ray diffraction methods by the heavy-atom method from counter data on 3252 reflections, and refined to *R* 0·058 by a full-matrix least-squares procedure. The monoclinic unit cell, space group *I*2/*a* (standard cell *C*2/*c*), has dimensions $a = 17{\cdot}88(1)$, $b = 12{\cdot}69(1)$, $c = 16{\cdot}79(1)$ Å, $\beta = 98{\cdot}32(10)°$ for $Z = 8$. The molecule has approximately C_{2v} symmetry. Two tropolonato-groups and the pyridine ligand are displaced slightly from the plane perpendicular to the linear uranyl group. The U–O(uranyl) distances are 1·78 and 1·79 Å; the four U–O(eq) distances are almost equal (2·37—2·38 Å) and U–N(py) is 2·61 Å.

CHELATES formed between tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one = Ht) and a wide range of elements are known.[1-7] In particular, the ability of tropolone to form very stable solid complexes with the uranyl(VI) ion in the ratios 2 : 1 and 3 : 1 has been pointed out,[8] but there is little information beyond the nature and co-ordination number of uranium in the 2 : 1 compound UO_2t_2.

Recently Plymale and Smith[9] prepared a compound of formula UO_2t_2 by drying *in vacuo* at 80 °C the product isolated from reaction in methanol between stoicheiometric amounts of uranyl salts and tropolone. The reddish orange compound which was hygroscopic, was characterized by several preliminary physicochemical measurements and was shown to be apparently monomeric by determination of the molecular weight in dimethyl sulphoxide solution.

We have repeated that preparation, with the same experimental conditions, and obtained the methanol adduct [UO_2t_2(MeOH)]. A non-hygroscopic product having elemental analysis fitting the formula UO_2t_2 (I), but an i.r. spectrum significantly different from that reported,[1] was obtained by drying the methanol adduct at *ca.* 140 °C *in vacuo*. The product reported in ref. 9 is different too from the [UO_2t_2(MeOH)] adduct as shown later.

By varying the experimental conditions and/or the starting materials, the same product, as small red microcrystals, and a yellow one (II) containing water were obtained. Since these compounds are virtually insoluble in all solvents that do not react with them, their physicochemical characterization was carried out by i.r. spectra, *X*-ray powder diffraction, and elemental and thermogravimetric analysis in the solid state. Their reactivities were investigated by the preparation of adducts with a series of neutral ligands (L) where L is either an oxygen donor (methanol, water, dimethyl sulphoxide, pyridine *N*-oxide, triphenylphosphine oxide, and cyclohexanone) or a nitrogen donor (pyridine or aniline). We report the crystal structure of the pyridine complex.

EXPERIMENTAL

Materials.—Reagent-grade uranyl nitrate and cyclohexanone were used without further purification. Commercial dimethyl sulphoxide, methanol, pyridine, aniline, and benzene were distilled before use. Pyridine *N*-oxide and triphenylphosphine oxide were prepared as described in refs. 10 and 11. Tropolone (Aldrich Chemicals) was recrystallized several times from isopentane (m.p. 48—50 °C).

Instruments.—I.r. (4000—400 cm^{-1}): Perkin-Elmer 337 and 621 spectrophotometers; visible and u.v.: Optica CF4R spectrophotometer; molecular weight: Mechrolab thermoelectric osmometer; density determinations: Mohr–Westphal balance; thermogravimetric analysis: Vacuum Mettler Analyser; *X*-ray powder spectra: Siemens automatic powder diffractometer. I.r. measurements were carried out with KBr discs or Nujol mulls, and electronic spectra in 1 cm quartz cells.

Dioxo(methanol)bis(tropolonato)uranium(VI).—A stoicheiometric quantity of tropolone in methanol was added to a solution of uranyl nitrate hexahydrate in methanol and the resulting mixture was stirred for *ca.* 2 h. The reddish orange microcrystalline solid which formed was washed with methanol, recrystallized (methanol), and dried *in vacuo*.

Dioxobis(tropolonato)uranium(VI), (I).—A sample of [UO_2t_2(MeOH)] when heated at 150 °C for 2 h *in vacuo*

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yielded a non-hygroscopic, red, very thin microcrystalline powder, which when heated under reflux in benzene, formed brilliant red microcrystals after *ca.* 30 h. (All attempts to grow single crystals suitable for *X*-ray analysis were unsuccessful.) The same product was obtained from (II), but without heating at 150 °C *in vacuo*.

Dioxobis(tropolonato)uranium(VI),xH$_2$O, (II).—Samples of (I) or of the various uranyl tropolonato-complexes (see later) were digested in benzene (H$_2$O *ca.* 0·02%) for several hours at room temperature. The yellow-orange flocculent product was washed with benzene and dried *in vacuo*.

Preparation of Addition Complexes.—In general the adducts were prepared by reaction of (I) or (II) with an excess of the appropriate ligand. In particular, the complexes with dimethyl sulphoxide, pyridine, aniline, and cyclohexanone were obtained by dissolving the starting materials in the liquid ligands at room temperature and removing the excess of ligand *in vacuo*. Triphenylphosphine and pyridine *N*-oxide complexes were obtained on treating (I) or (II) with concentrated solutions of the ligands in anhydrous benzene. The solids obtained on concentrating the resulting solutions were rapidly washed with benzene and then dried *in vacuo*. [UO$_2$t$_2$(H$_2$O)] was obtained by heating the starting materials under reflux in water. The same adducts were obtained from [UO$_2$t$_2$(MeOH)] by analogous experimental procedures. Uranium was determined gravimetrically as the tetraphenylarsonium salt of uranyl (2,6-dipicolinate).[12] Water content was determined thermogravimetrically. Analytical data are reported in Table 1.

TABLE 1

Analytical data (%) for the complexes

		U	C	H	N	S	H$_2$O
(I) (UO$_2$t$_2$)$_n$	Found	46·6	32·7	2·0			0
	Calc.	46·48	32·81	1·95			0
(II) (UO$_2$t$_2$,xH$_2$O)$_n$	Found	44·5	32·0	2·3			3·6
			30·9	2·2			2·6
			31·8	2·4			3·65
			32·05	2·1			2·5
	Calc.	44·9	31·69	2·2			3·39
[UO$_2$t$_2$(H$_2$O)]	Found	44·65	31·3	2·3			3·4
	Calc.	44·90	31·69	2·26			3·39
[UO$_2$t$_2$(MeOH)]	Found	43·75	33·1	2·55			
	Calc.	43·74	33·00	2·57			
[UO$_2$t$_2$(Me$_2$SO)]	Found	40·3	33·0	2·8		5·45	
	Calc.	40·32	32·53	2·71		5·42	
[UO$_2$t$_2$(Ph$_3$PO)]	Found	29·95	49·0	3·1			
	Calc.	30·10	48·60	3·16			
[UO$_2$t$_2$(pyNO)]	Found	39·3	37·45	2·6	2·25		
	Calc.	39·20	37·55	2·47	2·30		
[UO$_2$t$_2$(cyclohexanone)]	Found	39·1	39·65	3·35			
	Calc.	39·01	39·01	3·28			
[UO$_2$t$_2$(py)]	Found	40·25	38·65	2·6	2·4		
	Calc.	40·26	38·58	2·54	2·37		
[UO$_2$t$_2$(aniline)]	Found	39·4	40·0	2·95	2·35		
	Calc.	39·34	39·67	2·81	2·31		

Crystal Structure Determination of UO$_2$t$_2$(py)

Crystal Data.—C$_{19}$H$_{15}$NO$_6$U, $M = 591$, Monoclinic, $a = 17·88(1)$, $b = 12·69(1)$, $c = 16·79(1)$ Å, $\beta = 98·32(10)°$, $U = 3764$ Å^3, $D_c = 2·09$, $Z = 8$, $D_m = 2·08$, $F(000) = 2208$, Mo-K_α radiation, $\lambda = 0·7107$ Å, μ(Mo-K_α) = 109 cm^{-1}. Space group $I2/a$ ($C2/c$ standard cell) from systematic absences: hkl when $h + k + l$ is odd, $h0l$ when h is odd, with the following equivalent positions: $\pm(x, y, z)$; $\pm(\frac{1}{2} - x, y, \bar{z})$; $\pm(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$; $\pm(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$.

Bright-red prismatic crystals (elongated along *b*) were obtained from pyridine. A fragment of dimensions 0·01 × 0·02 × 0·01 cm was used for the measurements. Approximate unit-cell parameters and the space group were determined from preliminary oscillation, Weissenberg, and precession photographs. Accurate values of the cell constants were derived by the method of least squares from 20 angle data recorded on a diffractometer.

Intensity Data.—The selected crystal was mounted with the [010] direction parallel to the ϕ axis of the goniometer. 3252 Independent reflections were collected on a computer-controlled Siemens AED., by the θ—2θ scan technique and the five-point measuring procedure, by use of zirconium-filtered Mo-radiation up to $\theta_{\text{max.}}$ 25°. 1085 Reflections having $I \leqslant 2\sigma(I)$ were considered unobserved and were given zero weight in the refinement. No absorption correction was applied. All calculations were performed with a CDC 6600 computer with programmes of ref. 13. Atomic scattering factors were taken from ref. 14. For uranium, the correction for anomalous scattering was applied.[15]

Structure Determination.—The structure was solved by the heavy-atom method. The uranium atom was correctly located from a sharpened Patterson function; remaining non-hydrogen atoms were successively located in subsequent three-dimensional electron-density maps. Refinement by full-matrix least-squares, with isotropic thermal parameters and $w = 1$, reduced R to 0·12. A weighting scheme of the form $w = \{1 + [(F_o - b)/a]^2\}^{-1}$ was introduced, the function minimized being $w(|F_o| - |F_c|)^2$; a and b were adjusted to 250 and 200 respectively. At this stage uranium and co-ordinated atoms were allocated anisotropic thermal parameters. Refinement proceeded until parameters shifts in both atomic positional and thermal parameters were $< 0·1\sigma$, those of the uranium atom being considerably less. The structure converged

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[15] Ref. 14, p. 216.

to the final R of 0·058, the weighted factor, R', being 0·066. (An attempt to refine all atoms anisotropically produced no significant changes either in the parameters of the co-ordinated atom or in the reliability factor.) A difference map computed after the final round of least-squares refinement revealed no significant peaks, and it was impossible to locate the hydrogen atoms. There was no evidence for disorder in the structure.

Final atomic positional and thermal parameters are given in Table 2, with least-squares estimated standard deviations, and bond distances and angles in Tables 3 and 4. Planes were calculated through each of the three ligands within the molecules, and the equations are given in Table 5. Intra- and inter-molecular contacts <4 Å are listed in Table 6. Observed and calculated structure factors are listed in Supplementary Publication No. 21001 (7 pp.).*

TABLE 2

Atomic fractional co-ordinates ($\times 10^4$) and thermal parameters, U (Å$^2 \times 10^2$), with estimated standard deviations in parentheses

	x	y	z	U
U	5670(1)	−257(1)	3347(1)	*
O(1)	5136(7)	−946(12)	2527(8)	*
O(2)	6169(7)	458(11)	4169(8)	*
O(3)	5068(6)	−1286(11)	4255(8)	*
O(4)	6276(7)	−1867(11)	3793(8)	*
O(5)	6772(6)	−290(12)	2700(8)	*
O(6)	5815(7)	1190(12)	2490(8)	*
N	4422(7)	771(13)	3454(9)	*
C(1)	4246(11)	1636(16)	3004(12)	5·1(4)
C(2)	3774(14)	2175(19)	3044(15)	5·2(6)
C(3)	3084(12)	1852(17)	3561(13)	5·3(5)
C(4)	3268(11)	994(16)	4016(12)	4·6(5)
C(5)	3954(11)	425(16)	3978(12)	5·2(5)
C(6)	6048(9)	−2521(13)	4295(10)	3·8(4)
C(7)	6445(12)	−3437(18)	4522(13)	6·4(5)
C(8)	6319(11)	−4259(18)	5069(12)	5·4(5)
C(9)	5743(11)	−4308(17)	5536(12)	6·2(5)
C(10)	5116(13)	−3612(18)	5554(14)	5·9(6)
C(11)	4958(10)	−2696(15)	5153(10)	4·7(4)
C(12)	5339(10)	−2152(14)	4575(11)	4·2(4)
C(13)	6426(11)	1333(16)	2151(12)	4·4(4)
C(14)	6481(14)	2305(19)	1698(15)	5·6(6)
C(15)	7061(12)	2579(17)	1261(13)	6·2(5)
C(16)	7763(15)	2081(21)	1194(16)	6·7(7)
C(17)	8027(13)	1108(18)	1526(14)	6·2(6)
C(18)	7673(12)	415(18)	1977(13)	5·0(5)
C(19)	6962(9)	478(13)	2254(10)	4·2(4)

* Anisotropic thermal parameters, U_{ij} (Å$^2 \times 10^4$) in the form: $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	388(4)	432(4)	470(4)	13(4)	175(3)	18(5)
O(1)	542(83)	759(101)	581(76)	−162(73)	186(64)	170(71)
O(2)	494(70)	700(108)	566(71)	−137(67)	153(56)	−5(66)
O(3)	401(63)	557(88)	606(75)	62(60)	264(56)	83(65)
O(4)	579(74)	580(86)	579(81)	26(63)	294(63)	126(66)
O(5)	424(63)	725(84)	709(80)	99(70)	405(59)	144(79)
O(6)	370(66)	815(98)	595(77)	160(64)	232(58)	225(68)
N	319(68)	494(95)	442(84)	−56(67)	137(61)	−89(74)

TABLE 3

Bond distances (Å), with estimated standard deviations in parentheses

U–O(1)	1·79(1)	N–C(1)	1·34(3)
U–O(2)	1·78(1)	C(1)–C(2)	1·39(3)
U–O(3)	2·38(1)	C(2)–C(3)	1·38(4)
U–O(4)	2·38(1)	C(3)–C(4)	1·34(3)
U–O(5)	2·38(1)	C(4)–C(5)	1·43(3)
U–O(6)	2·37(1)	C(5)–N	1·37(3)
U–N	2·61(1)	O(3)–C(12)	1·29(2)
O(5)–C(19)	1·30(2)	O(4)–C(6)	1·29(2)
O(6)–C(13)	1·31(3)	C(6)–C(7)	1·38(3)
C(13)–C(14)	1·46(3)	C(7)–C(8)	1·43(3)
C(14)–C(15)	1·40(3)	C(8)–C(9)	1·38(3)
C(15)–C(16)	1·42(3)	C(9)–C(10)	1·43(3)
C(16)–C(17)	1·41(3)	C(10)–C(11)	1·35(3)
C(17)–C(18)	1·37(3)	C(11)–C(12)	1·44(3)
C(18)–C(19)	1·42(3)	C(12)–C(6)	1·49(3)
C(19)–C(13)	1·44(3)		

TABLE 4

Bond angles (°), with estimated standard deviations in parentheses

O(1)–U–O(2)	178(1)	O(4)–C(6)–C(7)	121(2)
O(3)–U–O(4)	64(1)	C(6)–C(7)–C(8)	132(2)
O(4)–U–O(5)	76(1)	C(7)–C(8)–C(9)	127(2)
O(5)–U–O(6)	64(1)	C(8)–C(9)–C(10)	129(2)
O(3)–U–N	76(1)	C(9)–C(10)–C(11)	129(2)
O(6)–U–N	80(1)	C(10)–C(11)–C(12)	131(2)
U–N–C(1)	120(1)	C(11)–C(12)–C(6)	125(2)
U–N–C(5)	119(1)	C(12)–C(6)–C(7)	127(2)
N–C(1)–C(2)	120(2)	O(5)–C(19)–C(13)	114(2)
C(1)–C(2)–C(3)	121(2)	O(5)–C(19)–C(18)	119(2)
C(2)–C(3)–C(4)	118(2)	O(6)–C(13)–C(19)	115(2)
C(3)–C(4)–C(5)	122(2)	O(6)–C(13)–C(14)	118(2)
C(4)–C(5)–N	118(2)	C(13)–C(14)–C(15)	126(2)
C(1)–N–C(5)	120(2)	C(14)–C(15)–C(16)	131(2)
U–O(3)–C(12)	124(1)	C(15)–C(16)–C(17)	127(2)
U–O(4)–C(6)	126(1)	C(16)–C(17)–C(18)	129(2)
O(3)–C(12)–C(6)	115(2)	C(17)–C(18)–C(10)	131(2)
O(3)–C(12)–C(11)	120(2)	C(18)–C(19)–C(13)	128(2)
O(4)–C(6)–C(12)	112(2)	C(19)–C(13)–C(14)	127(2)

TABLE 5

Equations of least-squares planes in the form $AX + BY + CZ + D = 0$, where X, Y, and Z are orthogonal co-ordinates (Å). Deviations (Å) of relevant atoms from the planes are given in square brackets

	A	B	C	D
Plane (1): U, O(3)—(6), N	0·384	0·500	0·776	7·690
[U 0·03, O(3) 0·05, O(4) −0·04, O(5) −0·01, O(6) 0·02, N −0·05]				
Plane (2): N, C(1)—(5)	0·377	0·578	0·724	7·375
[N −0·01, C(1) 0·01, C(2) 0·00, C(3) 0·00, C(4) 0·00, C(5) 0·00]				
Plane (3): O(3), O(4), C(6)—(12)	0·436	0·503	0·746	7·960
[O(3) −001, O(4) 0·03, C(6) 0·00, C(7) −0·02, C(8) −0·02, C(9) 0·02, C(10) 0·00, C(11) 0·01, C(12) 0·00]				
Plane (4): O(5), O(6), C(13)—(19)	0·331	0·454	0·827	7·329
[O(5) −0·01, O(6) 0·01, C(13) 0·01, C(14) 0·02, C(15) −0·04, C(16) 0·00, C(17) 0·03, C(18) 0·00, C(19) −0·03]				

Angles (°) between the planes:

(1)–(2)	5·4	(2)–(3)	5·6
(1)–(3)	3·5	(2)–(4)	9·6
(1)–(4)	4·9	(3)–(4)	8·1

RESULTS AND DISCUSSION

The Scheme summarizes the transformations which the various compounds undergo under suitable conditions. The methanol complex was also obtained by use of the same experimental conditions reported by Plymale and Smith for the preparation of their UO_2t_2 compound. The product precipitated rapidly as reddish orange microcrystals and can be recrystallized from methanol as needles.

The $[UO_2t_2(MeOH)]$ complex remains unchanged on heating at 80 °C *in vacuo*,[9] but the methanol is removed at 142—172 °C. The product obtained (I) is not

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TABLE 6

Some intra- and inter-molecular contacts (Å) in the structure

N ··· O(3)	3·08		
N ··· O(6)	3·21		
O(4) ··· O(5)	2·94	C(8) ··· C($10^{\rm II}$)	3·76
O(3) ··· O(4)	2·51	C(9) ··· C($9^{\rm II}$)	3·46
O(5) ··· O(6)	2·53	C(9) ··· C($10^{\rm II}$)	3·44
N ··· C($10^{\rm I}$)	4·00	C(13) ··· C($15^{\rm III}$)	3·77
N ··· C($11^{\rm I}$)	3·45	C(13) ··· C($16^{\rm III}$)	3·56
N ··· C($12^{\rm I}$)	3·71	C(13) ··· C($17^{\rm III}$)	3·97
C(1) ··· C($10^{\rm I}$)	3·55	C(14) ··· C($15^{\rm III}$)	4·00
C(1) ··· C($11^{\rm I}$)	3·48	C(14) ··· C($16^{\rm III}$)	3·68
C(2) ··· C($8^{\rm I}$)	4·11	C(14) ··· C($17^{\rm III}$)	3·60
C(2) ··· C($9^{\rm I}$)	3·69	C(14) ··· C($18^{\rm III}$)	3·82
C(2) ··· C($10^{\rm I}$)	3·57	C(15) ··· C($18^{\rm III}$)	3·88
C(2) ··· C($11^{\rm I}$)	3·77	C(15) ··· C($19^{\rm III}$)	3·75
C(3) ··· C($6^{\rm I}$)	3·80		
C(3) ··· C($7^{\rm I}$)	3·78	N ··· C($18^{\rm IV}$)	3·99
C(3) ··· C($8^{\rm I}$)	3·88	C(2) ··· C($18^{\rm IV}$)	3·97
C(3) ··· C($9^{\rm I}$)	3·93	C(3) ··· C($18^{\rm IV}$)	3·91
C(3) ··· C($11^{\rm I}$)	3·98	C(4) ··· C($18^{\rm IV}$)	3·87
C(3) ··· C($12^{\rm I}$)	3·92	C(4) ··· C($19^{\rm IV}$)	3·96
C(4) ··· C($7^{\rm I}$)	3·94	C(5) ··· C($18^{\rm IV}$)	3·93
C(4) ··· C($11^{\rm I}$)	3·92		
C(4) ··· C($12^{\rm I}$)	3·50		
C(5) ··· C($6^{\rm I}$)	3·93		
C(5) ··· C($11^{\rm I}$)	3·66		
C(5) ··· C($12^{\rm I}$)	3·38		

The superscripts refer to the following transformations of the atomic co-ordinates x, y, z:

I $1 - x, \bar{y}, 1 - z$

II $1 - x, -1 - y, 1 - z$

III $1{\cdot}5 - x, \frac{1}{2} - y, \frac{1}{2} - z$

IV $-\frac{1}{2} + x, \bar{y}, z$

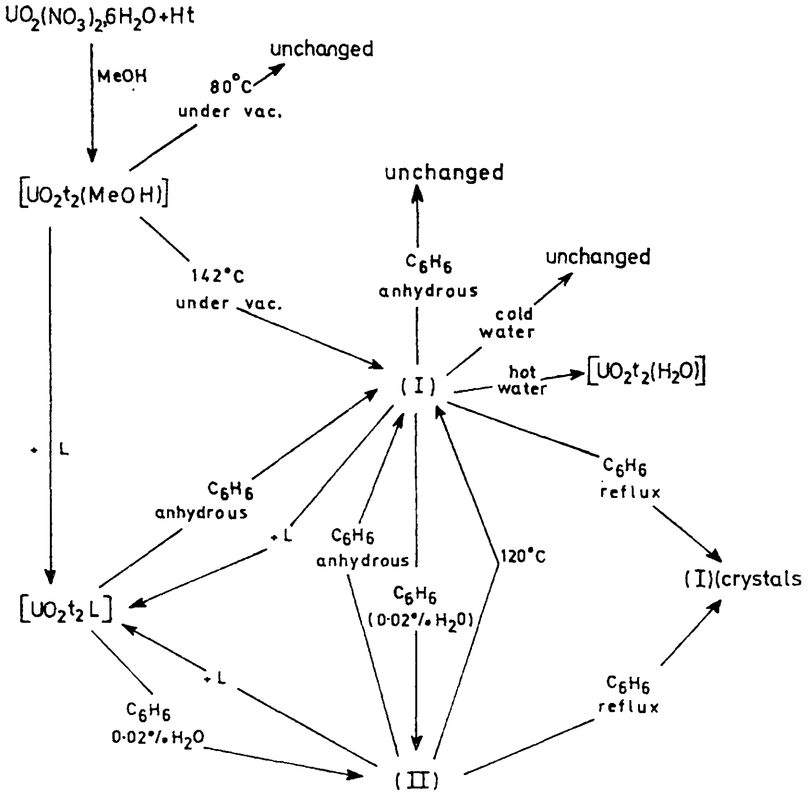
hygroscopic, as shown by the i.r. spectrum and lack of change of weight on long exposure to moist air.

The non-hygroscopic behaviour, elemental analysis, i.r., *X*-ray spectra, and density showed that the same compound (I) can also be obtained by heating (II) under reflux in a Soxhlet apparatus with benzene. The *X*-ray powder spectra (see Supplementary Publication No. 21001) clearly show that (I) is quite different both from the compound reported by Plymale and Smith and from the methanol adduct, which are both different from each other.

On digestion in benzene containing *ca.* 0·02% water (but not in anhydrous benzene) (I) gives the product (II).

The yellow-orange flocculent product (II), which is insoluble in benzene, has an i.r. spectrum quite different from that of product (I), displaying in particular a minor complexity in the region 800—1300 cm^{-1} and some indication of the presence of water; also the absorptions characteristic of water were different from those of the complex [$UO_2t_2(H_2O)$] (see Supplementary Publication No. 21001).

This product gave an extremely poor-quality *X*-ray powder pattern and elemental analyses of samples from different preparations gave variable values for hydrogen and carbon, higher and lower respectively than corresponding to the formula UO_2t_2. Thermogravimetric analysis showed variable water content. This did not influence the i.r. spectrum, the ν_{as}(O–U–O) frequency being generally found at 915 cm^{-1}, whereas for [$UO_2t_2(H_2O)$] it was at 906 cm^{-1}. These factors



SCHEME

Scheme summarizing the observed transformations and the lower temperature at which the water is lost (114 °C), compared with 135 °C for [$UO_2t_2(H_2O)$], could indicate that no direct U–OH_2 bonds are present in (II). However, in an attempt to obtain an anhydrous form of (II) by heating at 120 °C or by digestion in anhydrous benzene, product (I) was formed.

A critical discussion on the nature of (I) and (II) is not simple owing to their very low solubilities in the solvents with which they do not react. Attempts to recrystallize them from co-ordinating organic solvents gave addition compounds, all of which contained one molecule of solvent directly co-ordinated to the uranium atom.

The molecular-weight values in dimethyl sulphoxide, in which (I) and (II) are very soluble, are not substantive because of co-ordination of the solvent to form the monomeric species [$UO_2t_2(Me_2SO)$]. This is shown to have occurred by comparison of the i.r. spectrum of the latter with those of (I) and (II) in dimethyl sulphoxide solution and in Nujol mulls. These conclusions are also supported by comparison of the u.v. and visible spectra of (I) and (II) in benzene solutions containing the various neutral ligands (see later).

Some characteristic features of the i.r. spectra in the region 1200—1300 cm^{-1} together with the ν_{as}(O–U–O) absorption bands are listed in Supplementary Publication No. 21001.

The physicochemical properties of (I) and (II) strongly support the conclusion that they are not monomers in the solid state. In fact, in agreement with previous studies on β-diketonate–uranyl complexes of formula [$UO_2(diket)_2$],[16,17] they are insoluble in inert organic solvents, and their observed densities [2·51 (I), and 2·64 g cm^{-3} (II)], are significantly higher than the values found for *e.g.* monomeric adducts with pyridine (2·08) and methanol (2·29), and also in the UO_2t_2 monomer obtained by Plymale and Smith (2·26 g cm^{-3}).

In addition, the i.r. spectra of (I) and (II) display a weak sharp band at *ca.* 1575 cm^{-1} (not present in the spectra of the monomeric adducts) which seems to be a common feature of 'polymeric' metal tropolonates in which there is a sharing of some of the chelate oxygen atoms between metal atoms.[18] Taking into account the relatively high stability of structures containing five-membered rings,[19] two possible structures could be suggested as shown diagrammatically in Figure 1.

As shown by molecular models, steric hindrance excludes other types of polymer structures with six-co-ordination on the equatorial plane.

The extra stability of (a) (Figure 1) with respect to (b) (because of the presence of $\overline{\mathrm{U}\cdots\mathrm{O}\text{–}\mathrm{U}\cdots\mathrm{O}}$ bonds in the former), could account for the physicochemical properties of (I). In fact the transformations of (II) into (I), on dehydrating, and the stability of (I) in water suggest that the structure of (I) is more stable. The polymeric form (b) could represent the structure of (II), the presence of water stabilizing this structure by hydrogen bonding between some of the chelate oxygen atoms.

The suggested models for (I) and (II) are in accordance with their i.r. spectra, which differ significantly only in the region 1200—1300 cm^{-1} (C–H in-plane deformations [20]) the spectrum being less complex for the polymeric species, owing to the expected greater steric effects.[6,21]

Visible and U.v. Spectra.—Absorption spectra of solutions of (I) and (II) in the region 320—520 nm in co-ordinating solvents such as methanol and dimethyl sulphoxide are not very different. The methanolic solution exhibits a shoulder at 324 nm (ε = 24,000), and intense peak at 334 nm (ε = 27,600) and a peak at 398 nm (ε = 7000), whereas in Me_2SO solution the absorptions are at 326 (ε = 24,900), 337 (ε = 28,900), and 401 nm (ε = 8000) respectively. These differences do not clearly indicate an interaction of the solvent with the central atom. However, the co-ordination is evident on considering the following results. Samples of *ca.* 50 mg of product (I) were suspended in anhydrous benzene (100 ml) containing the appropriate ligands L (L = MeOH, Me_2SO) at suitable concentrations. The solutions were thermostatted at 20 °C until equilibrium was reached. In every case the solid, always present in the heterogeneous mixture, was found (by i.r. spectra) to be unchanged (I). The spectra in the 320—520 nm region of the filtered solutions were run at the same temperature, and preliminary results show that in both cases the absorbance is a linear function of the ligand concentration, the form of the spectra being very similar to those reported above for MeOH and Me_2SO solutions respectively.

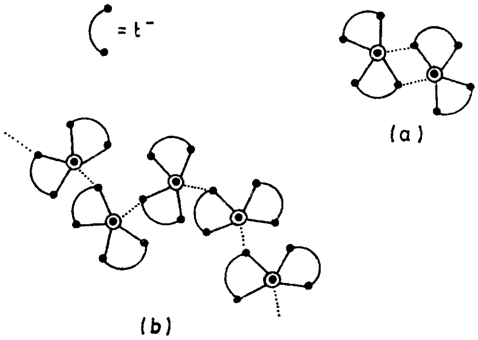


FIGURE 1 Diagrammatic representation of possible structures of compounds (I) and (II)

I.r. Spectral Results.—Infrared absorptions in the solid state of the compounds (I) and (II), and of the adducts, together with some tentative assignments are listed in the Supplementary Publication.

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The C=O and C=C vibrations in the free tropolone are shifted to lower frequencies in the complexes, the positions of these bands being remarkably constant in all the compounds examined. This seems to be quite general behaviour for an homogeneous series of uranyl β-diketonates. In particular no significant variations were observed for well established monomeric and polymeric species of uranyl acetylacetonates.[22,23] Relative to the spectrum of tropolone,[20] a new strong and very sharp band is observed in all the compounds in the narrow region 495—500 cm^{-1}. This band may be associated with metal–oxygen vibrations.[4] As far as the antisymmetric (O–U–O) stretching frequencies are concerned the general behaviour of the shift on co-ordination [24] is also found in this case. In fact ν_{as} occurs at 912 and 915 cm^{-1} for compounds (I) and (II) respectively, but in the range 895—906 cm^{-1} for the adducts not strongly affected by the nature of the co-ordinated neutral ligand.

The anomalously high ν_{as}(O–U–O) absorption (914 cm^{-1}) for [UO_2t_2(cyclohexanone)] and the ν(C=O) at 1696 cm^{-1} (1715 cm^{-1} in free cyclohexanone) indicate a weak interaction of the neutral ligand towards the central atom.

In this respect it is significant to note that we were unable to isolate the adduct with acetone.

The co-ordination of the neutral ligands results in characteristic shifts with respect to free-ligand vibrations (see Supplementary Publication No. 21001).

The presence of MeOH in the co-ordination sphere of the complex [UO_2t_2(MeOH)] is not fully evident in the i.r. spectrum, but was independently confirmed by thermogravimetric and elemental analysis. As far as the [UO_2t_2(py)] complex is concerned it seems possible to apply Gill's statement 'each band in the spectrum of pyridine is faithfully reproduced with only minor shifts or splittings in the spectra of the complexes' [25] in the region free from bands due to co-ordinated tropolone. In particular the spectrum displays a strong sharp band at 630 cm^{-1}, not present in all other adducts, and very near to the fundamental absorption of pure pyridine at 605 cm^{-1}.[26,27]

With the aim of better characterizing the molecular structure of the adducts UO_2t_2L, an *X*-ray single-crystal analysis has been carried out on the [UO_2t_2(pyridine)] compound.[28]

Crystal Structure of [UO_2t_2(py)].—Figures 2 and 3 show the molecule of [UO_2t_2(py)] with the numbering scheme used and a projection of the unit-cell contents along [010]. The co-ordination polyhedron has the expected geometry with the uranyl group perpendicular to the equatorial plane in which four oxygens from two tropolonato-groups, and the nitrogen from the pyridine, are co-ordinated to uranium. The molecule has approximately C_{2v} symmetry.

Calculations by least-squares fitting of the mean plane for pyridine and for the atoms of each tropolonato-skeleton show them to be planar, within experimental error, and to form angles of a few degrees with the co-ordination plane (Table 5). The resulting distortion results in a slight twisting of the two tropolonato-groups about the line passing through N and U. Some departure from C_{2v} symmetry in the molecule arises also from incomplete equivalence of the N ··· O contact distances between nitrogen and the two adjacent oxygen atoms, and in the N ··· U ··· O angles (Table 6),

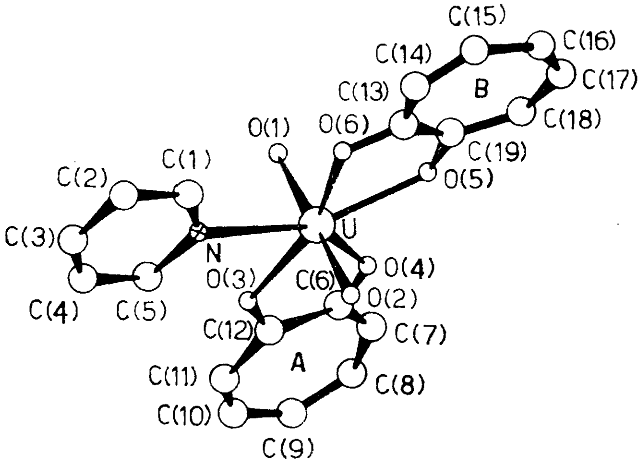

FIGURE 2 A molecule of [UO_2t_2(py)] showing the atom numbering system used

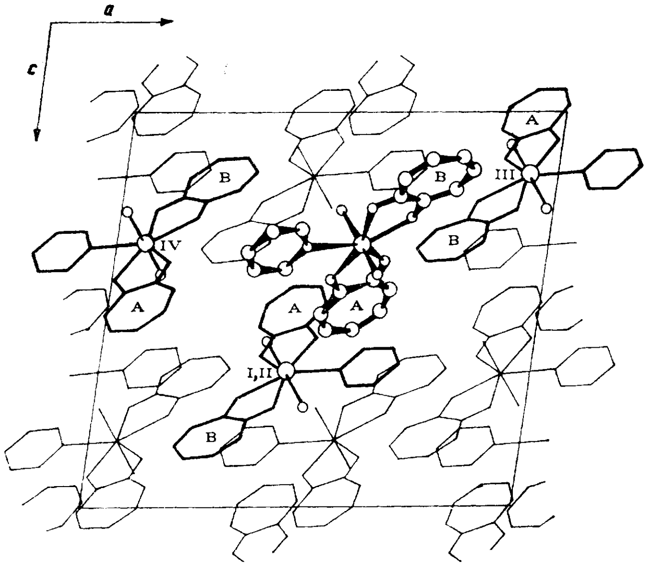

FIGURE 3 Projection of the unit-cell contents along [010]

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but this distortion seems to have structural significance only in connection with the crystal packing.

The two U–O(uranyl) bond lengths [1·78(1) and 1·79(1) Å] are equal; the four U–O(eq) bond lengths are very close to those found in many structures in which five oxygen atoms are equatorially bonded to uranium.[29,30] The pentagonal girdle in the molecule carries two O · · · O contacts of 2·51 and 2·53 Å which represent the normal 'bite' of the tropolonato-ligand; the contact of 2·94 Å between oxygens of adjacent groups, and the two O · · · N contacts of 3·21 and 3·08 Å are greater than the sum of the van der Waals radii (2·80 and 2·90 Å), excluding the presence of destabilizing energy.

In addition the two contacts C(1) · · · O(6) [3·10(2) Å] and C(5) · · · O(3) [2·94(2) Å] strongly suggest the presence of hydrogen bonds. In fact, according to the criterion of ref. 31, both distances between the calculated positions of the two hydrogen and the corresponding oxygen atoms are shorter than 2·4 Å.

The four C–O bond distances in the two tropolonato-ligands are of the same order as those found in tropolonato-complexes of iron 1·294,[32] thorium 1·277,[33] tin 1·287, 1·285,[34] and in sodium tropolonate 1·284 Å.[35] However, the fact that two independent tropolonato-groups (A and B in Figure 3) are unequally influenced by crystal packing force, seems to have some influence on the C–C bond lengths. In ligand A, C(6)–C(12) [1·49(3) Å] has the predicted value for a C(sp^2)–C(sp^2) single bond.[32,36,37] In addition, the other six C–C lengths show the regular bond alternation already found in Cut$_2$.[38] In ligand B, no bond alternation is observed in the six corresponding C–C distances while the C(13)–C(19) distance [1·44(3) Å] does not differ significantly from the corresponding value in A.

The molecules are arranged in the crystal to form infinite parallel layers, approximately perpendicular to the crystallographic direction [223]. The separation between successive layers is *ca.* 3·7 Å, with minor fluctuations for the planes of the single ligands due to the fact that they do not exactly coincide with the co-ordination plane. Two important points may be noted about this mode of packing. The separation between layers is small and the pyridine ring (which in principle could assume any position around the U–N direction) lies in the plane of the molecule. These points suggest the presence of some weak interaction between the layers which would be associated with an increase in crystal binding energy and would make hydrogen bonding possible, as already mentioned. Thus, as shown in Table 6, the pyridine ring makes with the tropolonato-ligand A at $1 - x, \bar{y}, 1 - z$, a number of short contacts which can be reasonably related to some degree of π interaction between the two aromatic systems, whereas it makes only few such contacts with ligand B at $x - \frac{1}{2}, \bar{y}, z$. Ligand B is in a less favourable position: it is not matched by other aromatic rings apart from a few contacts with the equivalent ring at $1{\cdot}5 - x, \frac{1}{2} - y, \frac{1}{2} - z$. It can therefore be concluded that only ligand A (in which alternation is observed) is directly involved in possible van der Waals interaction in the crystal.

On the other hand it has been suggested [32] that in the crystal the molecules can adopt a state in which there is a large measure of π-electron localization, with consequent reduction in the electron delocalization energy, provided that the loss of delocalization energy is balanced by an increase in crystal binding energy. Thus, the observed alternation in bond length of the tropolonato-ligand A, which is nevertheless at best only just significant, could be ascribed to the decrease in π-electron delocalization required to maximize the crystal binding energy. In this way the crystal could have a higher total electronic binding energy than would be possible if π-electron delocalization were complete.

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[3/1082 *Received*, 25*th May*, 1973]

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