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The Crystal and Molecular Structure of Dichlorobis(hexamethylphosphoramide)-dioxouranium(VI): $UO_2Cl_2.2(HMPA)$

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The title compound is tetragonal with $a = 10{\cdot}430\,(5)$, $c = 23{\cdot}82\,(1)$ Å, $Z = 4$, space group $P4_12_12$. The structure was determined by Patterson and Fourier methods and refined by full-matrix least squares to a final R of 0·037 for 924 observed reflexions. The U atom is octahedrally coordinated with the HMPA ligands in the *trans* position.

Introduction

Although numerous structures of complexes containing the uranyl ion, UO_2^{2+}, have been published, no comparison has yet been made with similar U^{IV} complexes. Our interest in the complex $UO_2Cl_2.2(HMPA)$ arose from an earlier study of $UCl_4.2(HMPA)$ (de Wet & Darlow, 1971). The former can be considered as being derived from the latter by replacement of two Cl^- ions by two O^{2-} ions, with a corresponding increase in oxidation state from U^{IV} to U^{VI}. The present study was undertaken to determine to what extent the tetragonal distortion, caused by the presence of two O^{2-} ions, affects the interactions between the central ion and the other ligand.

Experimental

The compound was prepared by mixing acetone solutions of $UO_2Cl_2.3H_2O$ and HMPA. The resulting yellow solid was recrystallized from a dichloromethane/ether mixture. The IR spectra of $UO_2Cl_2.2(HMPA)$ and $UCl_4.2(HMPA)$ were recorded on a PE 457 grating instrument, as Nujol mulls pressed between CsI plates. A single crystal was ground to a sphere of radius 0·15 mm and the lattice constants were determined by least squares from the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation. The crystal data are listed in Table 1. The density was measured by flotation in a mixture of xylene and iodomethane.

Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the ω–2θ scan mode (scan width $0{\cdot}8^\circ\theta$, scan speed $0{\cdot}03^\circ\theta s^{-1}$). With graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), 1005 reflexions up to $2\theta = 46^\circ$ were measured. Three reference reflexions were recorded after every 63 reflexions, and remained constant to ±1%. With the criterion $I(\text{rel.}) > 2\sigma I(\text{rel.})$ for an observed reflexion, 147 reflexions were omitted as unobserved. The remaining 929 reflexions were employed in the analysis. The data were corrected for Lorentz–polarization effects but not for absorption.

The U atom was located from a Patterson map. The space group requires U to lie in a special position at $x,x,0$ on a twofold axis. A subsequent difference map showed the two Cl atoms to be on this same axis and revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with U, Cl anisotropic, and remaining non-hydrogen atoms isotropic, yielded an R of 0·044. At this stage a difference map showed the positions of some of the H atoms. Final refinement was carried out with the methyl H atoms constrained at 1·08 Å from their corresponding C atoms, the methyls being refined as rigid groups (Sheldrick, 1977). The isotropic temperature factors of the H atoms were refined as one common parameter which had a final value of $U = 0{\cdot}112$ Å^2. The refine-

Table 1. *Crystal data*

Molecular formula $C_{12}H_{36}Cl_2N_6O_4P_2U$

$M_r = 699{\cdot}3$
$a = 10{\cdot}430\,(5)$ Å
$c = 23{\cdot}82\,(1)$
$V = 2591{\cdot}3$ Å^3

Space group $P4_12_12$
$D_m = 1{\cdot}83$ g cm^{-3}
$D_c = 1{\cdot}85$ for $Z = 4$
$\mu(\text{Mo } K\alpha) = 63{\cdot}1$ cm^{-1}
$F(000) = 1352$

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Table 2. *Fractional atomic coordinates* ($\times 10^4$), *temperature factors* ($\times 10^3$) *and e.s.d.'s of the heavy atoms*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	261 (0)	261 (0)	0 (0)	37 (3)	37 (3)	35 (4)	0 (2)	0 (2)	10 (3)
Cl(1)	2059 (3)	2059 (3)	0 (0)	57 (2)	57 (2)	117 (5)	−4 (3)	4 (3)	−14 (3)
Cl(2)	−1545 (3)	−1545 (3)	0 (0)	69 (3)	69 (3)	94 (4)	0 (3)	0 (3)	−19 (3)

	x	y	z	U_{iso}		x	y	z	U_{iso}
O(1)	176 (7)	328 (8)	734 (3)	61 (2)	C(11)	4721 (21)	−434 (18)	116 (8)	108 (6)
O(2)	1830 (8)	−1242 (8)	62 (4)	62 (3)	C(12)	4766 (19)	−1907 (20)	892 (8)	109 (7)
P(1)	2890 (3)	−2215 (3)	114 (1)	45 (1)	C(21)	4473 (26)	−3101 (27)	−682 (10)	163 (10)
N(1)	4169 (13)	−1594 (13)	364 (5)	71 (4)	C(22)	2184 (23)	−3136 (22)	−871 (9)	122 (8)
N(2)	3241 (13)	−2759 (12)	−509 (5)	73 (4)	C(31)	2953 (17)	−4644 (17)	508 (8)	87 (5)
N(3)	2412 (11)	−3342 (11)	529 (5)	55 (3)	C(32)	1551 (18)	−3097 (21)	988 (7)	93 (6)

Table 3. *Fractional atomic coordinates of the hydrogen atoms* ($\times 10^3$)

	x	y	z
H(111)	429	−30	−30
H(112)	575	−48	7
H(113)	447	35	39
H(121)	447	−273	114
H(122)	499	−112	117
H(123)	560	−215	65
H(211)	535	−290	−46
H(212)	453	−269	−110
H(213)	435	−413	−72
H(221)	116	−307	−91
H(222)	247	−413	−91
H(223)	264	−257	−120
H(311)	362	−498	19
H(312)	209	−522	49
H(313)	339	−473	92
H(321)	108	−219	106
H(322)	205	−340	136
H(323)	84	−381	88

ment converged to $R = 0{\cdot}037$ and $R_w = 0{\cdot}032$, with $w = 1/\sigma^2$. Tables 2 and 3 list the atomic positions and thermal parameters. Bond lengths and angles are given in Table 4.*

Table 4. *Bond lengths* (Å) *and angles* (°)

Cl(1)–U(1)	2·653 (5)	O(2)–U(1)–Cl(2)	91·2 (2)
Cl(2)–U(1)	2·663 (5)	O(2)–U(1)–O(1)	89·9 (4)
O(1)–U(1)	1·753 (8)	P(1)–O(2)–U(1)	178·5 (6)
O(2)–U(1)	2·272 (9)	N(1)–P(1)–O(2)	111·7 (6)
P(1)–O(2)	1·50 (1)	N(2)–P(1)–O(2)	109·0 (6)
N(1)–P(1)	1·60 (1)	N(2)–P(1)–N(1)	107·1 (7)
N(2)–P(1)	1·63 (1)	N(3)–P(1)–O(2)	108·3 (6)
N(3)–P(1)	1·62 (1)	N(3)–P(1)–N(1)	108·9 (7)
C(11)–N(1)	1·46 (2)	N(3)–P(1)–N(2)	111·9 (7)
C(12)–N(1)	1·44 (2)	C(11)–N(1)–P(1)	121 (1)
C(21)–N(2)	1·40 (2)	C(12)–N(1)–P(1)	127 (1)
C(22)–N(2)	1·45 (2)	C(12)–N(1)–C(11)	112 (2)
C(31)–N(3)	1·47 (2)	C(21)–N(2)–P(1)	124 (1)
C(32)–N(3)	1·44 (2)	C(22)–N(2)–P(1)	118 (1)
Cl(2)–U(1)–Cl(1)	180·0 (0)	C(22)–N(2)–C(21)	117 (2)
O(1)–U(1)–Cl(1)	90·4 (2)	C(31)–N(3)–P(1)	122 (1)
O(1)–U(1)–Cl(2)	89·6 (2)	C(32)–N(3)–P(1)	122 (1)
O(2)–U(1)–Cl(1)	88·8 (2)	C(32)–N(3)–C(31)	116 (1)

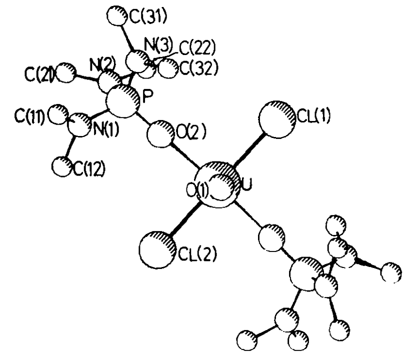

Fig. 1. Perspective view of the molecule with atomic nomenclature.

Description of the structure and discussion

The molecular structure and atomic nomenclature are shown in Fig. 1. U is six-coordinate with the neutral ligands in a *trans* arrangement. The uranyl group is linear and normal to the equatorial plane defined by the Cl and neutral O atoms. The U–O (ligand) and U–Cl lengths [2·272 (9) and 2·658 (5) Å] may be compared with those in $UCl_4.2(HMPA)$ [2·31 (1) and 2·615 (6) Å] (du Preez, Gellatly, Jackson, Nassimbeni & Rodgers, 1976), and suggest that the Lewis acidity of UO_2^{2+} in the equatorial plane is slightly less than U^{4+}, the presence of the O^{2-} ions more than compensating for the increase in oxidation state. Previously reported potentiometric results from the measurements of the Lewis acidity of UCl_4 and UO_2Cl_2 in acetone solution are in agreement with this (du Preez, Gellatly, Gibson, Groot & Rohwer, 1976). One striking feature of $UO_2Cl_2.2(HMPA)$ is the almost linear U–O–P arrangement (178·5°). The only other phosphine oxide

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32385 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

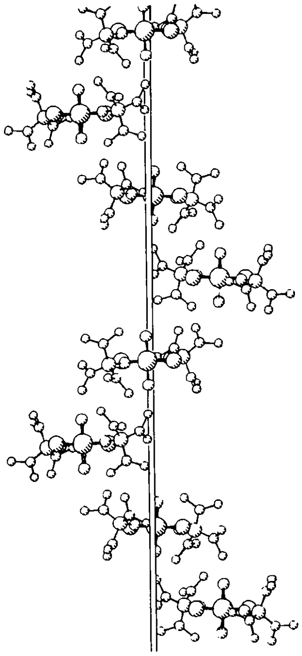

Fig. 2. Stacking of the molecules about 4_1 axis viewed along **b**.

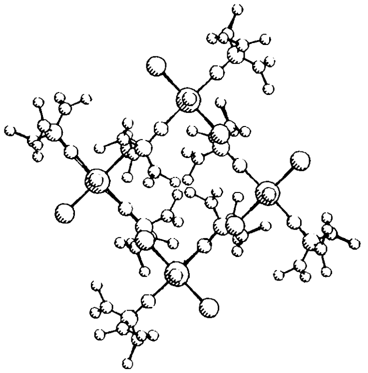

Fig. 3. Stacking of the molecules about 4_1 axis viewed along **c**.

complex known where the *M*—O—P group is linear is $Cu_4OCl_6.4(TPPO)$ (TPPO = tetraphenylphosphine oxide) (Bertrand, 1967). This is, however, symmetry imposed, with Cu, O and P lying on a threefold axis. The IR spectrum of this compound shows a P=O stretching frequency virtually unchanged from the free ligand [ν(P=O) 1195 cm^{-1}]. However, in $UO_2Cl_2.2(HMPA)$ ν(P=O) occurs at 1086 cm^{-1}, which, although higher than ν(P=O) in $UCl_4.2(HMPA)$ (1036 cm^{-1}), is significantly lower than in the free ligand, HMPA (1201 cm^{-1}). Although the U—O—P angles are different in these compounds [$UO_2Cl_2.2(HMPA)$, 178·5°; $UCl_4.2(HMPA)$, 163·7°] the P=O lengths are very similar [1·50 (1) Å]. It seems therefore that in some cases the P=O stretching frequency is not dependent on only the P=O length and the *M*—O—P angle, and care should be exercised in correlating the shift in P=O stretching frequency with P—O interaction and consequently with metal–ligand interaction.

Table 5. *Packing densities of related uranium compounds expressed as mean volume $\bar{V}$ per non-hydrogen atom*

TEASO = triethylarsine oxide, TMPO = trimethylphosphine oxide, HMPA = hexamethylphosphoramide, TPPA = tetramethylphenylphosphoramide, TPPO = triphenylphosphine oxide.

Compound	$\bar{V}$(Å^3)	Reference
$UCl_4.2(TEASO)$	27·4	*a*
$UCl_4.6(TMPO)$	27·2	*b*
$UCl_4.2(HMPA)$	25·0	*c*
$UO_2Cl_2.2(HMPA)$	24·0	*d*
$UCl_4.2(TPPA)$	24·0	*e*
$UO_2.4(HMPA).2ClO_4$	22·1	*f*
$UCl_5.(TPPO)$	21·8	*b*
$UCl_4.2(TPPO)$	20·9	*g*

References: (*a*) Sommerville & Laing (1976). (*b*) Bombieri, Forsellini, Brown, Whittaker & Mealli (1975). (*c*) Du Preez, Gellatly, Jackson, Nassimbeni & Rodgers (1976). (*d*) Present work. (*e*) Caira & Nassimbeni (1976). (*f*) Nassimbeni & Rodgers (1976). (*g*) Bombieri, Brown & Graziani (1975).

Figs. 2 and 3 show the arrangement of the molecules viewed perpendicular to and along the 4_1 axis respectively. There are no intermolecular contacts shorter than 3·5 Å so that packing forces cannot be readily invoked to account for the almost linear U—O—P arrangement. In this connexion we have analysed the packing densities of a series of similar compounds. These are expressed as a mean volume per non-hydrogen atom (Table 5). The values vary from 27·4 Å^3 for $UCl_4.2(TEASO)$, in which the C_2H_5 groups in the TEASO ligand are folded in an irregular manner and result in loose packing, to 20·9 Å^3 for $UCl_4.2(TPPO)$, in which there are significant intra- and intermolecular close contacts. There is no correlation between packing density and the U—O—P angles.

All calculations were carried out on a Univac 1106 computer at the University of Cape Town.

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The Crystal Structures of Three New Solvates of 5,5′,6,6′-Tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine Iodide

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Two solvate crystals of the title dye (DYE), the 2 : 1 methanol : DYE (DYE2M) and the 1 : 1 acetonitrile : DYE (DYEA), were investigated previously [Smith & Luss, *Acta Cryst.* (1972), B**28**, 2793–2806]. Three new solvates, the 1 : 1 ethanol : DYE (DYEE), the 1 : 1 methanol : DYE (DYE1M) and the 2 : 1 dichloromethane : DYE (DYEDC), were studied to find the effect of intermolecular interactions between the dye molecules. The crystal structures were determined from single-crystal X-ray data. DYEE is monoclinic, $P2_1/c$, with a = 16·490 (1), b = 10·990 (1), c = 17·876 (1) Å, β = 108·72 (1)°, and Z = 4; DYE1M is isomorphous with DYEE, with a = 16·262 (1), b = 10·912 (1), c = 17·579 (1) Å, β = 108·04 (1)°, and Z = 4; DYEDC is monoclinic, $P2_1/c$, with a = 14·426 (1), b = 18·237 (1), c = 14·741 (1) Å, β = 118·33 (1)°, and Z = 4. The final R values are 0·096 for DYEE, 0·071 for DYE1M and 0·124 for DYEDC. The bond distances and angles agree with the values reported for DYE2M and DYEA. The crystal structures of five dye solvates are classified into two types; DYE2M, DYEA and DYEDC are grouped into type I, in which the cations pack plane-to-plane in sheets; DYEE and DYE1M belong to type II, in which the cations form dimers and each dimer is linked to another behind it through the overlap of half a dye-cation ring. Close Cl · · · Cl contacts were found, which may indicate a specific interaction between the substituent Cl atoms. The correlation of the crystal structures with the electronic spectra of aggregates is discussed.

Introduction

Cyanine dyes form several different kinds of aggregates which exhibit spectral shifts of the order of ±100 nm from the solution monomer spectrum. Aggregates with red-shifted intense sharp absorption maxima were found by Jelley (1936) and Scheibe (1936) in solution, and were called *J* aggregates. Blue-shifted aggregates were also found in solution, and some of them show intense sharp absorption spectra which were called *H** bands (West, Lovell & Cooper, 1970; Herz, 1974). Molecular and crystal structures of cyanine dyes have been investigated by many investigators and several types of stacking modes were observed (Wheatley, 1959*a*,*b*; Dammeier & Hoppe, 1971; Yoshioka & Nakatsu, 1971; Smith & Barrett, 1971; Nakatsu, Yoshioka & Aoki, 1972; Smith & Luss, 1972, 1975; Potenza & Mastropaolo, 1974).

Scheibe, Muller & Schiffmann (1941) proposed the ladder and staircase models for the *J* aggregate of 2,2′-cyanine dyes, but these models were revised by Daltrozzo, Scheibe, Gschwind & Haimerl (1974) based on the X-ray structural result of Dammeier & Hoppe (1971). Bird and his group (Emerson, Conlin, Rosenoff, Norland, Rodriguez, Chin & Bird, 1967; Bird, Zuckerman & Ames, 1968) proposed the model for the *J* and *H* aggregates of thiacarbocyanine dyes.

The title compound (DYE) is an efficient spectral sensitizer of the silver halide photographic system to green light and the crystal structures of two solvates, the 2 : 1 methanol : DYE (DYE2M)* and the 1 : 1 acetonitrile : DYE (DYEA), were determined by Smith

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* The crystal was named as DYEM by Smith & Luss, but in this paper it is called DYE2M to distinguish it from the 1 : 1 methanol : DYE solvate (DYE1M).