Crystal and Molecular Structure of Bis(3-chloropentane-2,4-dionato)-dioxo(triphenylphosphine oxide)uranium(VI) and Dioxobis(pentane-2,4-dionato)(triphenylphosphine oxide)uranium(VI)–Benzene (1/1)

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The crystal structures of the title complexes have been determined by single-crystal *X*-ray diffraction. The first, $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$, is monoclinic and the second, $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$, belongs to the triclinic system. Both structures are molecular, with no strong association between molecules except for van der Waals forces and possible weak hydrogen-bond attractions. In each crystal the uranium co-ordination polyhedron is a pentagonal bipyramid. The packing of the complex molecules in the two structures is quite different, owing to the presence of the large chlorine atom in the first crystal and the solvent molecule in the second. In the chlorodiketonate the molecular planes are both mutually perpendicular and parallel, but in the unsubstituted diketonate are parallel only. The pentane-2,4-dionate molecules and the pentagonal ring have an L-shaped system in the chloro-derivative and a chair shape in the unsubstituted derivative.

NUMEROUS uranyl complexes with β-diketones, for example pentane-2,4-dione (Hpd) or hexafluoropentane-2,4-dione (Hhfpd), have been prepared with the stoicheiometric composition $[UO_2(\text{diketone})_2L]$ [L = a neutral unidentate ligand such as $PO(OMe)_3$ or PPh_3O]. In general, these complexes have the yellow colour typical of complexes of $[UO_2]^{2+}$ with aliphatic ligands.[1] Under special conditions, red or orange polymorphs have been obtained for some complexes, such as with $[UO_2(pd)_2(OH_2)]$,[2] but these are unstable and revert to the yellow form when recrystallised. Recently, in these laboratories the first crystal structures of these polymorphs have been determined, namely the yellow α and orange β forms of $[UO_2(hfpd)_2\{PO(OMe)_3\}]$.[3,4]

The title complex containing the 3-chloro-substituted pentane-2,4-dionate ligand, $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$, is unusual because it forms crystals with a bright orange colour which is retained when the complex is recrystallised from such solvents as hexane, benzene, methanol and chloroform. A previous ethanol analogue of this complex, $[UO_2(3Cl\text{-}pd)_2(HOEt)]$ was also found to form stable golden-orange crystals.[5] It appears that the presence of the chlorine atom produces rather different crystal structures for these complexes and for this reason the structure of the PPh_3O complex was determined.

The structure of the orange chloro-substituted complex has been compared with that of the analogous unsubstituted complex, $[UO_2(pd)_2(PPh_3O)]$. It was found that the latter crystallised as the solvate $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$ with the normal yellow colour. In order to compare molecular dimensions in the substituted and unsubstituted forms and to see why only the unsubstituted complex forms solvates, the crystal structure of the solvate was determined. The present analyses are the first structural studies of uranyl pentane-2,4-dionates except for $[UO_2(pd)_2(OH_2)]$.[6]

EXPERIMENTAL

Reagents.—Triphenylphosphine oxide and pentane-2,4-dione were obtained from B.D.H. and used without further purification. The 3Cl-pd was prepared from the reaction of Hpd with *N*-chlorosuccinimide in boiling chloroform, and purified *via* the copper complex.[7]

Preparation of Complexes.—The complexes were prepared by the reaction of stoicheiometric quantities of $UO_3\cdot 2H_2O$, PPh_3O, and the diketone in benzene. Crystals were obtained by evaporating off the benzene in a stream of dry nitrogen. Elemental analysis of the uranyl complex containing the unsubstituted pentane-2,4-dionate ligand indicates a benzene solvate with the composition $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$. Crystallisations from hexane and chloroform also produce the corresponding solvates. {Found: C, 49.0; H, 4.25; P, 3.80; U, 28.4. Calc. for $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$: C, 49.5; H, 4.25; P, 3.75; U, 28.9. Found: C, 41.5; H, 3.35; Cl, 8.80; U, 29.0. Calc. for $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$: C, 41.25; H, 3.35; Cl, 8.70; U, 29.2%}.

Infrared Spectra.—Spectra were recorded of KBr discs on a Perkin-Elmer 225 grating spectrophotometer. Those of the two complexes $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$ and $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$ were essentially the same, the main difference being the presence of only a singlet band at *ca.* 1 575 cm^{-1} for the former complex, a feature characteristic of pentane-2,4-dionato-complexes having a group other than hydrogen at the central carbon.[8] Only a small difference occurred in the O–U–O asymmetric frequencies (908 and 907 cm^{-1}).

Crystal-structure Determination.—Faces of crystals used and their distance from the crystal centre were: for the chlorodiketonate, ±(001) (0.007 5), ±(100) (0.001 5), (010) (0.006 1), (0–41) (0.006 1), and (0–4–1) (0.006 1); for the diketonate, ±(100) (0.002 7), ±(010) (0.008 5), ±(001) (0.011 5), and ±(01–2) (0.011 5 cm). Rotation and Weissenberg photographs established the crystal

TABLE 1

Crystal data

	$[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$	$[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$
M	815.42	824.65
a/Å	16.289(26)	11.121(3)
b/Å	13.625(22)	15.710(4)
c/Å	14.717(24)	11.229(5)
α/°	90	104.32(2)
β/°	112.051(13)	112.98(2)
γ/°	90	90.20(1)
Space group	$P2_1/c$	$P\bar{1}$
U/Å^3	3 027	1 739
D_c/g cm^{-3}	1.789	1.575
μ(Cu-K_α)/cm^{-1}	212	172
Z	4	2
Colour	Orange	Yellow

symmetry, and three-dimensional X-ray diffraction data (1 542 independent reflections for the chlorodiketonate and 1 704 for the diketonate) were collected on a four-circle diffractometer [solid-state detector, Cu-K_α radiation (λ 1.541 8 Å), $0 < \theta < 70°$, ω—2θ scans]. The intensities were normalised to a standard reflection. Absorption corrections were applied;[9] the computed transmission factors were between 12 and 54% for the chlorodiketonate and 9 and 42% for the diketonate. The crystal data are given in Table 1.

Table 2

Positional parameters ($\times 10^3$)

Atom	$[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$			$[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$		
	x	y	z	x	y	z
U	817.5(2)	19.6(2)	712.4(2)	186.9(2)	214.0(2)	493.3(2)
O(1)	760(3)	−55(3)	770(3)	77(4)	261(3)	381(4)
O(2)	878(3)	89(3)	659(3)	297(4)	167(3)	605(4)
pd (Molecule 1)						
C(1)	1 102(4)	16(5)	950(5)	359(9)	491(7)	818(11)
C(2)	1 031(4)	−19(5)	860(5)	366(9)	417(6)	698(9)
C(3)	1 048(4)	−87(5)	799(5)	459(8)	414(6)	636(10)
C(4)	984(5)	−136(5)	717(5)	446(8)	352(6)	530(9)
C(5)	1 003(4)	−220(5)	664(5)	542(8)	362(5)	462(9)
O(3)	951(3)	008(3)	846(3)	259(4)	358(3)	654(5)
O(4)	903(3)	−115(3)	694(3)	355(4)	287(3)	466(5)
Cl(1)	1 157.6(14)	−121.5(16)	821(7)(17)			
(Molecule 2)						
C(6)	788(5)	265(6)	925(6)	262(7)	12(5)	144(8)
C(7)	754(5)	220(5)	821(5)	179(8)	46(5)	228(8)
C(8)	687(4)	241(5)	737(5)	62(7)	7(4)	201(7)
C(9)	658(5)	205(6)	645(6)	−6(8)	23(5)	278(9)
C(10)	585(5)	242(6)	557(6)	−140(7)	−27(5)	253(7)
O(5)	810(3)	146(4)	824(3)	245(4)	112(3)	332(5)
O(6)	694(3)	120(4)	636(3)	33(5)	82(3)	399(5)
Cl(2)	628.0(18)	347.1(16)	754.3(22)			
PPh_3O						
P	707.2(12)	−133.1(13)	483.1(13)	−25(2)	269(1)	696(2)
O(7)	731(3)	−59(3)	567(3)	45(4)	237(3)	608(4)
C(11)	686(4)	−255(5)	519(5)	−60(6)	379(5)	696(8)
C(12)	731(4)	−279(5)	617(5)	−79(7)	409(5)	583(7)
C(13)	721(5)	−376(5)	655(5)	−118(7)	495(5)	575(8)
C(14)	658(5)	−438(5)	589(6)	−131(8)	549(5)	687(9)
C(15)	609(5)	−413(6)	497(6)	−117(8)	520(6)	800(9)
C(16)	622(4)	−318(5)	456(5)	−72(8)	434(6)	811(9)
C(17)	606(4)	−91(5)	383(5)	−182(7)	203(5)	633(7)
C(18)	556(4)	−21(5)	409(5)	−281(8)	233(5)	669(8)
C(19)	473(5)	5(5)	337(6)	−400(9)	179(6)	610(10)
C(20)	444(5)	−36(5)	246(6)	−421(7)	103(5)	519(8)
C(21)	495(5)	−105(5)	217(5)	−327(8)	66(5)	488(8)
C(22)	582(5)	−135(5)	293(6)	−199(7)	120(5)	535(8)
C(23)	794(4)	−146(5)	440(5)	67(6)	265(4)	865(6)
C(24)	841(5)	−58(5)	436(5)	9(6)	236(4)	940(7)
C(25)	915(5)	−68(5)	403(5)	92(7)	232(4)	1 068(7)
C(26)	941(4)	−158(5)	380(5)	224(7)	252(4)	1 121(7)
C(27)	891(4)	−242(5)	380(5)	285(7)	284(5)	1 049(8)
C(28)	818(4)	−238(5)	411(4)	201(7)	288(4)	918(7)
C_6H_6						
C(29)				542(9)	192(7)	949(9)
C(30)				540(11)	139(8)	1 033(13)
C(31)				642(14)	159(8)	1 167(14)
C(32)				745(10)	216(8)	1 177(11)
C(33)				750(10)	271(7)	1 112(12)
C(34)				627(11)	262(8)	972(11)

Structural analyses. Each structure was determined by locating the uranium atom in the Patterson synthesis, and subsequently calculating difference syntheses. When all the non-hydrogen atoms were finally located, final refinement was carried out with the program LINUS.[10] All atoms were given isotropic temperature factors except U, P, and Cl in the chlorodiketonate and U and P in the diketonate. Hydrogen atoms were not located. The scattering factor for uranium included the anomalous dispersion terms $\Delta f' = -4.9$ e and $\Delta f'' = 11.3$ e. The neutral-atom scattering curves were taken from ref. 11. The final weighted and unweighted R factors were 0.062 and 0.057 for the chlorodiketonate and 0.075 and 0.064 for the diketonate.

The positional parameters are given in Table 2 and some interatomic distances and angles in Table 3. A list of observed and calculated structure factors is available as Supplementary Publication No. SUP 22420 (12 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

RESULTS AND DISCUSSION

The bond lengths and angles in Table 3 are normal. The uranyl bond lengths in the chlorodiketonate may be slightly longer than in the diketonate, and the other U–O bonds slightly shorter, although these differences could not be observed in the i.r. spectra.[12] The dimensions of the pd molecules in both structures are in agreement with structural studies of transition-metal pentane-2,4-dionates.[13-16] The uranium co-ordination polyhedron in both structures is the usual pentagonal bipyramid.

TABLE 3

Interatomic distances and angles

	[UO$_2$(3Cl-pd)$_2$(PPh$_3$O)]	[UO$_2$(pd)$_2$(PPh$_3$O)]·C$_6$H$_6$
(a) Bonds (Å)		
Uranyl		
U–O(1)	1.79(2)	1.71(2)
U–O(2)	1.76(2)	1.70(2)
U–O Pentagon		
U–O(3)	2.32(2)	2.42(2)
U–O(4)	2.37(2)	2.35(2)
U–O(5)	2.41(2)	2.40(2)
U–O(6)	2.34(2)	2.41(2)
U–O(7)	2.33(2)	2.37(2)
PPh$_3$O		
P–O(7)	1.53(2)	1.49(2)
P–C(11)	1.82(3)	1.77(3)
P–C(17)	1.84(3)	1.82(3)
P–C(23)	1.76(3)	1.79(3)
C(11)–C(12)	1.39(3)	1.40(4)
C(12)–C(13)	1.47(4)	1.43(4)
C(13)–C(14)	1.40(4)	1.39(4)
C(14)–C(15)	1.33(4)	1.41(5)
C(15)–C(16)	1.48(4)	1.47(5)
C(16)–C(11)	1.40(3)	1.42(4)
C(17)–C(18)	1.40(3)	1.36(4)
C(18)–C(19)	1.41(3)	1.39(4)
C(19)–C(20)	1.37(4)	1.31(4)
C(20)–C(21)	1.42(4)	1.32(4)
C(21)–C(22)	1.49(4)	1.49(4)
C(22)–C(17)	1.37(4)	1.43(4)
C(23)–C(24)	1.44(3)	1.41(4)
C(24)–C(25)	1.47(4)	1.38(4)
C(25)–C(26)	1.38(3)	1.36(4)
C(26)–C(27)	1.40(3)	1.41(4)
C(27)–C(28)	1.41(3)	1.42(4)
C(28)–C(23)	1.42(3)	1.38(3)
pd (Molecule 1)		
O(3)–C(2)	1.31(2)	1.36(4)
C(2)–C(1)	1.47(3)	1.57(5)
C(2)–C(3)	1.39(3)	1.45(5)
C(3)–Cl(1)	1.75(3)	
C(3)–C(4)	1.42(3)	1.30(5)
C(4)–C(5)	1.49(3)	1.57(5)
C(4)–O(4)	1.26(3)	1.28(4)
(Molecule 2)		
O(5)–C(7)	1.34(3)	1.31(4)
C(7)–C(6)	1.55(4)	1.57(4)
C(7)–C(8)	1.33(3)	1.32(4)
C(8)–Cl(2)	1.80(3)	
C(8)–C(9)	1.35(3)	1.33(4)
C(9)–C(10)	1.47(4)	1.57(4)
C(9)–O(6)	1.32(3)	1.35(4)
Lattice C$_6$H$_6$		
C(29)–C(30)		1.41(6)
C(30)–C(31)		1.44(7)
C(31)–C(32)		1.41(7)
C(32)–C(33)		1.27(6)
C(33)–C(34)		1.60(6)
C(34)–C(29)		1.35(5)
(b) Angles (°)		
Uranyl		
O(1)–U–O(2)	177(1)	180(1)
Ring pentagon		
O(5)–U–O(6)	70(1)	72(1)
O(6)–U–O(7)	73(1)	74(1)
O(7)–U–O(4)	74(1)	O(7)–U–O(3) 73(1)
O(4)–U–O(3)	69(1)	70(1)
O(3)–U–O(5)	75(1)	O(3)–U–O(7) 73(1)

TABLE 3 (*Continued*)

pd (Molecule 1)		
O(3)–C(2)–C(3)	121(2)	126(4)
C(2)–C(3)–C(4)	126(2)	121(4)
C(3)–C(4)–O(4)	119(3)	128(4)
O(3)–C(2)–C(1)	117(3)	106(4)
C(1)–C(2)–C(3)	122(3)	129(4)
C(2)–C(3)–Cl(1)	119(2)	
Cl(1)–C(3)–C(4)	114(4)	
C(3)–C(4)–C(5)	124(3)	117(4)
C(5)–C(4)–O(4)	116(2)	116(4)
(Molecule 2)		
O(5)–C(7)–C(8)	121(3)	125(4)
C(7)–C(8)–C(9)	134(3)	128(4)
C(8)–C(9)–O(6)	115(3)	126(3)
O(6)–C(9)–C(10)	117(3)	106(3)
C(10)–C(9)–C(8)	129(3)	128(4)
C(9)–C(8)–Cl(2)	115(2)	
Cl(2)–C(8)–C(7)	111(2)	
C(8)–C(7)–C(6)	133(3)	124(4)
C(6)–C(7)–O(5)	106(3)	111(3)

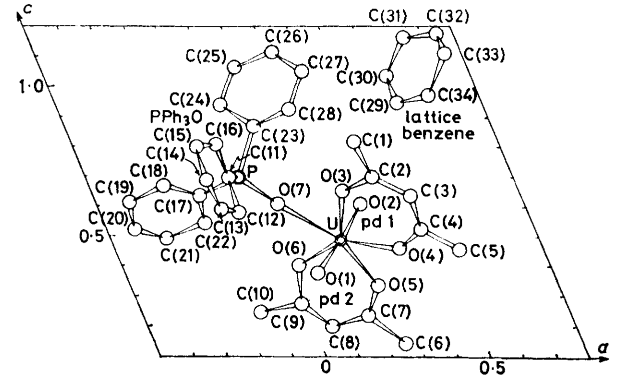

FIGURE 1 Projection of [UO$_2$(pd)$_2$(PPh$_3$O)]·C$_6$H$_6$ on the (*ac*) face of the unit cell

Diagrams of one molecule in the unit cell of each complex are shown in Figures 1 and 2, and Figures 3 and 4 illustrate the packing of the molecules in the crystal. In the diketonate, where the only symmetry element is a centre of symmetry, layers of [UO$_2$(pd)$_2$(PPh$_3$O)] molecules are arranged in parallel fashion, and the benzene molecule of crystallisation is trapped by four surrounding large molecules. Adjacent layers are similar, but reversed in direction. The centre of symmetry implies that the pentane-2,4-dionate pentagonal ring and the benzene planes are parallel throughout the structure. The pd molecules and the pentagonal ring form a chair-shaped system.

On the other hand, the chlorodiketonate structure is completely different. The large chlorine atoms on the periphery of the molecule have an effect in the crystallisation process, and no solvent molecules are incorporated. As well as centres of symmetry and two-fold screw axes, molecules are related by *c*-glide planes, which make pd molecular planes *ca.* 90° to each other. The large chlorine atoms probably prevent the chlorodiketonate from crystallising in a structure resembling that of the diketonate. The molecular planes are both parallel and mutually perpendicular in the chlorodiketonate, in the higher-symmetry space group $P2_1/c$. The pd molecules and the pentagonal rings form an L-shaped system in this crystal.

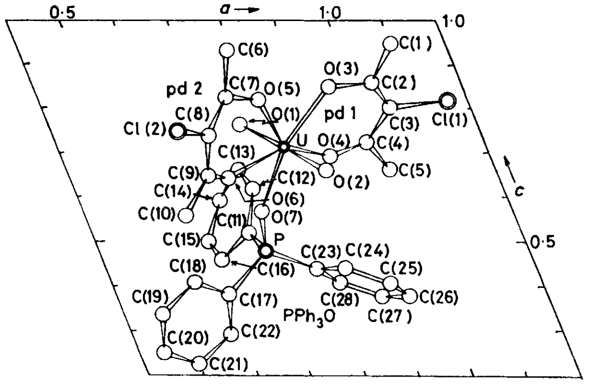

FIGURE 2 Projection on the (*ac*) face of $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$

Least-squares planes were calculated for the atoms of each pd molecule in both structures. No deviation from the mean plane was greater than 2 σ so the pd molecules are planar within the errors. The pentagonal rings show deviations of up to 2.9 σ [O(6) in the chlorodiketonate] and 3.2 σ [O(4) in the diketonate]. These border on being significant, and may be caused by slight mutual twisting of the pd molecules. The angle between the pd 1 and pd 2 planes is 9(2)° in the diketonate and 31(1)° in the chlorodiketonate. In the latter, pd 2 is coplanar with the pentagonal ring [mutual inclination = 2(1)°], while pd 1 is inclined at 23(1)° to the pentagonal plane; this is strictly L-shaped rather than boat-shaped. In the diketonate, pd 1 is inclined at 11(2)° to the pentagonal ring, and pd 2 at −10°. This is a true chair shape. Least-squares planes are given in Table 4.

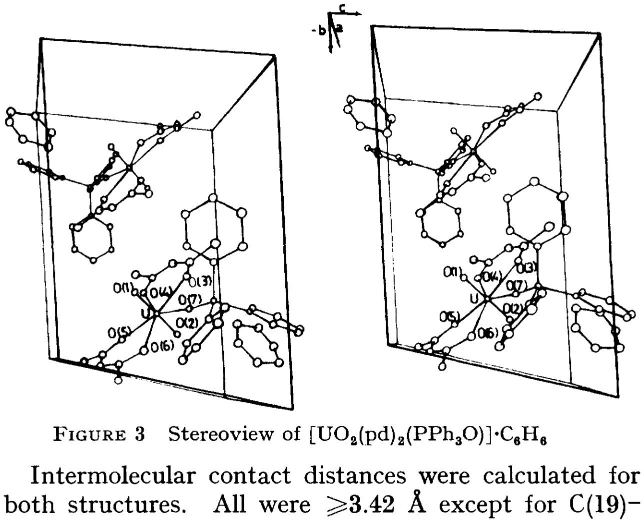

FIGURE 3 Stereoview of $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$

Intermolecular contact distances were calculated for both structures. All were ⩾3.42 Å except for C(19)–O(4) 3.29, C(14)–O(1) 3.35, C(19)–O(2) 3.35, and C(19)–C(4) 3.34 Å in the diketonate, and C(19)–O(6) 3.36 Å in the chlorodiketonate. These are possibly weak hydrogen bonds (the C · · · O distance of 3.6 Å corresponds to the van der Waals separation[17]). The packing is, however, largely of the van der Waals type. Similar C · · · O and C · · · F separations occur in α- and β-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$.[3,4]

Since no significant differences occur in the bond lengths around the uranium atom in both structures or in the intermolecular contact distances, the differences in colour may be due to the conformation of the pd rings or the molecular packing scheme. The orange complexes (β-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$ and the present chlorodiketonate) have at least one pd ring which is

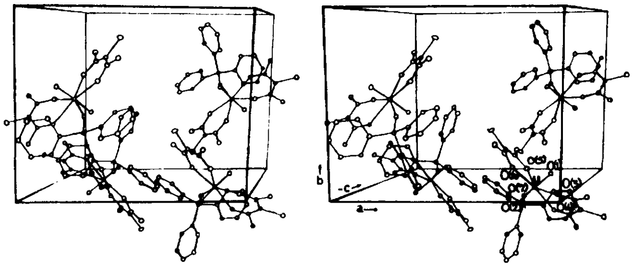

FIGURE 4 Stereoview of $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$

TABLE 4

Least-squares planes

(*a*) Equations in the form $Ax + By + Cz = D$ where *x*, *y*, and *z* are the positional co-ordinates in Table 2 (the *y* co-ordinates are translated by ½)

	$[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$				$[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$			
	A	*B*	*C*	*D*	*A*	*B*	*C*	*D*
pd 1	0.336	0.728	−0.680	1.78	0.380	−0.709	0.558	−4.33
pd 2	0.768	0.558	−0.522	8.91	0.281	−0.809	0.551	−4.91
Pentagon plane	0.675	0.588	−0.667	6.16	0.391	−0.601	0.619	−2.52

(*b*) Deviations (×10² Å). (A) refers to $[UO_2(3Cl\text{-}pd)_2(PPh_3O)]$ and (B) to $[UO_2(pd)_2(PPh_3O)]\cdot C_6H_6$

(*i*) pd molecule 1

Atom	C(1)	C(2)	C(3)	C(4)
Deviation (A)	−13(8)	3(8)	6(8)	5(8)
Deviation (B)	−6(10)	4(10)	8(10)	5(10)
Atom	C(5)	O(3)	O(4)	Cl
Deviation (A)	−15(8)	0(6)	4(6)	9(2)
Deviation (B)	−8(10)	−3(4)	−1(4)	

(*ii*) pd molecule 2

Atom	C(6)	C(7)	C(8)	C(9)
Deviation (A)	−1(8)	0(8)	−2(8)	3(8)
Deviation (B)	11(8)	−6(8)	−9(8)	−3(8)
Atom	C(10)	O(5)	O(6)	Cl(2)
Deviation (A)	9(8)	9(7)	−13(7)	−4(3)
Deviation (B)	3(8)	−5(4)	9(4)	

(*iii*) Pentagonal plane

Atom	U	O(3)	O(4)	O(5)
Deviation (A)	0(1)	7(7)	5(7)	−16(7)
Deviation (B)	2(1)	9(4)	−13(4)	11(4)
Atom	O(6)	O(7)		
Deviation (A)	20(7)	−15(7)		
Deviation (B)	−6(4)	−2(4)		

coplanar with the pentagonal ring, while in the yellow complexes all the pd or hfpd rings are not coplanar.

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