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(Chloromethyl)diphenylphosphine Oxide Complexes of Tin and Uranium

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Abstract. The reactions between (chloromethyl)diphenylphosphine oxide, $ClCH_2P(O)Ph_2$ (**L**) and Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl and $UO_2(NO_3)_2$ form complexes **1**, **2**, **3** and **4** respectively. The organotin complexes **1**, **2**, **3**, exhibit a 1:1 ligand metal stoichiometry while the uranyl nitrate (**4**) complex is a 2:1 complex. The complexes have been characterized by ^{13}C, ^{119}Sn and ^{31}P NMR spectroscopy and their single crystal X-ray structures have also been determined. The chlorine atom of the (chloromethyl)diphenylphosphine oxide does not directly interact either intramolecularly or intermolecularly with either the uranium or tin center as determined by the internuclear distances being greater than the sum of their respective Van der Waal's radii. However, in **1** and **4** there are clear dipolar interactions that result in conformational and molecular alignments due to the presence of the CH_2Cl group.

Keywords: (Chloromethyl)diphenyl phosphine oxide, Tin, Uranium, complexes, stoichiometry.

Resumen. Las reacciones entre el óxido de (clorometil)difenilfosfina $ClCH_2P(O)Ph_2$ (**L**), y Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl y $UO_2(NO_3)$ forman los complejos **1, 2, 3** y **4** respectivamente. Los complejos de organoestaño **1, 2** y **3,** exhiben una estequiometría metal ligando 1:1 mientras que en el complejo de nitrato de uranilo (**4**) esta es 2:1. Los complejos se han caracterizado por RMN de ^{13}C, ^{119}Sn y ^{31}P y su estructura cristalina ha sido determinada por difracción de rayos X de sus respectivos monocristales. El átomo de cloro del óxido de (clorometil)difenilfosfina no interactúa, ya sea intramolecular o intermolecularmente con el centro métalico uranio o estaño dado que las distancias internucleares son mayores que la suma de los correspondientes radios de Van der Waal's. Sin embargo, en **1** y **4** se manifiesta una clara interacción dipolar que da como resultado un alineamiento conformacional de las moléculas en la estructura cristalina debido a la presencia del grupo CH_2Cl.

Palabras clave: (Clorometil)difenilfosfina, estaño, uranio, complejos, estequiometría.

Introduction

Phosphine oxide ligands have found a wide applicability to the extraction and separation of metals, especially the lanthanides and actinides [1,2] A particular series of phosphine oxide derivatives, the carbamoylphosphine oxides, CMPO, $R_2P(O)CH_2C(O)NR_2$, are extremely useful in the separation of actinides [3,4]. Metal-CMPO complexes exhibit both a bidentate mode of coordination *via* the P(O) and C(O) groups [5-8], and in a mondentate mode where the C(O) group does not function *via* direct bonding but, for example, coordinates *via* a bridging water molecule [9]. In this regard we recently reported the synthesis, structural and spectroscopic characterization of uranyl and stannyl derivatives of di(p-tert-butylphenyl)-N,N-di(iso-butyl)carbamoylmethylphosphine oxide and observed both monodentate, *via* P(**O**), and bidentate, *via* P(**O**) and C(**O**) groups [10a].

Halogen atoms are also known to coordinate to metal ions directly as terminal and bridging ligands toward both main group and transition metals [11,12]. We are interested in the modification of phosphine oxide ligands and in the search for a possible role of chlorine as a Lewis base to form a bidentate or pseudo-bidentate stabilizing coordination. We now report the properties of (chloromethyl)diphenylphosphineoxide, $Ph_2P(O)CH_2Cl$, hereafter designated as **L** with respect to its reactions with $UO_2(NO_3)_2$, Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl.

Experimental

All reactions were performed in dry, oxygen-free, solvents under an atmosphere of nitrogen or argon. Chloromethyldiphenylphosphine oxide was prepared by using a modified literature procedure [13]; Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl were purchased from Gelest; $ClPh_2P$ and $UO_2(NO_3)_2.6H_2O$ were purchased from Aldrich and all reagents were used as received. NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of hydroxymethyldiphenylphosphine oxide. To chlorodiphenylphosphine (12.2 g, 56.0 mmol) was added to 37% aqueous formaldehyde solution (100 mL, 1.2 mol), concentrated hydrochloric acid (100 mL) and the mixture was heated at 100 °C overnight. Evaporation of the reaction mixture at reduced pressure produced an oil which was neutralized with aqueous sodium bicarbonate solution and extracted with chloroform (3 × 40 ml). The organic layers were combined, dried over magnesium sulfate, filtered and the solvents were removed under reduced pressure to give hydroxymethylphosphine oxide as a white solid (9.0 g, 38.8 mmol, 70%) m.pt. 138-139 °C.

Synthesis of chloromethyldiphenylphosphine oxide. To a solution of hydroxymethyldiphenylphosphine oxide (4.0 g,

17.2 mmol) dissolved in dichloromethane (25 mL) was added thionyl chloride (2.5 mL, 34.3 mmol) and the mixture was stirred for 3 h at room temperature. The solution was quenched with water (~50 mL), neutralized with aqueous sodium bicarbonate and extracted with dichloromethane. The organic layers were combined, dried with magnesium sulphate, filtered, and the solvent removed under reduced pressure to give (chloromethyl)diphenylphosphine oxide as a white solid (2.9 g, 11.6 mmol, 67%) m. pt. 137-138 ^{o}C**.**

^{1}H NMR (300 MHz) 3.94 (2H, d, $^{2}J_{PH}$ = 6.5 Hz, CH_2), 7.39 (6H,m, aryl), 7.73 (4H,m, aryl): ^{13}C NMR (75.4 MHz): 37.6 (d, $^{1}J_{PC}$ = 72.0 Hz, CH_2), 128.7 (d, ^{2}JPC = 12.2 Hz, CH, m-aryl), 129.60 (d, $^{1}J_{PC}$ = 104.0 Hz, aryl, ipso C), 131.4 (d, $^{3}J_{PC}$ = 9.42 Hz) 132.5 (d, $^{4}J_{PC}$ = 2.70 Hz, p-aryl C): ^{31}P NMR, 29.6; IR (ν P=O, cm^{-1}, THF): 1103.

Synthesis of $(Ph)_2P(O)CH_2Cl.Me_2SnCl_2$ (1) and $(Ph)_2P(O)CH_2Cl.Ph_2SnCl_2$ (2). To 10 mL of a warm ethanol solution of the ligand (1.25 g, 5 mmol) was added an equimolar amount of respective organotin compound in 10 mL of warm ethanol. The mixture was refluxed overnight and upon removal of the solvent a white crystalline solid was obtained. The solid was recrystallized from a ethanol/hexane solvent in overall yields between 70-80 %, m. pts: **1**, 110-111 ^{o}C; **2**, 128-129 ^{o}C.

1. ^{1}H NMR, 1.08(3H, *J* = 80.4 Hz); 4.10 (2H, d, *J* = 6.3 Hz); 7.47- 7.66 (m, 10H aryl): ^{13}C NMR, 11.2 ($SnCH_3$), 36.9 (2H, d, ^{2}J = 73.2 Hz), 127.5 (d, *J* = 106 Hz), 129.0 (d, *J* = 12.5 Hz), 131.7 (d, *J* = 9.9 Hz;), 133.4: ^{119}Sn NMR, -8.34: ^{31}P NMR, 33.4: IR (ν P=O, cm^{-1},THF) 1047: Elemental analysis, Found, C, 37.71; H,3.69. Calcd. C, 38.30; H, 3.85%.

2. ^{1}H NMR, 3.91(2H, d, *J* = 7.1 Hz, CH_2); 7.18-7.67 (20H m, aryl): ^{13}C NMR, 36.5 (d, *J* = 73.5 Hz), 127.0 (d, *J* = 107 Hz), 128.9 (d, *J* = 46.6 Hz), 128.9 (d, *J* = 12.4), 130.5, 132.0 (d, *J* = 10.0 Hz), 133.3 (d, *J* = 2.4 Hz) 135.3 (d, *J* = 32.3 Hz), 142.4: ^{119}Sn NMR, -180.0, ^{31}P NMR, 35.6: IR (ν P = O, cm^{-1}, THF), 1049: Elemental analysis, Found, C, 49.8; H, 3.75; Calc. C, 50.5; H, 3.73 %.

Synthesis of $(Ph)_2P(O)CH_2Cl.Ph_3SnCl$ (3). To 10 mL of a warm ethylacetate solution of the ligand (1.25 g, 5 mmol) was added an equimolar amount of triphenyltinchloride, Ph_3SnCl, in 10 mL of warm ethylacetate. The clear solution was refluxed for 5 min. Upon cooling a precipitate of white shining crystals of **3** were obtained in 80% yield, m. p. 150-152^{o}C. Further recrystallisation from ethylacetate produced X-ray quality crystals.

3. ^{1}H NMR, 3.82 (2H, d, *J* = 6.6 Hz, CH_2), 7.18-7.67 (25H, m, aryl): ^{13}C NMR 37.27 (d, *J* = 72.4 Hz), 128.59 (d, *J* = 12.1Hz), 130.11 (*J* = 7.0 Hz) 131.6 (d, *J* = 9.6 Hz), 132.7 (d, *J* = 2.7 Hz) 129.0, (d, *J* = 32.0 Hz); 136.1 (d, *J* = 24.2 Hz), 138.8 (d, *J* = 6.5 Hz): ^{119}Sn NMR-82.9: ^{31}P NMR, 30.6: IR (ν P = O, cm^{-1},THF):1068. Elemental analysis, Found: C, 58.63; H, 4.61; Calc: C, 58.53: H, 4.28 %.

Synthesis of $\{(Ph)_2P(O)CH_2Cl\}_2.UO_2(NO_3)_2$ (4). The ligand (1.25 g, 5 mmol) was combined with $UO_2(NO_3)_2.6H_2O$ (1.25 g, 2.5 mmol) in 20 mL of ethanol. The solution was allowed to evaporate slowly and a yellow crystalline solid was obtained. The resulting compound was recrystallised from ethyl alcohol, (1.8 g, 2.0 mmol, 79%), m. pt: 182-183^{o}C.

4.^{1}H NMR, 4.36 (2H, d, *J* = 5.4 Hz, CH_2), 7.47-7.87 (20H, m, aryl): ^{13}C NMR, 37.0 (2H, d, *J* = 74.4 Hz), 127.4 (d, *J* = 110.0 Hz), 129.3 (d, *J* = 12.74 Hz), 132.1 (d, *J* = 10.4), 133.8 (d *J* = 2.4): ^{31}P NMR, 47.2: IR (ν P = O, cm^{-1}, THF) 1085: Elemental analysis, Found: C, 34.55, H, 2.76 ; Calc: C, 34.87 , H, 2.70 %.

Single Crystal X-ray analysis.

Crystals of **1**, **2** , **3** and **4** were mounted on glass fibers and the X-ray intensity data were measured on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKá fine-focus sealed tube (l = 0.71073Å). Frames were collected at 296k for **1, 3, 4** and 100k for **2** with a scan width of 0.30º in w and an exposure time of 10 sec/frame using the Bruker SMART software [14a]. The frames were integrated with the Bruker SAINT software using a narrow-frame integration algorithm [14b]. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multi-scan technique with Bruker SADABS program [14c]. The corresponding experimental parameters for each compound are summarized in Table 1.

The structures were solved by direct methods and refined using the Bruker SHELXTL software Package [14d] with all non-hydrogen atoms refined anisotropically and hydrogen atoms placed at calculated positions and refined as riding atoms.

The structure of **2** was first solved at room temperature and showed some disorder in one of the phenyl rings, then, data were collected at 100 K and the dynamic disorder observed at room temperature was no longer present .

The numbering schemes are shown in Figures 1-4 that were produced with the XSHELL graphics program in the SHELXTL suite [14d]. Selected bond lengths and bond angles for **1** -**4** are presented in Table 2, respectively.

Results and Discussion

Crystalline complexes between **L** and the metal species Me_2SnCl_2, Ph_2SnCl_2, Ph_3SnCl and $UO_2(NO_3)_2$ were readily formed. In the case of the organotin chlorides 1:1 complexes were obtained, $R_2SnCl_2.L$ (R = Me (**1**), Ph (**2**) and $Ph_3SnCl.L$ (**3**) whereas for the uranyl nitrate a 2:1 complex $UO_2(NO_3)_2.L_2$ (**4**) was obtained.

Spectroscopic characterization

The use of ^{31}P NMR data for characterization of phosphine oxide complexes is well-established and resonance of the free

Table 1. Experimental and refinement data for crystallography of compounds **1**-**4**

Compound	**1**	**2**	**3**	**4**
Identification code	54RK	169RK	49RK	50RK
Empirical formula	C15 H18Cl3OP Sn	C25 H22 Cl3OP Sn	C31 H27 Cl2OP Sn	C26H24Cl2N2O10P2U
Formula weight	470.3	594.44	636.09	895.34
Temperature (K)	296(2)	100(2)	296(2)	296(2)
Wavelength (?)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm)	0.40 × 0.10 × 0.04	0.30 × 0.30 × 0.10	0.10 × 0.08 × 0.08	0.30 × 0.10 × 0.10
Crystal habit	colorless chunk	colorless fragment	colorless chunk	colorless prism
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	Pc	P2(1)/n	P-1
Unit cell (Å): a	9.030(2)	9.3145(6)	8.8798(4)	a = 9.1077(5)
b	9.498(2)	15.6861(10)	9.2817(4)	b = 9.9186(6)
c	11.913(3)	17.0586(11)	35.2403(17)	c = 10.2132(6)
α	94.895(4)°	90°	90°	77.4160(10)°
β	110.828(4)°	91.1540(10)°	94.1650(10)°	63.8090(10)°
γ	97.486(4)°	90°	90°	79.9160(10)°
Volume, Å^3	937.3(4)	2491.9(3)	2896.8(2)	804.71(8) Å3
Z	2	4	4	2
Density (calc.) Mg/m^3	1.666	1.584	1.458	1.848
Absorption coeff. (mm^{-1})	1.871	1.427	1.144	5.363
F(000)	464	1184	1280	430
Detector distance (cm)	5.96	5.96	5.96	5.97
Theta range for data collection (º)	1.85 to 23.28	1.30 to 23.71	1.16 to 28.29	2.11 to 28.29
Index ranges	-9 £ *h* £ 10	-10£ *h* £ 10	-11 £ *h* £ 11	-11 £ *h* £ 12
	-9 £ *k* £ 10	-17 £ *k* £ 16	-12 £ *k* £ 11	-13 = h = 13
	-13 £ *l* £ 13	-18 £ *l* £ 13	-45 £ *l* £ 47	-13 £ *l* £ 13
Reflections collected	4269	10967	32970	9379
Independent reflections	2670 [R(int) = 0.0161]	6104 [R(int) = 0.0185]	6949 [R(int) = 0.0289]	3735 [R(int) = 0.0210]
Coverage of independent reflections	98.90%	94.80%	96.60%	93.40%
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max. / min. transmission	0.5215 / 0.9289	0.8705 / 0.6742	0.9141 / 0.8942	0.6161 / 0.2961
Refinement technique	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Function minimized	S w(Fo^2 - Fc^2)^2	S w(Fo^2 - Fc^2)^2	S w(Fo^2 - Fc^2)^2	S w(Fo^2 - Fc^2)^2
Data/restraint /parameters	2670 / 0 / 192	6104 / 2 / 559	6949 / 0 / 325	3735 / 0 / 196
Goodness-of-fit on F^2	1.001	1.09	1.14	1.076
R1; I > 2σ(I)	0.031, 2446 data	0.0320, 5945 data	0.0469, 5727 data	0.0251, 3735 data
wR2; I > 2σ(I)	0.0735, 2446 data	0.0779, 5945 data	0.1026, 5727 data	0.0593, 3735 data
R1 all data	0.0344	0.0329	0.0604	0.0251
wR2 all data	0.0756	0.0785	0.11	0.0593
Largest diff. peak and hole	0.461 and -0.308 eÅ^{-3}	1.173 and -0.32 eÅ^{-3}	0.788 and -0.299 eÅ^{-3}	1.562 and -0.486 eÅ^{-3}

ligand at 29.6 ppm shifts to 47.2 ppm for the uranyl complex **1** (Δδ = 17.6 ppm) whereas only modest Δδ values of ~ 4-6 ppm to 33.4, 35.6 and 30.6 ppm were noted for **1** and **2** and **3**, respectively. Such results are similar to the data obtained for CMPO complexes of the uranyl nitrate and organotin chloride complexes previously reported [10a]. In that case the bidentate character of the CMPO-uranyl complex cf. mondentate tin complexes was suggested to be responsible, *vide infra*.

The ^{119}Sn NMR spectra of **1**, **2** and **3** exhibit substantial chemical shifts compared to the uncoordinated compounds as would be expected for a change from tetrahedral geometry to trigonal bipyramidal. The resonances, which are in general broad, appear at –8.3 ppm for Me_2SnCl_2.L, (Δδ = -150 ppm); -180.0 ppm for Ph_2SnCl_2.L, (Δδ = -152 ppm); and –83 ppm for Ph_3SnCl.L, (Δδ = -38 ppm). These shifts are similar to those noted for the CMPO organotinchloride complexes [10] and the $Ph_3P(O)$ complexes of Ph_3SnCl and Et_2SnCl_2 [10b].

^{13}C and ^{1}H NMR data exhibit no significant changes from those resonances for the uncoordinated ligand, but the P=O stretching frequency of the free ligand at 1103 cm^{-1} shifts to

Table [2] Selected bond lengths and angles for compounds 1-4.

Compound **1**					
Sn-C15	2.092(4)	Sn-C14	2.100(4)	Sn-O	2.356(3)
Sn-Cl2		2.3732(12)	Sn-Cl3	2.4808(13)	P-O
1.485(3)					
Cl1-C1		1.780(4)			
C15-Sn-C14	143.5(2)	C15-Sn-O	84.23(17)	C14-Sn-O	86.12(15)
C15-Sn-Cl2	106.55(15)	C14-Sn-Cl2	107.85(14)	O-Sn-Cl2	86.56(8)
C15-Sn-Cl3	94.48(16)	C14-Sn-Cl3	94.23(14)	O-Sn-Cl3	178.22(7)
Cl2-Sn-Cl3	94.99(4)				
Compound **2**					
Sn1-C1	2.103(5)	Sn1-C7	2.130(6)	Sn1-O1	2.264(4)
Sn1-Cl2	2.3942(17)	Sn1-Cl1	2.4549(15)	Sn2-C32	2.105(5)
Sn2-C26	2.105(5)	Sn2-O2	2.272(4)	Sn2-Cl5	2.3814(16)
Sn2-Cl4	2.4425(15)	P2-O2		1.473(4)	P1-O1
1.486(4)					
C25-Cl3	1.763(6)	C50-Cl6	1.747(6)		
C1-Sn1-C7	125.7(2	C1-Sn1-O1	87.00(18)	C7-Sn1-O1	85.15(18)
C1-Sn1-Cl2	112.87(16)	C7-Sn1-Cl2	119.81(18)	O1-Sn1-Cl2	85.13(11)
C1-Sn1-Cl1	98.95(16)	C7-Sn1-Cl1	93.37(16)	O1-Sn1-Cl1	173.51(11)
Cl2-Sn1-Cl1	90.15(6)	C32-Sn2-C26	124.8(2)	C32-Sn2-O2	84.02(17)
C26-Sn2-O2 84.95(18)	C32-Sn2-Cl5	120.11(17)	C26-Sn2-Cl5	112.60(15)	
O2-Sn2-Cl5 85.29(11)	C32-Sn2-Cl4	95.11(15)	C26-Sn2-Cl4	98.58(16)	
O2-Sn2-Cl4 176.16(11)	Cl5-Sn2-Cl4	91.94(6)			
Compound **3**					
Sn1-C26	2.128(3)	Sn1-C20	2.132(3)	Sn1-C14	2.135(3)
Sn1-O1	2.347(2)	Sn1-Cl1	2.5046(9)	P-O	
1.489(2)					
Cl2-C1	1.765(4)				
C26-Sn1-C20 115.87(12) C26-Sn1-C14 120.24(12)	C20-Sn1-C14	122.13(11)			
C26-Sn1-O1 85.26(10) C20-Sn1-O1	86.85(11)	C14-Sn1-O1	84.69(10)		
C26-Sn1-Cl1 92.85(8) C20-Sn1-Cl1	98.11(10)	C14-Sn1-Cl1	92.31(9)		
O1-Sn1-Cl1 175.02(6)					
Compound **4**					
U-O5A 1.755(2) U-O5 1.755(2)	U-O1	2.363(2)			
U-O1A 2.363(2) U-O3A 2.534(3) U-O3	2.534(3)				
U-O2A 2.564(3) U-O2 2.564(3)					
O5A-U-O5	180.00(17)	O5A-U-O1	89.10(10)	O5-U-O1	90.90(10)
O5A-U-O1A	90.90(10)	O5-U-O1A	89.10(10)	O1-U-O1A	180.00(10)
O5A-U-O3A	90.50(12)	O5-U-O3A	89.50(12)		

expected lower values upon coordination: 1047cm^{-1} (**1**); 1049 cm^{-1} (**2**); 1068 cm^{-1} (**3**); 1085 cm^{-1} (**4**).

Structural characterization

Selected bond lengths and bond angles for complexes **1-4** are presented in Table 2 and their strucvtures illustrated in Figures 1-4. All the complexes exhibit coordination of the chloromethylphosphine oxide in a monodentate fashion with no well-characterized Cl...metal bonding. For the tin complexes **1-3** the P=**O-Sn** bond distances are in the range 2.264(4) – 2.356(3)Å with no significant distinction between the dichloro- and mono-chloro tin complexes. Likewise the **P=O** bond lengths for the same complexes range form 1.473(4)–1.489(2)Å representing a difference from the bond length in the free ligand of 1.493Å.

The structure of **1** reveals a typical dimerization of the dichlorotin unit *via* intermolecular bridging Cl——Sn interactions. The intermolecular Sn——Cl distance of 3.883 Å and Sn-Cl——Sn angle of 177.7º results in a distorted octahedral

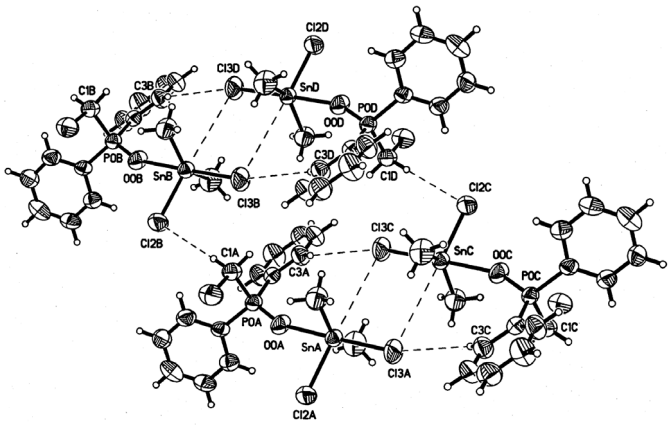

Fig. 1. Structure of $Me_2SnCl_2.L$

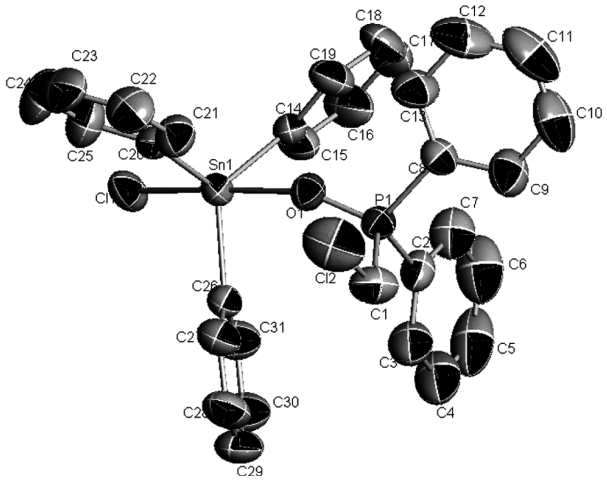

Fig. 3. Structure of $Ph_3SnCl.L$

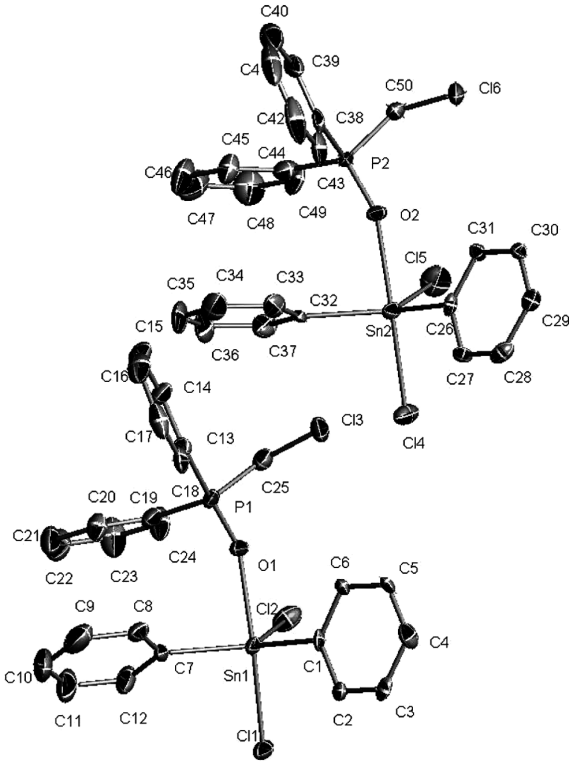

Fig. 2. Structure of $Ph_2SnCl_2.L$

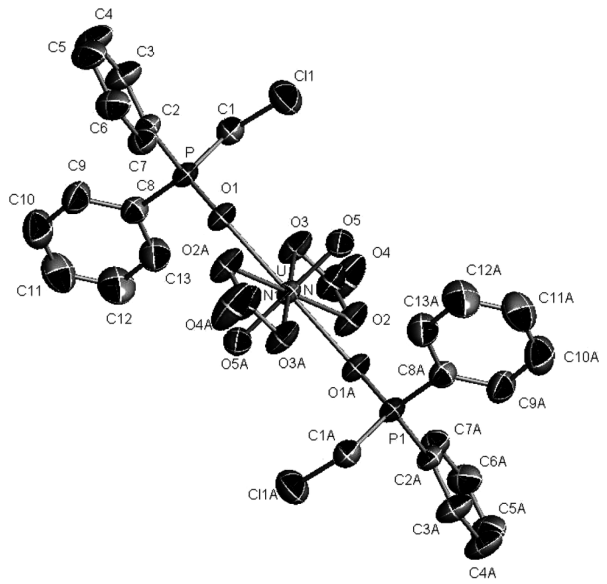

Fig. 4. Structure of $UO_2(NO_3)_2.2L$

coordination for the tin atom as illustrated in Figure 1. This arrangement also permits a weak interaction between the tin coordinated chlorines and the symmetry related hydrogens to H1a (distance H1bd——Cl 2c = 2.833 Å; C1d-H1——Cl 2c angle = 175.3º) and H3a (distance H3c——Cl2c = 2.864 Å; C 3c-H3c——Cl 3a angle = 133.8º) in vicinal molecules favoring the alignment of the dimeric units in a self-assembled infinite chain. The intramolecular Sn…Cl internuclear distance of 4.809Å is well beyond any normal bonding interaction limit.

The structures of **2** and **3** consist of discrete molecules showing no clear Sn——Cl intra- and intermolecular interaction. In both compounds the tin atom is in a distorted trigonal bi-pyramidal coordination as reported in Table 2. However, as can be seen from the unit cell of **2**, the two molecules in the unit cell orient in such a manner that the Cl atom of the choromethyl group aligns well with the tin atom of the adjacent molecule. The internuclear Sn2-Cl3 distance of 4.970Å is well beyond the sum of their van der Waals radii of ~3.85Å; however, it is clear that some form of supramolecular order is imposed upon the solid state structure.

In compound **4** the uranium atom is located at the center of symmetry in the origin of the unit cell resulting in eight oxygen atoms around the uranium, four of them from the nitrate ions and two from the chloromethyldiphenylphosphine oxides distributed in the equatorial plane leaving the remain-

ing two oxygens in the axial positions in a pseudo-octahedral fashion. The intramolecular U…Cl internuclear bond distance of 4.671Å is well above that of the sum of their respective Van der Waals radii; however, as in the case of **2** a clear conformational preference of the CH_2Cl group aligns it with the metal centre, in this case in an intramolecular manner as opposed to the intermolecular fashion of **2**.

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