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Dithiophosphinate Complexes of the Actinides. II. Preparation and Characterisation of the Compounds $UO_2(S_2PR_2)_2\cdot R'OH$, $[Et_4N][UO_2(S_2PR_2)_2Cl]$ and $UO_2(S_2PR_2)_2\cdot Me_3PO$. The Crystal Structures of $UO_2(S_2PR_2)_2\cdot EtOH$, R = Ph and C_6H_{11}, $[Et_4N][UO_2(S_2PR_2)_2Cl]$, R = Me and Ph, and $UO_2(S_2PMe_2)_2\cdot Me_3PO$

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Salts of dithiophosphinic acids, R_2PS_2H, react with UO_2Cl_2 in alcoholic, R'OH, solution to yield the complexes $UO_2(S_2PR_2)_2\cdot R'OH$. In the presence of excess chloride ion the alcohol is displaced to form the anionic chloro-complexes, which may be isolated as their $[Et_4N]^+$ salts. Similar reactions with UCl_4 in the air yield the same compounds in a novel double oxidation reaction. The initially formed U(IV) complexes are rapidly oxidised by the air to yield the corresponding uranyl compound and, at the same time, two ligands are oxidised to form the dimer, $[R_2PS_2]_2$. When $[UCl_6]^{2-}$ is employed, only the chloro-complexes are obtained. The complexes for R = Me, Et, Pr^i, OMe, OEt, OPr^i, Ph and C_6H_{11} have been characterised by elemental analysis, IR and NMR spectroscopy.

From one reaction of UCl_4 and NaS_2PMe_2, the complex $UO_2(S_2PMe_2)_2\cdot Me_3PO$ was obtained by an unknown route.

The crystal structures have been determined for two alcohol adducts, two chlorocomplexes and the phosphine oxide adduct.

$UO_2(S_2PPh_2)_2\cdot EtOH$: Triclinic, a = *11.589(2),* b = *11.6928(8),* c = *13.273(2)* Å, *α = 113.205(8), β = 110.849(9), γ = 92.979(9)°, $P\bar{1}$, R = 0.057.*

$UO_2\{S_2P(C_6H_{11})_2\}_2\cdot EtOH$: Monoclinic, a = *12.765(1),* b = *16.502(2),* c = *15.813(2)* Å, *β = 90.622(9)°, $P2_1/n$, R = 0.044.*

$[Et_4N][UO_2(S_2PMe_2)_2Cl]$: Orthorhombic, a = *10.770(1),* b = *11.730(2),* c = *20.079(2)* Å, *$P2_12_12_1$, R = 0.033.*

$[Et_4N][UO_2(S_2PPh_2)_2Cl]$: Monoclinic, a = *11.341 (2),* b = *20.889(3),* c = *16.172(2)* Å, *β = 101.79(1)°, $P2_1/n$, R = 0.046.*

$UO_2(S_2PMe_2)_2\cdot Me_3PO$: Orthorhombic, a = *11.499 (1),* b = *13.079(1),* c = *14.362(1)* Å, *Pcmn, R = 0.050.*

All five complexes have pentagonal bipyramidal structures. The pentagonal plane contains four sulphur atoms from the two bidentate dithiophosphinate ligands (U–S = 2.873 Å*) and one oxygen or chlorine atom from the coordinated ethanol (U–O = 2.41* Å*), phosphine oxide (U–O = 2.32* Å*) or chloride (U–Cl = 2.677* Å*). The uranyl group is linear (U–O = 1.76* Å*) and perpendicular to the equatorial plane. In both ethanol adducts the ethyl groups of the alcohol are disordered. The phosphine oxide adduct has crystallographic m symmetry.*

No more than two bidentate ligands could be attached to the uranium; however, a fifth equatorial coordination site is always occupied by an additional ligand, even when the substituents at phosphorus are bulky.

Introduction

We have been investigating dithiophosphinate complexes of the lanthanides for several years [1]. Our interest in this type of compound lies in the characterisation of complexes of hard metal ions with soft donor ligands. When the donor atom is as polarisable as sulphur, effects due to covalent contributions to the bonding are seen to be amplified *e.g.* we have been able to measure appreciable hyperfine couplings to the phosphorus nuclei from the NMR spectra of the paramagnetic lanthanide ions [2, 3].

We have recently turned our attention to the actinides where a more varied chemistry is to be expected. In the first paper in this series [4] we reported the preparation, characterisation and crystal structures of complexes of thorium(IV) of the type $Th(S_2PR_2)_4$. This study has now been extended to uranium for which a greater number of oxidation

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states are accessible, and in this paper we report the preparation and characterisation of a series of uranyl complexes. We have chosen to start with these uranium(VI) species as preliminary studies showed uranium(IV) to be rapidly oxidised under our experimental conditions. The uranium(IV) analogues will be described in a later publication [5].

To our knowledge, the only uranyl complexes containing dithiophosphinate ligands wich have been well characterised are a series of mixed ligand complexes where the additional ligand was a phosphine oxide [6]. Brief communications [7–10] have also appeared reporting complexes with the formula $UO_2(S_2PR_2)_2$, but in the light of the work that we report here it seems unlikely that these formulations are correct. Under the reaction conditions employed, it is far more likely that an additional solvent molecule is bound to uranium. The present study will also shed some light on the species present when dithiophosphinates are used in the solvent extraction of uranium(VI) [11].

The chemistry of the actinides with sulphur donor ligands is not vast [12]. Perhaps the best characterised analogues of the present compounds are complexes formed with diethyldithiocarbamate. Again, these are mainly of the type $UO_2(S_2CNEt_2)_2 \cdot L$ where L is an additional monodentate oxygen donor.

In the present study we were interested in the influence of the steric properties of the ligands on the possible coordination around the linear UO_2^{2+} moiety. We wished to know whether it would be possible to prepare $[UO_2(S_2PR_2)_3]^-$ or $UO_2(S_2PR_2)_2$ species, or whether the only complexes formed would be of the type $UO_2(S_2PR_2)_2 \cdot L$ where L is an additional monodentate ligand. We have thus carried out a systematic study of these systems, including five X-ray structure determinations, and report our results herein.

Experimental

Solvents were purified by standard methods [13]. $UO_2Cl_2 \cdot 3H_2O$ was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ and HCl (12 *M*) by repeated evaporation and crystallised over NaOH. UCl_4 was used as supplied (ICN Pharmaceuticals Inc). $[Et_4N]_2[UCl_6]$ was prepared by bubbling HCl gas through an ethanolic solution of UCl_4 and Et_4NCl. Salts of dithiophosphinic acids were prepared by literature methods [14].

Infrared spectra were recorded as nujol mulls or KBr discs with a Perkin-Elmer PE 577 spectrometer. Proton NMR spectra were obtained from CD_2Cl_2 solutions with Bruker WP 60, WH 80, or WVH 360 Instruments, and chemical shifts are reported relative to $SiMe_4$.

Micro-analyses (C, H, S, Cl) were carried out by Herrn. W. Manser, ETH, Zurich.

$UO_2(S_2PR_2)_2 \cdot R'OH$

From $UO_2Cl_2 \cdot 3H_2O$

One mol of $UO_2Cl_2 \cdot 3H_2O$ was allowed to react with two mol of MS_2PR_2 (M = Na^+, NH_4^+; R = Me, Et, Pr^i, OMe, OEt, OPr^i, Ph, C_6H_{11}) in hot ethanol (methanol for R = OMe, isopropanol for R = OPr^i) for about 30 minutes. The resulting orange solution was taken to dryness and the complexes extracted from the MCl residue with CH_2Cl_2. The products were recrystallised after solvent removal from a small amount of the appropriate alcohol diluted with toluene at about 0 °C. For R = Et, the diluting solvent was n-heptane. In the case of R = C_6H_{11}, the complex is only sparingly soluble in both ethanol and CH_2Cl_2, hence the synthesis was carried out in enough ethanol to prevent precipitation of NH_4Cl, and the product filtered off.

From UCl_4

One mol of UCl_4 was allowed to react with four mol of MS_2PR_2 (R = Et, Ph) in hot ethanol in the open air for about 30 minutes. The initially green solution rapidly turned orange. After solvent removal, the solid was extracted with CH_2Cl_2 and the filtrate evaporated. The residue was re-extracted with ether and the insoluble (complex) and soluble (dimerised ligand) fractions recrystallised from ethanol. For R = C_6H_{11}, the complex is insoluble in ethanol, hence, enough solvent was used to prevent precipitation of NH_4Cl and the complex filtered off. The ligand dimer was then recovered from the filtrate as above.

$[Et_4N][UO_2(S_2PR_2)_2Cl]$

From $UO_2Cl_2 \cdot 3H_2O$

One mol of $UO_2Cl_2 \cdot 3H_2O$ and one mol of Et_4NCl were allowed to react with two mol of MS_2PR_2 (M = Na^+, NH_4^+; R = Me, Et, Pr^i, OMe, OEt, OPr^i, Ph, C_6H_{11}) in refluxing ethanol for *ca.* 20 min (methanol for R = OMe, isopropanol for R = OPr^i, acetonitrile/dioxan for R = C_6H_{11}). The resulting orange solution was filtered, evaporated in vacuo, and the solid extracted with CH_2Cl_2. After solvent removal, the product was recrystallised from the appropriate alcohol (with addition of CH_2Cl_2 in the case of R = Me, Et, Ph, or ether for R = OEt). The product for R = C_6H_{11} was recrystallised from acetonitrile.

From UCl_4

One mol of UCl_4, one mol of Et_4NCl and four mol of MS_2PR_2 (R = Et, Ph) were refluxed in ethanol for *ca.* 20 min. During this time the initially green solution became yellow/orange. After filtration and solvent removal, the residue was extracted with CH_2Cl_2 to eliminate MCl. The resulting solution was filtered and evaporated and the product extracted with ether. Both the ether soluble and insoluble fractions were recrystallised from ethanol. The ether insoluble products are identical to the complexes prepared above, and the ether soluble products are the ligand dimers.

From $[Et_4N]_2[UCl_6]$

One mol of $[Et_4N]_2[UCl_6]$ and four mol of MS_2PR_2 (R = Et, Ph, C_6H_{11}) were allowed to react as above, but for R = C_6H_{11} acetonitrile was employed as solvent. The reaction times were longer due to the lower solubility of the uranium salt. The resulting orange solutions were worked up in the same way to give identical uranyl complexes and dimerised ligand.

$UO_2(S_2PMe_2)_2 \cdot Me_3PO$

One mol of UCl_4 was allowed to react with four mol of NaS_2PMe_2 in hot ethanolic solution in the air. After solvent removal the solid was extracted with CH_2Cl_2. The product thus extracted was crystallised from ethanol. Initially a crop of colourless crystals of the ligand dimer was obtained. After standing for three weeks, orange crystals of composition $UO_2(S_2PMe_2)_2 \cdot Me_3PO$ were obtained.

Yields and elemental analyses are given in Table I.

Crystallography

Suitable quality crystals of $UO_2(S_2PPh_2)_2 \cdot EtOH$ and the two chlorocomplexes were grown from $EtOH/CH_2Cl_2$ solution. The crystals of $UO_2\{S_2P(C_6H_{11})_2\}_2 \cdot EtOH$ were obtained from a diffusion controlled synthesis in ethanol. The crystals obtained from the synthesis of $UO_2(S_2PMe_2)_2 \cdot Me_3PO$ were used directly. Intensity measurements were carried out with a Syntex $P2_1$ automatic diffractometer and corrected for absorption as described previously [15]. Backgrounds were obtained from analysis of the scan profile [16]. Crystal data, intensity measurement, structure solution and refinement are summarised in Table II. Scattering factors for the neutral atoms were taken from Cromer and Mann [17], and anomalous dispersion coefficients from Cromer and Libermann [18]. Computer

TABLE I. Elemental Analyses and Yields.

$UO_2(S_2PR_2)_2 \cdot R'OH$

R	R′	C %	H %	S %	Yield %
Me	Me	10.17(10.87)	2.58(2.92)		70
Me	Et			21.90(22.64)	
Et	Pr^i	20.15(20.76)	4.35(4.43)	19.80(20.15)	68
Pr^i	Et	24.89(24.78)	4.91(5.05)	19.16(18.90)	
Pr^i	Pr^i	25.54(26.01)	5.29(5.24)	19.00(18.51)	54
OMe	Me	9.60(9.74)	2.64(2.62)	19.90(20.80)	80
OEt	Et	17.30(17.50)	3.74(3.82)	18.40(18.68)	65
OPr^i	Pr^i	23.48(23.81)	4.59(4.80)	16.66(16.95)	71
OPr^i	Et	23.39(22.64)	4.64(4.61)	17.70(17.27)	
Ph	Et	38.21(38.33)	3.21(3.22)	15.75(15.74)	63
C_6H_{11}	Et	37.22(37.23)	5.82(6.01)	16.14(15.29)	80

$[Et_4N][UO_2(S_2PR_2)_2Cl$

R	C %	H %	N %	S %	Cl %	Yield %
Me	21.03(21.01)	4.72(4.70)	1.98(2.04)	19.22(18.69)	4.95(5.17)	54
Et	26.16(25.89)	5.31(5.43)	2.10(1.89)	16.80(17.28)		72
Pr^i	30.09(30.09)	6.14(6.06)	1.75(1.75)	16.70(16.07)	4.37(4.44)	55
OMe	19.30(19.22)	4.32(4.30)	1.97(1.87)	17.10(17.10)	4.88(4.73)	62
OEt	24.00(23.84)	4.92(5.00)	1.74(1.74)	15.70(15.91)	4.10(4.40)	15
OPr^i	27.90(27.86)	5.54(5.61)	1.72(1.62)	14.79(14.87)	4.69(4.11)	61
C_6H_{11}	40.13(40.10)	6.76(6.73)	1.58(1.46)	13.00(13.38)	3.82(3.70)	20
Ph	40.62(41.14)	4.25(4.32)	1.39(1.50)	14.28(13.73)	3.79(3.79)	83

$UO_2(S_2PMe_2)_2 \cdot Me_3PO$

R	C %	H %	S %
Me	15.29(13.73)	3.65(3.47)	20.91(20.93)

TABLE II. Summary of Crystal Data, Intensity Measurements, Structure Solution and Refinement for $UO_2(S_2PR_2)_2 \cdot L^a$.

Compound	I	II	III	IV	V
Formula	$UO_3S_4P_2C_{26}H_{26}$	$UO_3S_4P_2C_{26}H_{50}$	$UO_2S_4P_2NClC_{12}H_{32}$	$UO_2S_4P_2NClC_{32}H_{40}$	$UO_3S_4P_3C_7H_{21}$
Molecular weight	814.7	838.9	686.1	934.3	612.4
Crystal dimensions (mm)	0.22 × 0.13 × 0.10	0.14 × 0.13 × 0.12	0.34 × 0.25 × 0.19	0.30 × 0.25 × 0.18	0.29 × 0.21 × 0.18
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
a (Å)	11.589(2)	12.765(1)	10.770(1)	11.341(2)	11.499(1)
b (Å)	11.6928(8)	16.502(2)	11.730(2)	20.889(3)	13.079(1)
c (Å)	13.273(2)	15.813(2)	20.079(2)	16.172(2)	14.362(1)
α (°)	113.205(8)				
β (°)	110.849(9)	90.622(9)		101.79(1)	
γ (°)	92.979(9)				
U (Å^3)	1505.8(3)	3330.8(6)	2536.6(6)	3750.4(9)	2160.0(4)
Z	2	4	4	4	4
d_{calc} (g cm^{-3})	1.80	1.67	1.80	1.65	1.88
d_{obsd} (g cm^{-3})	1.81	1.66	1.80	1.63	
F_{000}	784	1664	1320	1883	1152
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	Pcmn
Radiation	Mo-Kα (niobium filtered)				
λ (Å)	0.71069				
μ (cm^{-1})	55.2	49.7	66.2	44.9	77.1
Scan method	$2\theta-\theta$				
$(\sin\theta/\lambda)_{max}$	0.54	0.54	0.54	0.54	0.60
No of unique reflections	3979	4366	1924	4934	2002
No of reflections $<3\sigma$	798	1626	228	1676	553
No of observations/ No of variables	21.1 (19.1^b)	23.2 (18.6^b)	9.2 (8.8^b)	23.2 (19.5^b)	21.8 (18.8^b)
Structure solution	Patterson & Fourier				
Refinement method	Full matrix least squares	Blocked matrix least squares			Full matrix least squares
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$				
w	$1/\sigma^2$				
R	0.057	0.044	0.033	0.046	0.050
R_w	0.067	0.054	0.038	0.046	0.073
Goodness of fit	2.57	2.41	3.27	2.16	4.33

[a] I = $UO_2(S_2PPh_2)_2 \cdot EtOH$, II = $UO_2\{S_2P(C_6H_{11})_2\}_2 \cdot EtOH$, III = $[Et_4N][UO_2(S_2PMe_2)_2Cl]$, IV = $[Et_4N][UO_2(S_2PPh_2)_2Cl]$, and V = $UO_2(S_2PMe_2)_2 \cdot Me_3PO$. [b] Only those reflections of I < 3σ with $\lvert F_c\rvert > \lvert F_o\rvert$ were included in the refinement.

programs for data reduction and structure solution were taken from the XRAY-72 program system [19], and the figure was prepared with the aid of the program ORTEP [20]. All of the structures were solved by Patterson and Fourier methods. A model for the partial disorder of the ethanol molecules in both ethanol adducts was found, and the structures successfully refined.

The structure of the phosphine oxide adduct was solved in the centric space group Pcmn with the crystallographic mirror plane bisecting the molecule. After refinement by full matrix least squares to R = 0.050 a refinement was attempted in the acentric space group $Pc2_1n$; however, no significant improvement in R or in goodness of fit was obtained.

Final atomic coordinates are reported in Tables III to VII, and derived bond lengths and angles in Table

TABLE III. Atomic Coordinates for $UO_2(S_2PPh_2)_2$·EtOH.

Atom	x	y	z	PP
U	0.10377(6)	0.06501(5)	0.24938(5)	
P(1)	0.2899(4)	0.3392(4)	0.5030(3)	
P(2)	−0.1256(4)	−0.1992(3)	0.1594(3)	
S(1)	0.2933(4)	0.2886(4)	0.3405(3)	
S(2)	0.1443(4)	0.2279(4)	0.4910(3)	
S(3)	−0.0539(4)	−0.1740(3)	0.0491(3)	
S(4)	−0.0754(4)	−0.0394(4)	0.3115(4)	
C(1)	0.282(1)	0.507(1)	0.568(1)	
C(2)	0.355(1)	0.595(1)	0.555(1)	
C(3)	0.346(2)	0.723(2)	0.603(1)	
C(4)	0.265(2)	0.761(2)	0.662(2)	
C(5)	0.194(2)	0.674(2)	0.674(2)	
C(6)	0.202(2)	0.541(1)	0.628(1)	
C(7)	0.440(1)	0.323(1)	0.599(1)	
C(8)	0.452(2)	0.200(2)	0.586(2)	
C(9)	0.572(2)	0.182(2)	0.645(2)	
C(10)	0.674(2)	0.283(2)	0.718(2)	
C(11)	0.662(2)	0.406(2)	0.734(2)	
C(12)	0.542(1)	0.427(1)	0.674(1)	
C(13)	−0.297(1)	−0.255(1)	0.082(1)	
C(14)	−0.361(2)	−0.279(2)	0.146(2)	
C(15)	−0.495(2)	−0.326(2)	0.090(2)	
C(16)	−0.559(2)	−0.349(2)	−0.030(2)	
C(17)	−0.496(2)	−0.320(2)	−0.092(2)	
C(18)	−0.363(2)	−0.276(1)	−0.037(1)	
C(19)	−0.071(1)	−0.331(1)	0.187(1)	
C(20)	−0.111(2)	−0.450(1)	0.088(1)	
C(21)	−0.066(2)	−0.556(2)	0.103(2)	
C(22)	0.016(2)	−0.533(2)	0.222(2)	
C(23)	0.052(2)	−0.422(2)	0.316(2)	
C(24)	0.010(2)	−0.309(1)	0.304(1)	
C(251)	0.266(5)	−0.070(5)	0.070(4)	0.5
C(252)	0.277(9)	−0.050(8)	0.062(8)	0.5
C(261)	0.404(4)	0.005(4)	0.136(4)	0.5
C(262)	0.363(5)	−0.030(5)	0.032(5)	0.5
O(1)	−0.011(1)	0.1426(9)	0.1869(9)	
O(2)	0.219(1)	−0.0190(9)	0.3002(9)	
O(3)	0.1848(9)	0.0245(8)	0.0979(8)	

TABLE IV. Atomic Coordinates for $UO_2\{S_2(C_6H_{11})_2\}_2$·EtOH.

Atom	x	y	z	PP
U	0.03748(5)	0.07784(4)	0.15707(4)	
P(1)	0.1044(3)	−0.0857(3)	0.2830(2)	
P(2)	−0.1310(3)	0.2405(3)	0.1362(3)	
S(1)	0.1805(3)	−0.0531(3)	0.1781(3)	
S(2)	−0.0102(3)	−0.0061(3)	0.3097(3)	
S(3)	−0.1310(3)	0.1617(3)	0.2337(3)	
S(4)	−0.0180(3)	0.2126(3)	0.0532(3)	
C(1)	0.200(1)	−0.0925(9)	0.3717(9)	
C(2)	0.253(1)	−0.007(1)	0.387(1)	
C(3)	0.337(1)	−0.016(1)	0.459(1)	
C(4)	0.284(2)	−0.046(1)	0.538(1)	
C(5)	0.228(2)	−0.126(1)	0.527(1)	
C(6)	0.143(1)	−0.120(1)	0.453(1)	
C(7)	0.048(1)	−0.1864(9)	0.2694(9)	
C(8)	−0.029(1)	−0.1872(9)	0.194(1)	
C(9)	−0.074(1)	−0.274(1)	0.181(1)	
C(10)	0.010(1)	−0.336(1)	0.167(1)	
C(11)	0.088(1)	−0.336(1)	0.243(1)	
C(12)	0.139(1)	−0.250(1)	0.256(1)	
C(13)	−0.110(1)	0.3442(9)	0.1741(9)	
C(14)	−0.203(1)	0.3696(9)	0.2319(9)	
C(15)	−0.182(1)	0.457(1)	0.267(1)	
C(16)	−0.075(1)	0.462(1)	0.313(1)	
C(17)	0.014(1)	0.437(1)	0.254(1)	
C(18)	−0.003(1)	0.3496(9)	0.2193(9)	
C(19)	−0.260(1)	0.2394(9)	0.0838(9)	
C(20)	−0.284(1)	0.152(1)	0.052(1)	
C(21)	−0.398(1)	0.153(1)	0.012(1)	
C(22)	−0.405(1)	0.216(1)	−0.062(1)	
C(23)	−0.377(1)	0.302(1)	−0.031(1)	
C(24)	−0.263(1)	0.304(1)	0.009(1)	
C(251)	0.259(4)	0.083(3)	0.017(3)	0.5
C(252)	0.223(3)	0.126(3)	−0.007(3)	0.5
C(261)	0.320(4)	0.112(3)	0.043(3)	0.5
C(262)	0.273(5)	0.165(3)	0.009(4)	0.5
O(1)	0.1300(8)	0.1405(6)	0.2075(6)	
O(2)	−0.0510(7)	0.0156(6)	0.1016(6)	
O(3)	0.1398(8)	0.0693(6)	0.0292(6)	

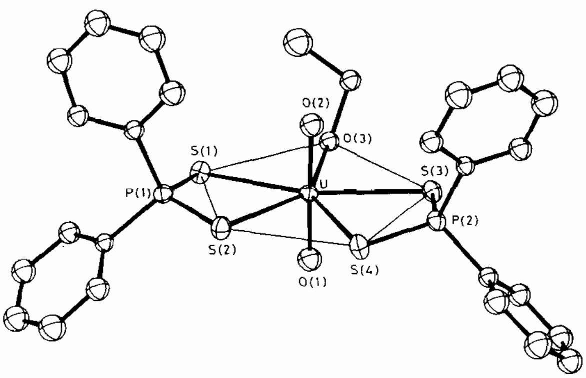

Fig. 1. A perspective view of the complex $UO_2(S_2PPh_2)_2$·EtOH (only one orientation of the disordered ethanol molecule is shown).

TABLE V. Final Atomic Coordinates for $[Et_4N][UO_2(S_2PPh_2)_2Cl]$.

Atom	x	y	z
U	0.14802(4)	0.14845(2)	0.28573(2)
Cl	0.3723(3)	0.1448(2)	0.2575(2)
P(1)	0.0803(3)	0.3015(2)	0.3500(2)
P(2)	0.0073(3)	−0.0011(2)	0.2515(2)
S(1)	0.2274(3)	0.2806(2)	0.3045(2)
S(2)	−0.0367(3)	0.2289(2)	0.3305(2)
S(3)	−0.0704(3)	0.0771(1)	0.2880(2)
S(4)	0.1829(3)	0.0142(2)	0.2586(2)
C(1)	0.011(1)	0.3747(6)	0.3029(6)
C(2)	0.080(1)	0.4306(7)	0.3182(8)
C(3)	0.028(1)	0.4899(8)	0.2848(9)
C(4)	−0.088(1)	0.4911(7)	0.2372(8)
C(5)	−0.156(1)	0.4360(8)	0.2242(9)
C(6)	−0.109(1)	0.3765(7)	0.2583(7)
C(7)	0.122(1)	0.3203(6)	0.4620(6)
C(8)	0.030(1)	0.3436(6)	0.4992(7)
C(9)	0.056(1)	0.3588(7)	0.5889(8)
C(10)	0.173(1)	0.3482(8)	0.6317(8)
C(11)	0.264(1)	0.3265(7)	0.5952(9)
C(12)	0.240(1)	0.3121(7)	0.5041(8)
C(13)	−0.0165(9)	−0.0666(6)	0.3188(6)
C(14)	−0.020(1)	−0.0541(6)	0.4027(7)
C(15)	−0.042(1)	−0.1047(7)	0.4554(8)
C(16)	−0.063(1)	−0.1654(7)	0.4253(8)
C(17)	−0.055(1)	−0.1787(8)	0.342(1)
C(18)	−0.029(1)	−0.1279(7)	0.2872(8)
C(19)	−0.062(1)	−0.0253(5)	0.1451(6)
C(20)	0.004(1)	−0.0616(6)	0.0965(7)
C(21)	−0.055(1)	−0.0815(7)	0.0127(8)
C(22)	−0.171(1)	−0.0653(7)	−0.0165(8)
C(23)	−0.245(1)	−0.0293(7)	0.0289(8)
C(24)	−0.182(1)	−0.0092(6)	0.1148(7)
C(25)	0.190(2)	0.384(1)	0.058(1)
C(26)	0.176(2)	0.449(1)	0.004(1)
C(27)	−0.013(1)	0.3381(7)	−0.0190(9)
C(28)	−0.062(1)	0.3427(8)	0.0624(9)
C(29)	0.169(1)	0.3254(8)	−0.0835(9)
C(30)	0.122(1)	0.2623(9)	−0.1319(9)
C(31)	0.152(2)	0.2714(9)	0.057(1)
C(32)	0.282(2)	0.246(1)	0.066(1)
N	0.125(1)	0.3294(6)	0.0011(7)
O(1)	0.0942(6)	0.1615(3)	0.1786(4)
O(2)	0.2023(6)	0.1356(4)	0.3927(4)

TABLE VI. Final Atomic Coordinates for $[Et_4N][UO_2(S_2PMe_2)_2Cl]$.

Atom	x	y	z
U	0.20537(6)	−0.00917(4)	0.13812(3)
Cl	0.0097(5)	−0.0070(5)	0.0559(2)
P(1)	0.4424(5)	0.1690(4)	0.0776(2)
P(2)	0.1494(5)	−0.1987(4)	0.2698(2)
S(1)	0.2776(6)	0.1404(4)	0.0323(2)
S(2)	0.4547(5)	0.0767(3)	0.1613(2)
S(3)	0.3059(5)	−0.1061(3)	0.2605(2)
S(4)	0.0314(6)	−0.1619(5)	0.1980(3)
C(1)	0.216(2)	0.771(1)	−0.1891(7)
C(2)	0.173(2)	0.665(1)	−0.2286(8)
C(3)	0.224(2)	0.658(1)	−0.0854(8)
C(4)	0.202(2)	0.656(1)	−0.0079(7)
C(5)	0.224(2)	0.874(1)	−0.083(1)
C(6)	0.366(2)	0.878(2)	−0.075(1)
C(7)	0.031(2)	0.769(2)	−0.106(1)
C(8)	−0.034(2)	0.863(1)	−0.1413(9)
C(9)	0.186(2)	−0.351(1)	0.266(1)
C(10)	0.079(2)	−0.175(2)	0.3512(9)
C(11)	0.566(2)	0.132(2)	0.0226(9)
C(12)	0.462(3)	0.322(1)	0.0978(9)
N(1)	0.174(1)	0.766(1)	−0.1162(6)
O(1)	0.269(1)	−0.1223(8)	0.0934(5)
O(2)	0.146(1)	0.1061(8)	0.1845(5)

TABLE VII. Final Atomic Coordinates for $UO_2(S_2PMe_2)_2 \cdot Me_3PO$.

Atom	x	y	z
U	0.02587(8)	0.25	0.23516(5)
P(1)	0.0213(4)	−0.0012(4)	0.3177(3)
P(2)	0.0787(8)	0.25	−0.0207(6)
S(1)	0.0326(5)	0.0386(4)	0.1827(3)
S(2)	0.0126(4)	0.1226(4)	0.3984(3)
C(1)	0.147(2)	−0.080(2)	0.349(1)
C(2)	−0.103(2)	−0.084(2)	0.333(1)
C(3)	−0.052(3)	0.25	−0.091(2)
C(4)	0.161(2)	0.378(2)	−0.038(2)
O(1)	0.177(1)	0.25	0.244(1)
O(2)	−0.125(1)	0.25	0.224(1)
O(3)	0.036(2)	0.25	0.074(1)

TABLE VIII. Bond Lengths (Å) and Angles (°) for $UO_2(S_2PR_2)_2 \cdot L^a$ with Estimated Standard Deviations in Parentheses.

Distances	I	II	III	IV	V
U–O(1)	1.79(1)	1.76(1)	1.74(1)	1.736(6)	1.75(1)
U–O(2)	1.80(1)	1.756(9)	1.76(1)	1.735(6)	1.75(1)
U–X	2.41(1)	2.423(9)	2.677(5)	2.676(3)	2.32(1)
U–S(1)	2.854(4)	2.845(4)	2.863(5)	2.900(3)	2.867(5)
U–S(2)	2.856(4)	2.855(4)	2.906(5)	2.891(3)	2.880(4)
U–S(3)	2.894(3)	2.839(4)	2.916(4)	2.898(3)	
U–S(4)	2.870(6)	2.850(4)	2.857(6)	2.879(4)	

(Continued on facing page)

TABLE VIII. *(Continued)*

P(1)–S(1)	2.015(6)	2.006(6)	2.022(8)	2.004(5)	2.013(6)
P(1)–S(2)	1.997(7)	2.014(6)	2.004(6)	1.998(5)	1.993(7)
P(1)–C(a)	1.83(1)	1.85(1)	1.78(2)	1.81(1)	1.83(2)
P(1)–C(b)	1.82(1)	1.82(2)	1.85(1)	1.82(1)	1.80(2)
P(2)–S(3)	2.026(7)	2.016(6)	2.014(7)	2.001(5)	
P(2)–S(4)	1.996(5)	2.014(6)	1.969(8)	1.998(5)	
P(2)–C(c)	1.82(1)	1.83(1)	1.84(2)	1.80(1)	
P(2)–C(d)	1.81(2)	1.84(2)	1.82(2)	1.81(1)	
S(1)....S(2)	3.306(8)	3.311(6)	3.302(7)	3.291(5)	3.295(6)
S(3)....S(4)	3.319(7)	3.319(6)	3.277(8)	3.281(5)	
Angles					
O(1)–U–O(2)	175.3(5)	176.9(4)	178.2(6)	179.8(3)	178.7(7)
O(1)–U–S(1)	88.0(3)	88.1(3)	88.7(3)	89.6(2)	89.5(2)
O(1)–U–S(2)	93.6(3)	92.9(3)	89.0(4)	91.9(2)	89.8(4)
O(1)–U–S(3)	87.5(3)	91.6(3)	89.5(3)	88.1(2)	
O(1)–U–S(4)	89.3(4)	87.9(3)	89.9(4)	91.8(2)	
O(1)–U–X	92.6(5)	92.7(4)	90.0(4)	89.2(2)	91.0(7)
O(2)–U–S(1)	92.4(3)	91.3(3)	91.2(3)	90.2(3)	90.2(2)
O(2)–U–S(2)	91.0(3)	89.8(3)	89.3(4)	88.1(3)	91.2(4)
O(2)–U–S(3)	89.7(3)	90.7(3)	89.4(3)	92.2(2)	
O(2)–U–S(4)	93.3(5)	90.8(3)	91.1(4)	88.2(3)	
O(2)–U–X	83.0(5)	84.2(4)	91.7(4)	90.6(2)	87.8(7)
S(1)–U–S(2)	70.8(1)	71.0(1)	69.8(1)	69.3(1)	70.0(1)
S(1)–U–S(3)	148.4(1)	143.9(1)	139.8(2)	137.42(9)	149.3(1)
S(1)–U–S(4)	140.9(1)	144.6(1)	151.0(2)	153.4(1)	140.7(1)
S(1)–U–X	74.9(2)	72.7(3)	75.6(2)	76.1(1)	74.69(9)
S(2)–U–S(3)	140.8(1)	72.9(1)	69.9(1)	68.34(9)	
S(2)–U–S(4)	70.5(1)	144.3(1)	139.1(2)	137.2(1)	70.7(1)
S(2)–U–X	144.9(2)	143.1(3)	145.4(1)	145.3(1)	144.64(9)
S(3)–U–S(4)	70.3(1)	71.4(1)	69.2(2)	69.21(9)	
S(3)–U–X	74.0(2)	143.3(3)	144.6(1)	146.4(1)	
S(4)–U–X	144.2(2)	72.4(3)	75.5(2)	77.4(1)	
U–S(1)–P(1)	88.3(2)	89.1(2)	90.4(2)	89.0(1)	89.7(2)
U–S(2)–P(1)	88.6(2)	88.7(2)	89.5(2)	89.4(2)	89.7(2)
U–S(3)–P(2)	87.8(1)	89.0(2)	88.7(2)	89.3(1)	
U–S(4)–P(2)	89.0(2)	88.7(2)	91.3(3)	89.9(2)	
S(1)–P(1)–S(2)	111.0(2)	110.9(3)	110.2(3)	110.6(2)	110.7(3)
S(1)–P(1)–C(a)	109.9(6)	108.9(5)	109.6(7)	110.6(4)	109.2(7)
S(1)–P(1)–C(b)	107.0(6)	109.9(5)	111.1(9)	110.3(4)	108.8(7)
S(2)–P(1)–C(a)	110.7(6)	110.7(5)	109.8(7)	110.9(4)	110.9(7)
S(2)–P(1)–C(b)	110.6(6)	109.5(5)	109.4(6)	110.4(4)	112.1(7)
C(a)–P(1)–C(b)	107.6(6)	106.8(7)	107(1)	103.8(5)	105(1)
S(3)–P(2)–S(4)	111.2(3)	110.9(3)	110.7(3)	110.3(2)	
S(3)–P(2)–C(c)	109.9(6)	110.7(5)	110.1(8)	108.2(4)	
S(3)–P(2)–C(d)	107.5(6)	109.3(5)	110.5(8)	112.2(4)	
S(4)–P(2)–C(c)	111.5(5)	108.8(5)	108.7(8)	111.0(4)	
S(4)–P(2)–C(d)	112.2(5)	110.5(5)	110.7(8)	109.4(4)	
C(c)–P(2)–C(d)	104.2(7)	106.6(7)	106(1)	105.9(5)	

[a] I = $UO_2(S_2PPh_2)_2 \cdot EtOH$, II = $UO_2\{S_2P(C_6H_{11})_2\}_2 \cdot EtOH$, III = $[Et_4N][UO_2(S_2PMe_2)_2 \cdot Cl$, IV = $[Et_4N][UO_2(S_2PPh_2)_2Cl$, V = $UO_2(S_2PMe_2)_2 \cdot Me_3PO$. Phenyl rings: C–C = 1.31(2)–1.49(2) Å; C–C–C = 114(1)–126(1)°. Cyclohexyl rings: C–C = 1.50(2)–1.59(2) Å; C–C–C = 107(1)–114(1)°. Tetraethylammonium ions: N–C = 1.50–1.56, C–C = 1.49–1.60 Å; C–N–C = 103–115, N–C–C = 106–115°. Phosphine oxide: P–O = 1.44(2), P–C = 1.81(3)–1.94(3) Å, U–O–P = 163(1), O–P–C = 104(1)–107(1), C–P–C = 109(1)–119(1)°. For I and II, X = O(3), C(a) = C(1), C(b) = C(7), C(c) = C(13), C(d) = C(19). For III, X = Cl, C(a) = C(11), C(b) = C(12), C(c) = C(9) and C(d) = C(10). For IV, X = Cl, C(a) = C(1), C(b) = C(7), C(c) = C(13) and C(d) = C(19). For V, X = O(3), S(3) and S(4) are generated by symmetry (m), C(a) = C(1), C(b) = C(2).

VIII. A perspective view of one of the complexes is presented in Fig. 1. The other coordination polyhedra are essentially the same. Lists of observed and calculated structure factors, as well as tables of thermal parameters, are available on request.

Results and Discussion

Salts of dithiophosphinic acids, MS_2PR_2 ($M = Na^+$, NH_4^+; R = Me, Et, Pr^i, OMe, OEt, OPr^i, Ph, C_6H_{11}) react readily with uranyl chloride in hot alcoholic solutions to form bis-complexes. The alcohol generally used was ethanol, but methanol and isopropanol were used where the ligands have R = OMe or OPr^i to avoid any trans-esterification reactions. In the absence of any other ligand, a molecule of solvent is always incorporated into the coordination polyhedron:

$$UO_2Cl_2 + 2MS_2PR_2 + R'OH \longrightarrow UO_2(S_2PR_2)_2 \cdot R'OH + 2MCl$$

The products may be extracted into CH_2Cl_2 after initial solvent removal, and recrystallised with some difficulty (due to their extreme solubility) from a small amount of the appropriate alcohol diluted with toluene or n-heptane (about 1:10). Many of the complexes were initially obtained as oils, and solid products were only obtained after several days at 0 °C.

The bound solvent is observed to be quite labile, hence care must be taken when isolating and recrystallising these compounds as solvent substitution may take place leading to a mixture of products. This lability is also demonstrated by the facile substitution of the alcohol molecule by chloride ion (see below).

The fact that we did not observe formation of non-solvated species is in contrast to previous preliminary reports [7–10] on similar systems. We suggest that in these previous studies under the reaction conditions employed it is highly probable that there was coordination of a solvent molecule which was not detected during the characterisation of the complexes. In the present work, even when the substitutents at phosphorus are as large as phenyl or cyclohexyl, a solvent molecule always binds.

When the reaction is carried out in the presence of excess Cl^- the resulting anionic chlorocomplexes may be isolated as their $[Et_4N]^+$ salts.

$$UO_2Cl_2 + 2MS_2PR_2 + Et_4NCl \longrightarrow [Et_4N][UO_2(S_2PR_2)_2Cl] + 2MCl$$

These products for R = Me, Et, Pr^i, OMe, OEt, OPr^i, Ph could be extracted into CH_2Cl_2 after removal of the reaction solvent, and finally recrystallised from alcohols or alcohol/CH_2Cl_2 or alcohol/ether mixtures according to their solubilities. The cyclohexyl analogue could not be obtained by this route, not because of the steric requirements of the C_6H_{11} groups, but because the ethanol adduct is very insoluble and this is the driving force for the reaction. It was, however, obtained from acetonitrile/dioxan solution and recrystallised from MeCN.

The alcohol adducts may also be obtained from UCl_4 by a novel double oxidation reaction, the oxidising agent being atmospheric oxygen.

$$UCl_4 + 4MS_2PR_2 + O_2 + R'OH \longrightarrow UO_2(S_2PR_2)_2 \cdot R'OH + [S_2PR_2]_2 + 4MCl$$

In this reaction the initial product formed is a uranium(IV) complex, as evidenced by the initial observation of a green solution. In the air, the colour rapidly changes to the orange of the final uranium(VI) product (R = Et, Ph, C_6H_{11}). At the same time, two ligands are oxidised to form the corresponding dimer.

The chlorocomplexes may also be prepared from UCl_4 or UCl_6^{2-} by a similar reaction (R = Et, Ph, C_6H_{11}). If UCl_4 is used, additional chloride ion must be added, but the necessary chloride is already present in UCl_6^{2-}.

$$UCl_4 + 4MS_2PR_2 + Cl^- + O_2 \longrightarrow [UO_2(S_2PR_2)_2Cl]^- + [S_2PR_2]_2 + 4MCl$$

$$UCl_6^{2-} + 4MS_2PR_2 + O_2 \longrightarrow [UO_2(S_2PR_2)_2Cl]^- + [S_2PR_2]_2 + 4MCl + Cl^-$$

As a preparative route, these reactions are wasteful in ligand, two mol being transformed into the complex and two more being oxidised to the corresponding dimer. The multistep separation process required due to the complexity of the reaction products also leads to low yields.

From the above we would expect the reaction of UCl_4 + $4NaS_2PMe_2$ + air in ethanol to give the complex $UO_2(S_2PMe_2)_2 \cdot EtOH$ along with one mol of the ligand dimer:

$$UCl_4 + 4NaS_2PMe_2 + EtOH + O_2 \longrightarrow UO_2(S_2PMe_2)_2 \cdot EtOH + [S_2PMe_2]_2 + 4NaCl$$

The initial colourless product isolated from the reaction was shown to be dimerised ligand. The second orange product was shown to be $UO_2(S_2PMe_2)_2 \cdot Me_3PO$ by elemental analysis and by the crystal structure described below.

In the presence of a phosphine oxide, others have shown that the coordinated ethanol in this type of complex is easily replaced to form the corresponding phosphine oxide adduct [6]. The presence of Me_3PO in the present case is not easy to explain, but must

TABLE IX. Selected I.r. Data.

$UO_2(S_2PR_2)_2 \cdot R'OH$						
R	R′	$\nu_{as}(UO_2)$	$\nu_s(UO_2)$	$\nu_s(PS_2)$	$\nu_{as}(PS_2)$	$\delta(UO_2)$
Me	Me	928vs	848w	598s	508m	256m
Et	Et	922vs	840m	607s	500s	257m
Pr^i	Et	919vs	889w	627vs 680s	507s	258m
OMe	Me	932vs	850w	605s 680s	540m	256m
OEt	Et	938vs	872m	668vs	540m 555m	258m
OPr^i	Pr^i	924vs	892s 839m	663s	547s 500s	253m
C_6H_5	Et	930vs	868m	618s 636vs	569vs	259m
C_6H_{11}	Et	916vs		620s	561vs	258m
$[UO_2(S_2PR_2)_2Cl]^-$						
Me		923vs	861w	607s	512s	240m
Et		920vs	–	610s	503s	240m
Pr^i		922vs	890w	629vs	506s	258m 240m
OMe		923vs	846w	660s 680s	560m	255m
OEt		926vs	–	665s 677s	560m	255m
OPr^i		930vs	892m	649s 662s	549m	252m
C_6H_5		927vs	–	621m 650s	578vs	240m
C_6H_{11}		923vs	851w	623s	561m	255m

be derived from the ligand, $Me_2PS_2^-$, or its dimer, there being no other source of phosphorus in the reaction mixture. It is perhaps important to note that the reaction mixture had stood for several weeks before the final product was isolated.

The dimers (R = Me, Et, Ph, C_6H_{11}) were identified by elemental analysis, and by comparing their melting points, IR and NMR spectra with those of authentic samples prepared by the iodine oxidation of the pure ligand salts [21].

The orange crytalline products are stable to the air; however, after prolonged exposure there is some evidence of hydrolysis. The colour of the complexes is derived from ligand to metal charge transfer transitions due to the reducing nature of the ligands and the high oxidation state of the metal.

IR Spectra

The most important bands observed in the IR spectra of these complexes are presented in Table IX. In all cases the strong absorption observed at *ca.* 930 cm^{-1} is assigned to the asymmetric stretching vibration (ν_3) of the linear uranyl group [22]. In all cases the symmetric stretch (ν_1) was weak or not observed for the present complexes. The UO_2 bending mode (ν_2) is observed at *ca.* 255 cm^{-1}. By analogy with previous studies [23] we were tempted to assign these bands to metal–sulphur vibrations. However, these vibrations must be shifted below 200 cm^{-1} due to the high atomic mass of the metal. Bands observed at 650–600 and 560–500 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of the PS_2 unit [23]. The stretching mode of the OH group of the coordinated alcohol occurs as a broad band at *ca.* 3400 cm^{-1}.

The infrared spectrum of the phosphine oxide adduct is complex in the region 950–850 cm^{-1}, thus we are unable to assign a value to ν_1 and ν_3 for the UO_2 group in this case. A broad intense band at 1135 cm^{-1} is assigned to ν(PO) [6].

TABLE Xa. ^1H NMR Data for $UO_2(S_2PR_2)_2 \cdot R'OH$[a].

R	R′	S_2PR_2		R′OH[b]	
Me	Et	$\delta(CH_3)$ 2.29;	$^2J_{HH}$ 13.2;	$\delta(CH_3)$ 1.46, $\delta(CH_2)$ 4.52;	$^3J_{HH}$ 6.8
Et	Pr^i	$\delta(CH_3)$ 1.36, $\delta(CH_2)$ 2.36;	$^3J_{HH}$ 7.4, $^2J_{PH}$ 10.7, $^3J_{PH}$ 22.1;	$\delta(CH_3)$ 1.61;	$^3J_{HH}$ 6.2
Pr^i	Et	$\delta(CH_3)$ 1.58, $\delta(CH)$ 2.64;	$^3J_{HH}$ 6.1, $^3J_{PH}$ 19.8, $^2J_{PH}$ 1.5;	$\delta(CH_3)$ 1.71, $\delta(CH_2)$ 4.59;	$^3J_{HH}$ 6.8
OMe	Me	$\delta(CH_3)$ 3.83;	$^3J_{PH}$ 15.1;	$\delta(CH_3)$ 5.25;	
OEt	Et	$\delta(CH_3)$ 1.40, $\delta(CH_2)$ 4.30;	$^3J_{HH}$ 7.0, $^3J_{PH}$ 7.0;	$\delta(CH_3)$ 1.63, $\delta(CH_2)$ 4.68;	$^3J_{HH}$ 6.9
OPr^i	Pr^i	$\delta(CH_3)$ 1.39, $\delta(CH)$ 4.92[c];	$^3J_{HH}$ 5.9;	$\delta(CH_3)$ 1.63;	$^3J_{HH}$ 5.9
Ph	Et	$\delta(Ph)$ 7.53[c], 8.11[c];		$\delta(CH_3)$ 1.48, $\delta(CH_2)$ 4.50;	$^3J_{HH}$ 6.5

[a] Chemical shifts are reported in ppm relative to $SiMe_4$, and coupling constants are in Hz. [b] Neither the CH protons of isopropanol nor the OH protons were observed. [c] Complex second order multiplets.

TABLE Xb. ^1H NMR Data for $[Et_4N][UO_2(S_2PR_2)_2Cl]$[a,b].

R		
Me	$\delta(CH_3)$ 2.23[d]	
Et	$\delta(CH_3)$ 1.31, $\delta(CH_2)$ 2.21;	$^3J_{HH}$ 7.5, $^2J_{PH}$ 10.9, $^3J_{PH}$ 21.2
Pr^i	$\delta(CH_3)$ 1.35, $\delta(CH)$ 2.42;	$^3J_{HH}$ 6.9, $^3J_{PH}$ 19.1, $^2J_{PH}$ 5.6
OMe	$\delta(CH_3)$ 3.86[d]	
OEt	$\delta(CH_3)$ 1.38, $\delta(CH_2)$ 4.25[d];	$^3J_{HH}$ 7.0
OPr^i	$\delta(CH_3)$ 1.39, $\delta(CH)$ 4.93[d];	$^3J_{HH}$ 6.3
Ph	$\delta(Ph)$ 7.44[d], 8.06[d]	
C_6H_{11}	$\delta(C_6H_{11})$ 1.7[c]	

[a] Chemical shifts are reported in ppm relative to $SiMe_4$, and coupling constants are in Hz. [b] The Et_4N^+ ions are observed as well resolved multiplets at 1.27 and 3.24 ppm. [c] Broad and poorly resolved. [d] Complex second order multiplets.

NMR Spectra

The proton NMR spectra (Table X) have been recorded in CD_2Cl_2 solution for all of the isolated complexes, except for the ethanol adduct for $R = C_6H_{11}$ which is too insoluble. For those of the spectra which are amenable to a first order analysis the relevant chemical shifts and coupling constants are reported. A number of the spectra are not first order, and for these only the observed chemical shifts of the multiplets are reported. The second order effects are in part due to magnetic non-equivalence of the ligands, derived from long range spin–spin coupling through the metal ion. The complete analysis of these spectra will be reported in a later publication [24].

The ^1H NMR spectrum of the phosphine oxide adduct consists of two doublets, the sulphur ligand signal being at 2.21 ppm with a coupling constant of 13.0 Hz, and that of the phosphine oxide at 1.91 ppm with a coupling constant of 14.4 Hz. The presence of a small amount of the expected complex, $UO_2(S_2PMe_2)_2 \cdot EtOH$, is evidenced by small multiplets due to the coordinated ethanol at 1.41 and 4.40 ppm. The ligand signal is obscured by that of the ligand in the main product.

No evidence was found for chemical inequivalence of the substituents at phosphorus, hence the puckering of the equatorial plane observed in the solid (see below) becomes fluxional in solution.

Crystal Structures

The crystal structures of the complexes $UO_2(S_2PR_2)_2 \cdot EtOH$ ($R = Ph, C_6H_{11}$) and $UO_2(S_2PMe_2)_2 \cdot Me_3PO$ consist of discrete monomeric neutral complexes, and those of the chlorocomplexes $[Et_4N][UO_2(S_2PR_2)_2Cl]$ ($R = Me$, Ph) monomeric anionic complexes and tetraethylammonium cations. A perspective view of the phenyl substituted ethanol adduct is shown in Fig. 1, and the coordination polyhedron of the other four complexes is similar. The ethyl group of the coordinated ethanol is disordered in both adducts. A model for the disorder was successfully refined with equal populations of two different orientations. Only one orientation is shown in the figure.

All five coordination polyhedra are pentagonal bipyramidal, typical for uranyl complexes [22]. The uranyl group is symmetrical, linear and perpendicular to the pentagonal plane. The average U–O distance

(1.76 Å) is quite typical [22]; however in the phenyl substituted ethanol adduct it is significantly longer (1.80 Å). The equatorial plane contains four sulphur atoms from the two bidentate dithiophosphinate ligands and the unique oxygen atom from the coordinated ethanol or phosphine oxide, or chlorine atom of the chlorocomplexes.

Although the equatorial plane is only slightly puckered for the methyl substituted chlorocomplex and the phosphine oxide adduct (max. deviation from the mean plane is 0.03 Å), the other three molecules have severely puckered pentagonal planes with deviations up to 0.15 Å. This distortion is fluxional in solution, hence the proton NMR spectra (see above) only record one chemical environment for all the substituents at phosphorus.

The four membered chelate rings in the methyl and cyclohexyl substituted compounds are essentially planar, the largest deviation measured as the bend about the S...S direction being 4.0°. The phenyl derivatives, however, are more severely distorted, the bend being as large as 14.7°. As has been previously observed with these ligands [1], the angles at sulphur are all close to 90°.

The uranium–sulphur bond distances observed here, 2.869 and 2.848 Å for the phenyl and cyclohexyl ethanol adducts, 2.886 and 2.892 Å for the methyl and phenyl chlorocomplexes, and 2.873 Å for the phosphine oxide adduct, may be compared with those found for the known dithiocarbamate complexes, $[UO_2(S_2CNEt_2)_3]^-$ (2.80 Å) [25], $UO_2(S_2CNEt_2)_2 \cdot Ph_3PO$ (2.84 Å) [26], $UO_2(S_2CNEt_2)_2 \cdot Ph_3AsO$ (2.85 Å) [26], and $UO_2(S_2CNEt_2)_2 \cdot Me_3NO$ (2.86 Å) [27]. The metal-oxygen (ethanol) distance (2.42 Å) is not surprisingly longer than that observed when the oxygen is derived from a phosphine oxide (2.32 Å). This is in agreement with the poorer ligating properties of the alcohol. The U–Cl bond length (2.677 Å) is identical to that found for the complex anion $[UO_2Cl_4]^{2-}$ [28].

The phosphine oxide adduct has crystallographic *m* symmetry, the mirror plane containing the UO_2 group and the P, O, and one C of the phosphine oxide.

Whereas it is possible to bind three dithiocarbamate ligands in the complex $[UO_2(S_2CNEt_2)_3]^-$ [25], we have not been able to prepare a dithiophosphinate analogue. We presume this to be a function of the smaller bite [29] of the dithiocarbamate (av. 2.85 Å) with respect to the dithiophosphinate (av. 3.10 Å). It is clear however that two ligands do not produce a coordinatively saturated uranyl complex as, even with the bulky phenyl and cyclohexyl ligands, the fifth equatorial site is always occupied.

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