# Synthesis and Characterization of Uranyl(VI) and Thorium(IV) Complexes with Phosphine Oxides. The Crystal Structure of $UO_2(NO_3)_2(NO_2\text{-}C_6H_4Ph_2PO)_2$

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## Abstract

Uranyl(VI) and thorium(IV) complexes of the type $UO_2(NO_3)_2(L^1)_2$, $UO_2(NO_3)_2(L^2)_2$, $UO_2(CH_3COO)_2L^1$, $UO_2(CH_3COO)_2L^2$, $Th(NO_3)_4(L^1)_2$ and $Th(NO_3)_4(L^2)_2$ ($L^1$ = (2-nitro)phenyl-bis-phenyl phosphine oxide, $L^2$ = triferrocenylphosphine oxide) are reported, together with their physico-chemical properties.

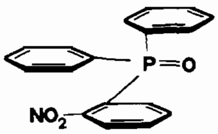
The crystal structure of $UO_2(NO_3)_2(L^1)_2$ is also reported. The crystals are monoclinic, space group $P2_1/n$ with $a$ = 17.78(1), $b$ = 13.88(1), $c$ = 17.37(1) Å, $\beta$ = 114.8(1)° for $Z$ = 4. The uranium atom is 8-coordinated, the uranyl(VI) group being equatorially surrounded by an irregular hexagon of six oxygen atoms from two *trans* neutral ligands and two nitrato groups.

## Introduction

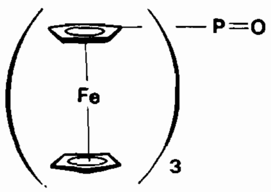
It is well known that arsine and phosphine-oxides strongly coordinate the lanthanide and actinide ions in various oxidation states [1].

Complexes with these ligands are widely used in the basic and applied chemistry of the 4f and 5f elements, for example in spectroscopic studies [1], in investigations regarding the relationship among polyhedra obtainable, steric hindrance of the ligand and ionic radius of the central metal ion [2], or the extraction of f-ions from aqueous into organic solvents [1, 3].

As a continuation of studies on interaction of neutral oxygen and nitrogen donor ligands with lanthanide and actinide ions [4] we have synthesized and characterized the uranyl(VI) and thorium(IV) complexes with the ligands $L^1$ and $L^2$ and determined the structure of $UO_2(NO_3)_2(L^1)_2$ by X-ray crystallography.



$L^1$



$L^2$

## Experimental

Triferrocenylphosphine oxide is a Strem Chemical; (2-nitro)phenyl-bis-phenylphosphine oxide was prepared according to literature [5], by reaction of *o*-dinitrobenzene with ethyldiphenylphosphonite [15].

$UO_2(NO_3)_2\cdot 6H_2O$, $UO_2(CH_3COO)_2\cdot 2H_2O$, $Th(NO_3)_4\cdot 5H_2O$, $Th(CH_3COO)_4$ and the solvents employed were Carlo Erba products, and were used without further purification.

### *Preparation of $UO_2(NO_3)_2(L^1)_2$*

To a methanolic solution of $UO_2(NO_3)_2\cdot 6H_2O$ (252 mg, 0.5 mmol), $L^1$ (293 mg, 1 mmol) was added. The resulting solution was stirred for 3 h. After removal of the solvent, the residue was dissolved in $CHCl_3$. The solvent was again removed and the product treated with the minimum quantity of methanol. The pale yellow product obtained was filtered and dried *in vacuo*. *Anal* Calc. for $C_{36}H_{28}P_2N_4O_{12}U$: C, 41.53; H, 2.69; N, 5.38. Found: C, 41.00; H, 2.71; N, 5.05%.

### *Preparation of $UO_2(OAc)_2(L^1)$*

To a methanolic solution of $UO_2(CH_3COO)_2\cdot 2H_2O$ (212 mg, 0.5 mmol), $L^1$ (293 mg, 1 mmol) was added.

The resulting solution was stirred for 3 h, then evaporated to dryness. The residue was dissolved in the minimum quantity of $CHCl_3$ and precipitated with diethylether. The yellow-gray product obtained was filtered, washed with diethylether and dried *in vacuo. Anal* Calc. for $C_{18}H_{20}NO_5PU$: C, 37.13; H, 2.81; N, 1.96. Found: C, 37.22; H, 2.63; N, 2.10%.

*Preparation of* $Th(NO_3)_4(L^1)_2$

To a methanolic solution of $Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol), $L^1$ (586 mg, 2 mmol) was added. The resulting solution was stirred for 3 h. The residue obtained by evaporation of the solvent at reduced pressure was dissolved in methanol. The white product obtained by addition of diethylether was filtered, washed with diethylether and dried *in vacua Anal.* Calc. for $C_{36}H_{18}P_2N_6O_{18}Th$: C, 38.36; H, 2.48; N, 7.46. Found: C, 38.45; H, 2.16; N, 7.83%.

*Preparation of* $UO_2(NO_3)_2(L^2_2)_2$

To a $CH_2Cl_2$ solution of the ligand $L^2$ (586 mg, 2 mmol) a methanolic solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (502 mg, 1 mmol) was added. From the orange-red solution obtained a yellow solid precipitated; it was filtered, washed with methanol and dried *in vacuo. Anal.* Calc. for $C_{60}H_{54}P_2O_{10}N_2Fe_6U$: C, 44.55; H, 3.34; N, 1.73. Found: C, 44.92; H, 3.40; N, 1.61%.

*Preparation of* $UO_2(OAc)_2(L^2)_2$

To a $CH_2Cl_2$ solution of the ligand (586 mg, 2 mmol), a methanolic solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$ (424 mg, 1 mmol) was added. The resulting solution was stirred under reflux for 24 h. After removal of the solvent, the residue was washed with methanol, hot 1,4 dioxane and diethylether, filtered and dried *in vacuo. Anal.* Calc. for $C_{34}H_{33}O_7Fe_3PU$: C, 41.21; H, 3.33. Found: C, 40.84; H, 3.32%.

*Preparation of* $Th(NO_3)_4(L^2)_2$

To a $CH_2Cl_2$ solution of the ligand $L^2$ (586 mg, 2 mmol), a methanolic solution of $Th(NO_3)_4 \cdot 5H_2O$ (424 mg, 1 mmol) was added. The resulting solution was stirred for 1 h, then evaporated to dryness. The residue, dried for 3 h, is insoluble in $CH_2Cl_2$. It was stirred in $CH_2Cl_2$ for 24 h. The precipitate was then filtered, washed with $CH_2Cl_2$ and dried *in vacuo. Anal.* Calc. for $C_{60}H_{54}P_2O_{14}N_4Fe_6Th$: C, 42.30; H, 3.17; N, 3.29. Found: C, 42.91; H, 3.21; N, 3.08%.

*Crystal Data for* $UO_2(NO_3)_2(L^1)_2$

$C_{36}H_{28}P_2N_4O_{12}U$, M = 1040, monoclinic, space group $P2_1/n(C^5_{2h})$, $a$ = 17.78(1), $b$ = 13.88(1), $c$ = 17.37(1) Å; $\beta$ = 114.8(1)°, $V$ = 3893 Å$^3$; $D$m(flotation) = 1.78, $D$c = 1.77 g cm$^{-3}$ for $Z$ = 4.

A prismatic crystal of approximate dimensions 0.1 × 0.2 × 0.1 mm was used for data collection. The X-ray experimental work was performed on a Philips PW 1100 four-circle diffractometer using Mo-K$\alpha$ radiation. Unit cell parameters were obtained by a least-squares refinement of 25 carefully determined angular settings. Intensities were collected over a range $\theta$ = 2.5–25° by the $\omega$–$2\theta$ scan mode with a scan rate of 2° min$^{-1}$. Two standard reflections, monitored before every 150 measurements, were constant within counting statistics. Of the 5819 independent reflections, 4382 were significantly above background, $I > 3\sigma(I)$, and were used in subsequent calculations. The data were corrected for Lp and for absorption [6]. Solution of the structure was achieved by standard methods. Refinement of scale-factor, positional and thermal parameters converged to the final $R$ of 0.078 when the largest parameters shift in the least cycle was about 0.5. The structure was refined by full-matrix least-squares, minimizing the function $\Sigma w \Delta F^2$ with $w$ = 1. A final difference-Fourier map showed no significant residuals. Scattering factors for $U$ were from ref. 7 and those of P, O, N, and C were supplied internally by the X-ray system [8] used for calculations. A correction for the anomalous dispersion of $U$ was also applied [9]. Final positional and thermal parameters are listed in Tables I and II, bond distances and angles are reported in Tables III and IV.

TABLE I. Final Fractional Atomic Coordinates. (e.s.d.s are in parentheses).

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| U | 0.5002(1) | 0.3183(1) | 0.2436(1) |
| O1 | 0.5118(12) | 0.3807(15) | 0.3406(13) |
| O2 | 0.4870(13) | 0.2547(17) | 0.1462(14) |
| O3 | 0.3940(11) | 0.2223(15) | 0.2493(13) |
| O4 | 0.6084(11) | 0.4166(15) | 0.2446(13) |
| O5 | 0.3568(14) | 0.3893(20) | 0.1635(17) |
| O6 | 0.4530(13) | 0.4700(19) | 0.1552(15) |
| O7 | 0.3316(18) | 0.5305(23) | 0.1025(21) |
| O8 | 0.6452(13) | 0.2450(18) | 0.3209(16) |
| O9 | 0.5507(12) | 0.1700(17) | 0.3409(15) |
| O10 | 0.6738(15) | 0.1184(20) | 0.4012(17) |
| O11 | 0.4897(17) | −0.0521(21) | 0.2316(19) |
| O12 | 0.3871(15) | 0.0482(20) | 0.1761(15) |
| O13 | 0.6105(17) | 0.5797(22) | 0.3385(18) |
| O14 | 0.5166(21) | 0.6911(24) | 0.2956(25) |
| N1 | 0.3784(20) | 0.4676(23) | 0.1391(20) |
| N2 | 0.6248(18) | 0.1732(20) | 0.3550(18) |
| N3 | 0.4318(21) | −0.0021(23) | 0.2337(22) |
| N4 | 0.9284(24) | 0.1363(25) | 0.2084(27) |
| P1 | 0.3335(4) | 0.1709(5) | 0.2732(4) |
| P2 | 0.6713(4) | 0.4793(5) | 0.2356(5) |
| C1 | 0.3079(17) | 0.2483(21) | 0.3404(18) |
| C2 | 0.3791(21) | 0.2842(26) | 0.4172(22) |
| C3 | 0.3657(24) | 0.3500(28) | 0.4778(24) |
| C4 | 0.2814(26) | 0.3775(31) | 0.4508(26) |

TABLE I. *(continued)*

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| C5 | 0.2145(24) | 0.3391(29) | 0.3882(25) |
| C6 | 0.2264(21) | 0.2724(26) | 0.3241(22) |
| C7 | 0.2404(16) | 0.1420(20) | 0.1866(17) |
| C8 | 0.1843(18) | 0.0800(23) | 0.1948(20) |
| C9 | 0.1073(20) | 0.0593(25) | 0.1233(21) |
| C10 | 0.0911(21) | 0.0992(26) | 0.0388(22) |
| C11 | 0.1506(21) | 0.1589(25) | 0.0305(22) |
| C12 | 0.2258(18) | 0.1843(24) | 0.1044(19) |
| C13 | 0.3721(16) | 0.0617(20) | 0.3316(18) |
| C14 | 0.4182(18) | −0.0120(22) | 0.3179(19) |
| C15 | 0.4506(23) | −0.0959(28) | 0.3661(24) |
| C16 | 0.4332(26) | −0.1082(33) | 0.4332(27) |
| C17 | 0.3873(25) | −0.0398(32) | 0.4576(26) |
| C18 | 0.3572(20) | 0.0446(25) | 0.4041(21) |
| C19 | 0.7117(18) | 0.4186(21) | 0.1705(19) |
| C20 | 0.6506(25) | 0.3748(30) | 0.0931(26) |
| C21 | 0.6750(31) | 0.3267(38) | 0.0262(31) |
| C22 | 0.7635(26) | 0.3261(32) | 0.0537(27) |
| C23 | 0.8188(29) | 0.3690(34) | 0.1195(29) |
| C24 | 0.7935(21) | 0.4162(26) | 0.1881(22) |
| C25 | 0.7574(17) | 0.5046(21) | 0.3315(18) |
| C26 | 0.7733(20) | 0.4406(24) | 0.4028(21) |
| C27 | 0.8447(22) | 0.4584(27) | 0.4829(22) |
| C28 | 0.8969(22) | 0.5317(27) | 0.4927(23) |
| C29 | 0.8828(26) | 0.5930(32) | 0.4240(27) |
| C30 | 0.8091(21) | 0.5820(26) | 0.3386(22) |
| C31 | 0.6296(17) | 0.5920(21) | 0.1835(18) |
| C32 | 0.5808(19) | 0.6581(23) | 0.2000(20) |
| C33 | 0.9559(24) | 0.2437(30) | 0.3475(25) |
| C34 | 0.9407(26) | 0.2656(32) | 0.4121(28) |
| C35 | 0.8911(25) | 0.2010(31) | 0.4379(26) |
| C36 | 0.6426(19) | 0.6177(24) | 0.1120(20) |

TABLE II. Thermal Parameters ($\times 10^2$).[a]

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| U | 3.1 | 3.9 | 2.2 | −0.3 | 1.9 | 0.1 |
| O(1) | 3.6 | 4.7 | 4.0 | −0.1 | 1.7 | −1.8 |
| O(2) | 4.8 | 6.5 | 3.6 | 0.2 | 2.0 | −2.1 |
| O(3) | 2.9 | 4.3 | 4.9 | −0.9 | 1.9 | −0.4 |
| O(4) | 3.3 | 4.2 | 4.9 | −0.4 | 2.0 | 0.5 |
| O(5) | 3.5 | 9.1 | 8.9 | 0.7 | 2.4 | 3.5 |
| O(6) | 3.3 | 7.5 | 7.8 | 0.0 | 2.6 | 2.1 |
| O(7) | 6.7 | 11.8 | 14.8 | 5.0 | 4.4 | 9.3 |
| O(8) | 3.7 | 6.4 | 7.4 | 1.0 | 2.7 | 1.8 |
| O(9) | 3.2 | 5.6 | 7.1 | −0.3 | 2.6 | 1.0 |
| O(10) | 5.9 | 9.3 | 9.3 | 4.3 | 4.1 | 6.3 |
| O(11) | 9.2 | 9.9 | 14.2 | −4.9 | 8.2 | −1.0 |
| O(12) | 6.2 | 7.8 | 4.5 | 1.7 | 2.2 | 0.2 |
| O(13) | 8.4 | 6.8 | 6.9 | 1.9 | 4.6 | 0.5 |
| O(14) | 13.2 | 10.5 | 21.9 | 6.1 | 15.1 | 5.3 |
| N(1) | 6.8 | 6.9 | 7.1 | 0.5 | 3.8 | 3.6 |
| N(2) | 6.8 | 4.0 | 5.2 | 0.4 | 4.2 | 0.5 |
| N(3) | 6.4 | 5.3 | 8.1 | −1.0 | 3.1 | −3.3 |
| N(4) | 9.6 | 6.7 | 11.9 | 2.6 | 9.2 | 3.6 |
| P(1) | 2.6 | 3.5 | 2.1 | −0.3 | 1.5 | 0.2 |
| P(2) | 3.0 | 3.3 | 3.0 | −0.3 | 2.1 | 0.3 |

| Atom | $U$ | | Atom | $U$ |
|---|---|---|---|---|
| C(1) | 3.5 | | C(19) | 3.7 |
| C(2) | 5.6 | | C(20) | 7.0 |
| C(3) | 6.6 | | C(21) | 10.1 |
| C(4) | 7.3 | | C(22) | 7.5 |
| C(5) | 6.5 | | C(23) | 8.6 |
| C(6) | 5.5 | | C(24) | 5.6 |
| C(7) | 3.0 | | C(25) | 3.5 |
| C(8) | 4.4 | | C(26) | 4.9 |
| C(9) | 5.1 | | C(27) | 5.7 |
| C(10) | 5.4 | | C(28) | 5.8 |
| C(11) | 5.2 | | C(29) | 7.7 |
| C(12) | 4.4 | | C(30) | 5.5 |
| C(13) | 3.3 | | C(31) | 3.4 |
| C(14) | 4.0 | | C(32) | 4.5 |
| C(15) | 6.1 | 6.1 | C(33) | 6.8 |
| C(16) | 7.7 | | C(34) | 7.7 |
| C(17) | 7.4 | | C(35) | 7.2 |
| C(18) | 5.0 | | C(36) | 4.5 |

[a] Anisotropic thermal parameters are in the form: $T = [-2\pi^2(\Sigma_{ij} U_{ij} h_i h_j a_i^* a_j^*)]$.

TABLE III. Bond Distances (A).[a]

| | | | |
|---|---|---|---|
| Coordination | | | |
| U–O(1) | 1.83(2) | U–O(5) | 2.54(2) |
| U–O(2) | 1.83(2) | U–O(6) | 2.53(2) |
| U–O(3) | 2.35(2) | U–O(8) | 2.57(2) |
| U–O(4) | 2.35(2) | U–O(9) | 2.57(2) |
| Ligands | | | |
| P(1)–O(3) | 1.49(2) | P(2)–O(4) | 1.48(2) |
| P(1)–C(1) | 1.78(2) | P(2)–C(19) | 1.78(2) |
| P(1)–C(7) | 1.75(2) | P(2)–C(25) | 1.76(2) |
| P(1)–C(13) | 1.79(2) | P(2)–C(31) | 1.80(2) |
| N(3)–C(14) | 1.58(4) | N(4)–C(32) | 1.69(4) |
| N(3)–O(11) | 1.25(5) | N(4)–O(13) | 1.13(4) |
| N(3)–O(12) | 1.21(4) | N(4)–O(14) | 1.26(5) |
| Nitrates | | | |
| N(1)–O(5) | 1.28(5) | N(2)–O(8) | 1.29(4) |
| N(1)–O(6) | 1.24(4) | N(2)–O(9) | 1.24(4) |
| N(1)–O(7) | 1.19(4) | N(2)–O(10) | 1.18(3) |

[a] C–C bond distances in the phenyl groups are normal, e.s.d.s are in parentheses.

TABLE IV. Bond Angles (deg) (e.s.d.s are in parentheses).

| | | | |
|---|---|---|---|
| Coordination | | | |
| O(1)–U–O(2) | 179.0(9) | | |
| O(3)–U–O(5) | 66.5(8) | | |
| O(3)–U–O(9) | 65.4(7) | | |
| O(4)–U–O(6) | 65.5(7) | | |
| O(4)–U–O(8) | 65.6(7) | | |
| O(5)–U–O(6) | 48.9(9) | | |
| O(8)–U–O(9) | 48.8(8) | | |
| Ligands[a,b] | | | |
| U–O(3)–P(1) | 167 | U–O(4)–P(2) | 174 |
| O(3)–P(1)–C(1) | 108 | O(4)–P(2)–O(19) | 108 |
| O(3)–P(1)–C(7) | 114 | O(4)–P(2)–C(25) | 114 |
| O(3)–P(1)–C(13) | 114 | O(4)–P(2)–C(31) | 113 |
| C(14)–N(3)–O(11) | 115 | C(32)–N(4)–O(13) | 122 |
| C(14)–N(3)–O(12) | 121 | C(32)–N(4)–O(14) | 109 |
| O(11)–N(3)–O(12) | 124 | O(13)–N(4)–O(14) | 129 |
| Nitrates | | | |
| U–O(5)–N(1) | 98 | U–O(8)–N(2) | 98 |
| U–O(6)–N(1) | 99 | U–O(9)–N(2) | 99 |
| O(5)–N(1)–O(6) | 113 | O(8)–N(2)–O(9) | 115 |
| O(5)–N(1)–O(7) | 124 | O(8)–N(2)–O(10) | 123 |
| O(6)–N(1)–O(7) | 123 | O(9)–N(2)–O(10) | 122 |

[a] C–C–C bond angles in the phenyl groups are normal. [b] e.s.d.s are 1°.

## Results and Discussion

The uranyl(VI) complexes of the type $UO_2(NO_3)_2(L)_2$ are easily prepared by reaction of $UO_2(NO_3)_2 \cdot 6H_2O$ with $L^1$ or $L^2$ in methanol in a 1:2 molar ratio.

The complexes can be almost completely extracted by $CH_2Cl_2$ or $CHCl_3$.

For $UO_2(NO_3)_2(L^1)_2$ and $UO_2(NO_3)_2(L^2)_2$ the bidentate coordination of the nitrate ion can be detected by the infrared spectra from the splitting of the $\nu_3$ stretching of free ion at 1390 $cm^{-1}$ into two infrared-active bands, one at higher (1550–1450 $cm^{-1}$) and one at lower frequency (1320–1260 $cm^{-1}$) [10]. In $UO_2(NO_3)_2(L^1)_2$ the two bands are at 1520 $cm^{-1}$ and at 1290 $cm^{-1}$, while in $UO_2(NO_3)_2(L^2)_2$ they lie at 1493 $cm^{-1}$ and at 1293 $cm^{-1}$.

The $\nu$ P–O is lowered to 1162 and 1100 $cm^{-1}$ upon coordination. The presence of the O–U–O group can be easily detected by the strong IR active band ($\nu_3$ O–U–O) at 939 $cm^{-1}$ for $UO_2(NO_3)_2(L^1)_2$ and 932 $cm^{-1}$ for $UO_2(NO_3)_2(L^2)_2$. These data are in agreement with the structure of $UO_2(NO_3)_2(L^1)_2$ determinated by X-ray crystallography.

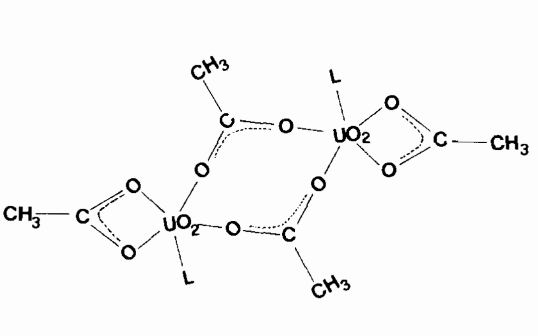
As shown in Scheme 1, the uranium atom is 8-coordinated, the uranyl group being equatorially surrounded by an irregular hexagon of six oxygen atoms from two *trans* neutral ligands and two chelate nitrato groups.

The molecule is quasi centrosymmetryc and bond lengths and angles in the structurally independent *trans* substituents are comparable. The molecule of $UO_2(NO_3)_2(NO_2\text{-}C_6H_4Ph_2PO)_2$ as a whole is basically similar to that of $UO_2(NO_3)_2(Ph_3AsO)_2$ [11] and the structural details strictly resemble those found in this compound. The P–O bonds 1.48(1) and 1.49(1) Å are about 0.16 Å shorter than the As–O in the above complex, which roughly correspond to the difference (0.14 Å) of the two covalent radii. A similar difference (1.49(3) *vs* 1.64(3) Å) was found in the isomorphous pair $UO_2((C_2H_5)_2NCS_2)_2Ph_3AsO$ and $UO_2((C_2H_5)_2NCS_2)_2Ph_3PO$ [12].

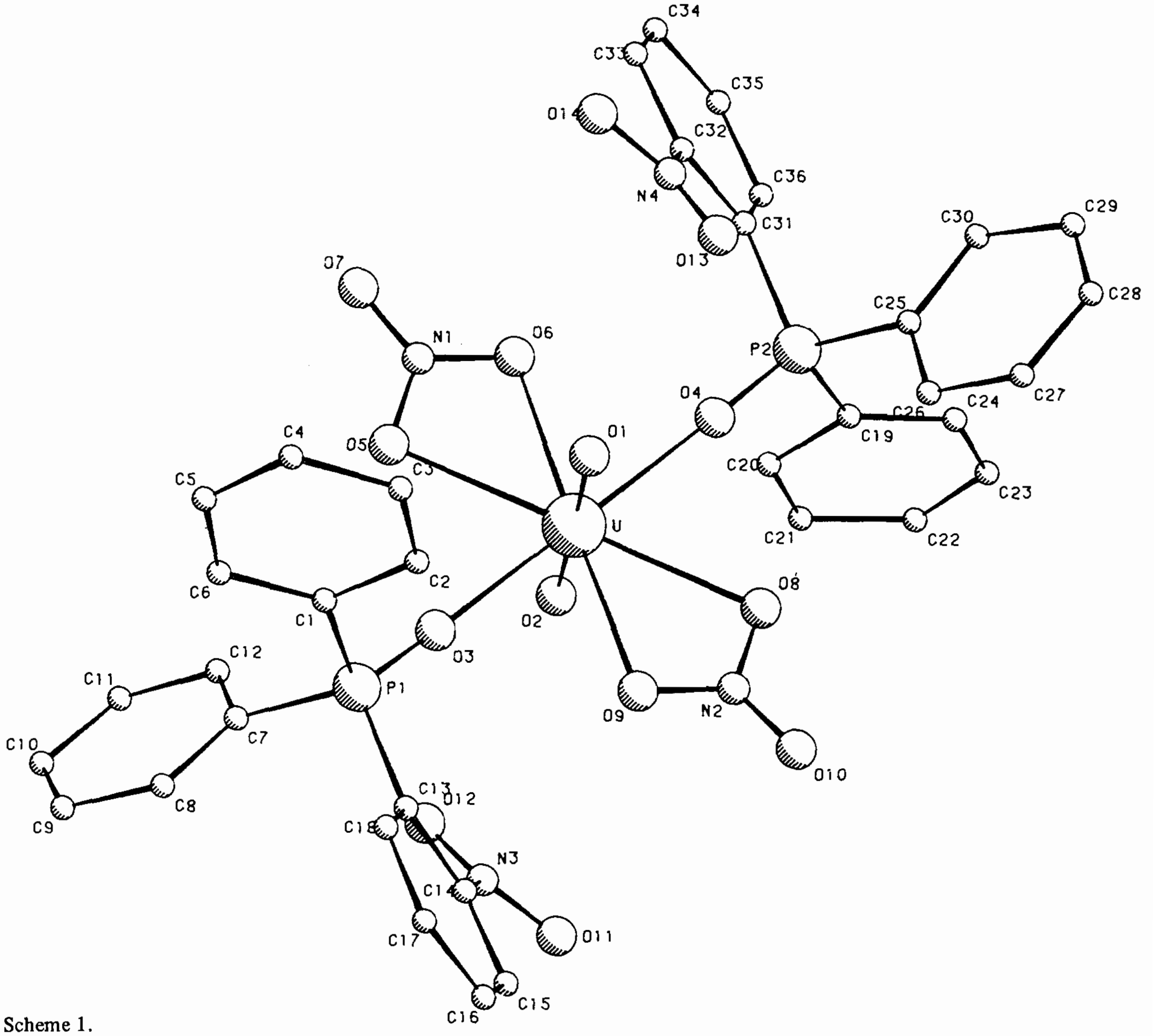
The molecule of $UO_2(NO_3)_2(Ph_3AsO)_2$ is strictly centrosymmetric so that the uranium atom lies on a crystallographic inversion center at the origin of the monoclinic cell which therefore contains two molecules; on the contrary $UO_2(NO_3)_2(NO_2\text{-}C_6H_4Ph_2PO)_2$, which is chemically very similar, is only approximately centrosymmetric so that the entire molecule is the asymmetric unit in a monoclinic cell which contains four molecules, and all atoms are in general positions. Nevertheless, both compounds have fully comparable densities, as expected.

The uranyl(VI) acetate complexes are of the type $UO_2(OAc)_2L$; their infrared spectra show two almost equally intense bands at 1590 and at 1460 $cm^{-1}$ $UO_2(OAc)_2L^1$; at 1525 $cm^{-1}$ and at 1412 $cm^{-1}$ $UO_2(OAc)_2L^2$ due to the antisymmetric and symmetric stretching frequencies of the $CH_3\text{–}CO_2$ carboxylic groups which coordinate to uranium as bidentate ligands. The coordination of the monodentate ligand is evidenced by the lowering of the $\nu$ P–O in comparison with the free ligands. The $\nu_3$ O–U–O lies at 925 $cm^{-1}$ for $UO_2(OAc)_2L^1$ and at 922 $cm^{-1}$ for $UO_2(OAc)_2L^2$.

A binuclear structure of the type:



might be reasonably suggested, in agreement with the structure found for $UO_2(OAc)_2(Ph_3PO)$ [13].



Scheme 1.

The thorium(IV) nitrate complexes are of the type $Th(NO_3)_4(L)_2$. The nitrates, according to the infrared data, act as bidentate and the two phosphine-oxide ligands can be supposed to be *trans* to each other in the apical position, as found for $Ce(NO_3)_4 \cdot (Ph_3PO)_2$ [16] and $Th(NO_3)_4 \cdot (Ph_3PO)_2$ [17].

In the complex $Th(NO_3)_4(L^1)_2$ there are two bands due to the bidentate nitrate groups at 1530 $cm^{-1}$ and 1285 $cm^{-1}$. The correct assignment of the higher band is partially precluded by other absorption bands of the monodentate ligands. This problem is not shown by $Th(NO_3)_4(L^2)_2$.

The bands due to the nitrate ions are at 1530 $cm^{-1}$ and at 1384 $cm^{-1}$; bands due to the triferrocenyl–phosphine oxides are not present in this region.

The coordination of the monodentate ligands is evidenced for $Th(NO_3)_4(L^1)_2$ by a strong $\nu$ P–O band at 1129 $cm^{-1}$ while for $Th(NO_3)_4(L^2)_2$ a $\nu$ P–O at 1180 $cm^{-1}$ was found. It is well known that thorium(IV) tetraacetate is a polymer, with the central metal ion being ten-coordinate [14].

For this reason also, it is not very soluble in organic solvents and is not very reactive towards neutral oxygen donor ligands. It does not react in alcoholic solution with $L^1$ and remains practically insoluble also when the methanolic mixture is treated under reflux for a long period of time.

This is a clear indication of the high crystal energy of the polymeric acetate structure.

On the contrary, under similar conditions $L^2$ reacts with $Th(OAc)_4$ giving rise to an orange-red solution. The complex $Th(CH_3COO)_4(L^2)_x$ probably formed cannot however be isolated in the solid state; only the original polymer acetate is obtained.

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