Inorganica Chimica Acta, 81 (1984) 47–54

Actinide and Lanthanide Complexes with Bidentate Ligands. Crystal Structure of Methanolbis(N-phenylbenzoylhydroxamato)dioxouranium(VI)

U. CASELLATO, P. A. VIGATO, S. TAMBURINI

Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Padua, Italy

R. GRAZIANI

Istituto di Chimica Generale, Università di Padova, Padua, Italy

and M. VIDALI

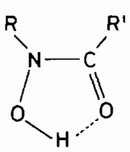
Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Italy

Received April 8, 1983

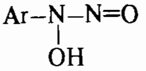
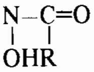
Some complexes of actinide and lanthanide ions with N-phenylbenzoylhydroxamato and cupferrato have been prepared and characterized, and the crystal structure of the title compound has been determined by X-ray diffraction. The compound is triclinic, space group $P\bar{1}$, *with* $a = 14.24(1)$, $b = 10.60(1)$, $c = 9.52(1)$ Å, $\alpha = 94.03(3)^\circ$, $\beta = 105.80(3)^\circ$, $\gamma = 107.92(3)^\circ$, *and* $Z = 2$. *Two bidentate hydroxamato ligands and one methanol molecule are equatorially bonded to the linear uranyl group in the pentagonal bipyramidal coordination geometry. The phenyl rings are inclined by about 50° to the equatorial plane. The five U–O (equatorial) bond distances are comprised between 2.35 and 2.42 Å with a mean value of 2.38 Å. The MeOH molecule is easily replaced by other neutral, more basic monodentate substituents ad* Ph_3PO, *dmso, dmf or py.*

Introduction

The hydroxamic acids (I) form somewhat stable uranyl compounds.

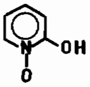


(I)

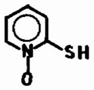
Complexes of (I) with Th^{4+} and La^{3+} are also stable and some X-ray structural determinations have been recently reported [1]. On the contrary, UCl_4 is quantitatively oxidized in an oxygen transfer reaction with two equivalents of the N-phenylbenzoylhydroxamic anion in THF to form a uranyl complex and benzanilide [2]. It is known that the naturally occurring sequestrating agents of the Fe^{3+} ion, produced by microbes, commonly contain hydroxamate or cathecolate. These groups could also play an important role in the complexation of the actinide ions and a better knowledge of the binding mode toward these ions can be useful with regard to their decorporation [1]. As far as the solvent extraction of metals is concerned nitrosoaryl hydroxylamines and their derivatives can be associated with the same class of ligands [3]. In all these ligands the hydrogen atom of the functional group  $\mathrm{Ar{-}\underset{\displaystyle OH}{N}{-}N{=}O}$ or  $\mathrm{Ar{-}\underset{\displaystyle OHR}{N{-}C}{=}O}$ can be replaced by an equivalent of a metal ion to form a five-membered ring.

Several studies on the physico-chemical properties of actinide complexes with the ligands N-phenylbenzoylhydroxamic acid (HL^1) and cupferron, the ammonium salt of N-nitrosophenylhydroxylamine (HL^2) have been published in the past. The structures of $UO_2(L^1)_2 \cdot 2H_2O$ and $TH(L^1)_4$ have been reported and $NH_4[UO_2(L^1)_3]$ and its structure have been known for a long time [11, 12].

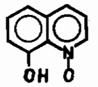
As a part of a study dealing with the interaction of the series of common and well known chelating ligands:



a)

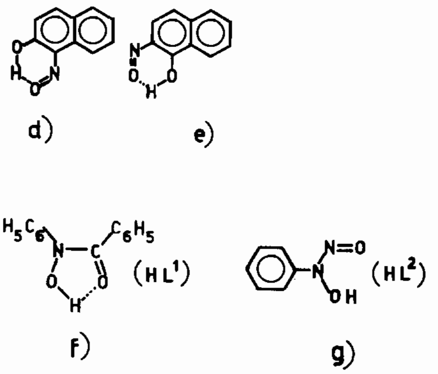


b)



c)

0020-1693/84/$3.00



(a) 2-hydroxypyridine N-oxide;
(b) 2-mercaptopyridine N-oxide;
(c) 8-hydroxyquinoline N-oxide;
(d) 1-nitroso-2-naphthol;
(e) 2-nitroso-1-naphthol;
(f) N-phenylbenzoylhydroxamic acid;
(g) N-nitrosophenylhydroxylamine

with some actinide and lanthanide ions [4], we report here the synthesis and the physico-chemical characterization of La^{3+}, Th^{4+} and UO_2^{2+} complexes of HL^1 and HL^2.

The crystal structure of methanolbis(N-phenylbenzoylhydroxamato)dioxouranium(VI), $[UO_2(L^1)_2 \cdot MeOH]$, is also reported.

Experimental

Preparation of Compounds

$[UO_2(L^1)_2MeOH]$

To a pale yellow methanolic solution of HL^1 (426 mg, 2 mmol) and LiOH (48 mg, 2 mmol) a solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (504 mg, 1 mmol) in the same solvent was added. The red solution obtained was stirred for 3 h at room temperature, reduced in volume and allowed to stand. A red precipitate of $[UO_2(L^1)_2MeOH]$ was obtained, and recrystallization from MeOH gave well formed crystals of the compound. (Found: C, 44.71; H, 3.42; N, 3.74%; calcd. for $C_{27}H_{24}O_7N_2U$: C, 44.62; H, 3.30; N, 3.85%).

$[UO_2(L^1)_2A]$ ($A = Ph_3PO$, dmf, py)

To a CH_2Cl_2 solution of $[UO_2(L^1)_2MeOH]$ an excess of the appropriate monodentate ligand was added. From the red solution, after stirring at room temperature for 3 h, the red complexes $[UO_2(L^1)_2A]$ were precipitated by addition of diethyl ether, washed with diethyl ether and dried *in vacuo*.

$UO_2(L^1)_2Ph_3PO$. Found: C, 54.31; H, 3.78; N, 2.66%; calcd. for $C_{44}H_{15}O_7N_2PU$: C, 54.32; H, 3.60; N, 2.88%.

$UO_2(L^1)_2dmf \cdot H_2O$. Found: C, 44.27; H, 3.64; N, 5.15%; calcd. for $C_{29}H_{17}O_7N_3U$: C, 44.33; H, 3.69; N, 5.35%.

$UO_2(L^1)_2py$. Found: C, 48.07; H, 3.45; N, 5.81%; calcd. for $C_{31}H_{15}O_6N_3U$: C, 48.12; H, 3.23; N, 5.43%.

$Th(L^1)_4 \cdot 4H_2O$

By reacting a water solution of $Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) with an excess of HL^1 (1280 mg, 6 mmol) and LiOH (144 mg, 6 mmol) a white precipitate of $Th(L^1)_4 \cdot 4H_2O$ was immediately obtained; it was washed with water and dried *in vacuo*. A compound which can be formulated as $Th(L^1)_3(OH) \cdot H_2O$, is obtained by reacting $Th(NO_3)_4 \cdot 5H_2O$ with HL^1 and LiOH in the ratio 1:4.

$Th(L^1)_4 \cdot 4H_2O$. Found: C, 54.72; H, 3.28; N, 4.86%; calcd. for $C_{52}H_{48}O_{12}N_4Th$: C, 54.16; H, 4.16; N, 4.86%.

$Th(L^1)_3(OH) \cdot H_2O$. Found: C, 51.67; H, 3.30; N, 5.83%; calcd. for $C_{39}H_{33}O_8N_3Th$: C, 51.82; H, 3.65; N, 4.65%.

$La(L^1)_3 \cdot 2H_2O$

By reacting a water solution of $La(NO_3)_3 \cdot 6H_2O$ (433 mg, 1 mmol) with HL^1 (639 mg, 3 mmol) and LiOH (72 mg, 3 mmol) a pale yellow precipitate of $La(L^1)_3 \cdot 2H_2O$ was immediately obtained. It was stirred for 3 h, washed with water, and dried *in vacuo*. Found: C, 57.84; H, 3.84; N, 5.07%; calcd. for $C_{39}H_{34}O_8N_3La$: C, 57.70; H, 4.19; N, 5.17%.

$UO_2(L^2)_2Ph_3PO \cdot 3H_2O$

By reacting $UO_2(NO_3)_2(Ph_3PO)_2$ (950 mg, 1 mmol) with cupferron (NH_4L^2) (310 mg, 2 mmol) in a H_2O/MeOH solution a yellow precipitate of $UO_2(L^2)_2Ph_3PO$ was immediately obtained. It was stirred for 3 h, washed with H_2O/MeOH solution, and dried *in vacuo*. Found: C, 45.13; H, 3.35; N, 6.11%; calcd. for $C_{36}H_{29}O_9N_4PU$: C, 45.56; H, 3.27; N, 5.90%.

$NH_4[UO_2(L^2)_3]$

An orange precipitate of $NH_4[UO_2(L^2)_3]$ was obtained by adding $UO_2(NO_3)_2 \cdot 6H_2O$ (252 mg, 0.5 mmol) to a EtOH solution of the ligand (233 mg, 1.5 mmol). It can be obtained also in a H_2O/MeOH solution with the 1:2 (salt to ligand) molar ratio. Found: C, 30.69; H, 3.18; N, 13.49%; calcd. for $C_{18}H_{10}O_8N_7U$: C, 30.90; H, 2.71; N, 14.02%.

$Th(L^2)_4 \cdot H_2O$

By reacting $Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) with cupferron (620 mg, 4 mmol) in H_2O/MeOH solution a white precipitate of $Th(L^2)_4 \cdot H_2O$ was immediately obtained. It was stirred for 3 h, washed with water and dried *in vacuo*. The presence of one molecule of water was confirmed by thermogravimetry. Found: C, 36.15; H, 2.59; N, 14.13%; calcd. for $C_{24}H_{22}N_8O_9Th$: C, 36.09; H, 2.75; N, 14.03%.

$Th(L^2)_4Ph_3PO$; $Th(L^2)_4py$; $Th(L^2)_4dma$

To a solution of $Th(L^2)_4 \cdot H_2O$ in $CHCl_3$ an excess of the neutral ligand was added. Addition of *n*-pentane to the resulting solutions caused the formation of the white solid adducts. They were washed with ether and dried *in vacuo.*

$Th(L^2)_4Ph_3PO$. Found: C, 47.50; H, 3.59; N, 9.94%; calcd. for $C_{42}H_{38}N_8O_9PTh$: C, 47.50; H, 3.58; N, 10.55%.

$Th(L^2)_4py$. Found: C, 40.49; H, 3.18; N, 14.22%; calcd. for $C_{29}H_{25}N_9O_8Th$: C, 40.51; H, 2.91; N, 14.66%.

$Th(L^2)_4dma$. Found: C, 38.95; H, 3.38; N, 14.61%; calcd. for $C_{28}H_{29}N_9O_9Th$: C, 38.75; H, 3.34; N, 14.53%.

$NH_4[Th(L^2)_5] \cdot H_2O$

By reacting $Th(NO_3)_4 \cdot 5H_2O$ (570 mg, 1 mmol) with the ligand (1.24 g, 8 mmol) in H_2O/MeOH solution, $NH_4[Th(L^2)_5] \cdot H_2O$ formed as an oil and precipitated as a white solid by addition of water. It was washed with water and dried *in vacuo.* Found: C, 37.62; H, 3.00; N, 15.18%; calcd. for $C_{30}H_{31}N_{11}O_{11}Th$: C, 37.77; H, 3.25; N, 16.15%.

$La(L^2)_3 \cdot H_2O$

By reacting $La(NO_3)_3 \cdot 6H_2O$ (433 mg, 1 mmol) with the ligand (465 mg, 3 mmol) in H_2O/MeOH solution a white precipitate of $La(L^2)_3 \cdot H_2O$ was immediately obtained. It was washed with water and dried *in vacuo.* Found: C, 38.40; H, 3.23; N, 14.47%; calcd. for $C_{18}H_{17}N_6O_7La$: C, 38.02; H, 2.99; N, 14.78%.

$La(L^2)_3(Ph_3PO)_2 \cdot 2H_2O$

To a solution of $La(L^2)_3 \cdot H_2O$ in hot ethyletate, an excess of Ph_3PO was added. Addition of n-hexane to the resulting solution caused the formation of $La(L^2)_3(Ph_3PO)_2 \cdot 2H_2O$ was a white solid. It was washed with ether and dried *in vacuo.* Found: C, 56.12; H, 3.74; N, 8.15%; calcd. for $C_{54}H_{49}N_6O_{10}P_2La$: C, 56.74; H, 4.29; N, 7.35%.

X-Ray Data for $UO_2(L^1)_2MeOH$

A small crystal of $UO_2(L^1)_2MeOH$ was used for the X-ray work. Cell dimensions were calculated from the accurate settings of 25 medium angle reflections on a PW-1100 Philips diffractometer with the MoKα radiation. Crystal data are: $C_{27}H_{24}O_7N_2U$, $M = 722$, triclinic, space group P1, cell parameters $a = 14.24(1)$, $b = 10.60(1)$, $c = 9.52(1)$ Å, $\alpha = 94.03(3)$, $\beta = 105.80(3)$, $\gamma = 107.92(3)^\circ$, $D_c = 1.85$ g cm^{-3} for $Z = 2$, μ(MoKα) = 150 cm^{-1}.

Intensities for reflections having $2^\circ < \theta < 25^\circ$ were measured with a scan speed of 2° min^{-1} and the ω–2θ scan. Of the 4615 reflections measured, 4026 with $I > 3\sigma(I)$ were considered to be observed. Corrections were made for Lp and for absorption. No deterioration of the crystal was observed during data collection. The structure is governed by the heavy atom and was solved by standard methods.

The ring hydrogen atoms were introduced in calculated positions with fixed temperature factors ($U_{iso} = 8$ Å^2). Refinement of positional and anisotropic thermal parameters converged to the final conventional R of 4.6%. Neutral scattering factors for U, O, N and C were those of Cromer and Mann [5], and for H those tabulated in the International Tables for X-ray Crystallography [6]. A dispersion correction was applied to the scattering factors of the uranium atom [7]. Calculations were performed using the X-ray program system [8]. Final atomic positional and thermal parameters, distances and angles, and selected mean planes are given in Tables I–IV.

Discussion

A projection of the $UO_2(L^1)_2MeOH$ molecule is shown in Fig. 1 together with the used numbering scheme. Two bidentate N-phenylbenzoylhydroxamato ions and one MeOH molecule are equatorially bonded to the uranyl group in the pentagonal bipyramidal coordination geometry. The coordinated solvent molecule confines with the NO group of one ligand and with the CO group of the other so that the entire molecule is asymmetric. The UO_2^{2+} group is linear with the usual values (1.75 Å) for the U–O distances; the equatorial U–O(L) distances (mean 2.39 Å) and the U–O (MeOH) distance of 2.37 Å are normal, but it is noteworthy that the longest one (U–O(3) = 2.42 Å) involves the O(3) oxygen atom which makes a relatively strong hydrogen bond (2.59 Å) with the MeOH oxygen atom of the centrosymmetric unit. The C–O (mean 1.30 Å) and the N–O (mean 1.36 Å) bonds are partially double, and also the N–C(7) and N–C(20) bonds (mean 1.30 Å) are shortened, indicating the presence of electronic mesomery over the chelate moieties. The two ligands basically behave in the same way with respect to the metal atom; nevertheless it seems that the hydrogen bonding to O(3) plays an important role in determining some observed differences. Thus we must note that, in addition to the above mentioned U–O(3) distance, the N(1)–O(3) distance is also significantly longer than the corresponding N(2)–O(5) and that the U–O(3)–N(1) angle is significantly smaller than U–O(4)–C(7), whereas the corresponding angles in the adjacent ligand are comparable.

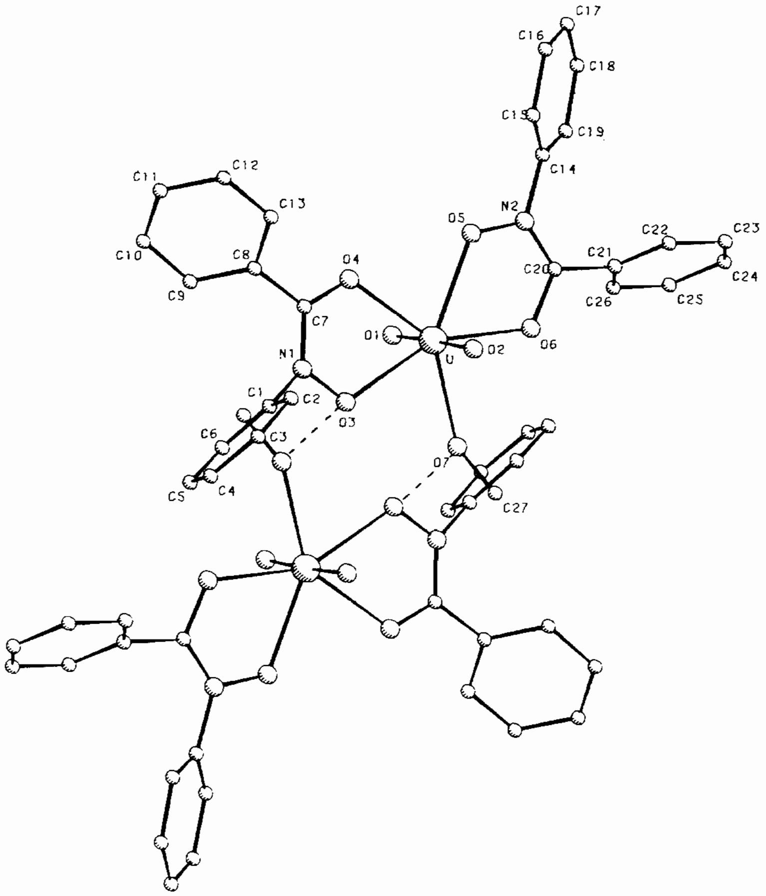


Fig. 1. The molecular structure of $UO_2(L^1)_2MeOH$.

TABLE I. Positional Parameters with e.s.d.s.

Atom	x	y	z
U	0.18782(3)	0.15476(4)	0.22478(5)
O(1)	0.1951(7)	0.0137(8)	0.1262(9)
O(2)	0.1743(7)	0.2929(8)	0.3191(10)
O(3)	0.0844(6)	0.1930(8)	−0.0048(8)
O(4)	0.2850(6)	0.2949(8)	0.0887(9)
O(5)	0.3625(6)	0.2242(9)	0.3820(9)
O(6)	0.2102(6)	0.0589(9)	0.4410(9)
O(7)	0.0145(6)	0.0238(8)	0.2001(9)
N(1)	0.1370(7)	0.2915(9)	−0.0718(10)
N(2)	0.3838(8)	0.1698(10)	0.5035(11)
C(1)	0.0754(9)	0.3601(12)	−0.1625(13)
C(2)	0.0875(13)	0.4896(16)	−0.1018(18)
C(3)	0.0258(17)	0.5545(19)	−0.1925(26)
C(4)	−0.0388(13)	0.4959(21)	−0.3252(24)
C(5)	−0.0493(12)	0.3672(19)	−0.3830(21)
C(6)	0.0070(11)	0.2970(15)	−0.2968(17)
C(7)	0.2395(8)	0.3345(11)	−0.0244(12)
C(8)	0.2997(8)	0.4243(11)	−0.1034(12)
C(9)	0.2776(9)	0.3921(12)	−0.2558(14)

(continued on facing page)

TABLE I. *(continued)*

Atom	x	y	z
C(10)	0.3414(11)	0.4721(13)	−0.3261(15)
C(11)	0.4238(11)	0.5828(14)	−0.2488(15)
C(12)	0.4464(11)	0.6142(14)	−0.0994(15)
C(13)	0.3839(10)	0.5356(13)	−0.0273(14)
C(14)	0.4936(8)	0.2075(10)	0.5880(11)
C(15)	0.5589(10)	0.3369(12)	0.6029(13)
C(16)	0.6650(10)	0.3724(14)	0.6738(15)
C(17)	0.7059(10)	0.2760(15)	0.7304(13)
C(18)	0.6394(10)	0.1473(14)	0.7159(14)
C(19)	0.5341(9)	0.1106(12)	0.6473(12)
C(20)	0.3065(8)	0.0896(11)	0.5337(11)
C(21)	0.3131(8)	0.0204(11)	0.6627(11)
C(22)	0.3511(9)	0.0912(12)	0.8028(13)
C(23)	0.3557(11)	0.0211(14)	0.9221(14)
C(24)	0.3232(12)	−0.1174(15)	0.8964(16)
C(25)	0.2845(12)	−0.1876(13)	0.7558(16)
C(26)	0.2784(11)	−0.1188(13)	0.6361(14)
C(27)	−0.0596(12)	0.0566(16)	0.2579(18)

Anisotropic thermal parameters ($\times 10^2$) in the form $T = \exp[-2\pi^2 \Sigma_i \Sigma_j h_i h_j a_i a_j U_{ij}]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	3.52	3.74	3.26	1.57	0.61	1.63
O(1)	6.33	4.58	4.76	2.50	1.71	1.49
O(2)	6.50	4.17	4.50	0.55	1.09	−0.50
O(3)	3.59	4.32	3.91	0.99	0.78	2.50
O(4)	3.55	5.84	5.11	1.78	0.97	2.88
O(5)	4.36	6.53	4.32	1.47	0.83	3.87
O(6)	4.36	6.71	4.43	0.050	0.11	3.57
O(7)	4.25	4.35	5.03	2.40	1.61	2.26
N(1)	3.94	3.81	3.72	1.09	1.12	2.16
N(2)	4.70	5.59	4.10	2.02	0.90	1.75
C(1)	3.92	4.90	4.41	2.03	1.33	2.72
C(2)	10.18	6.67	7.95	5.78	4.42	3.48
C(3)	13.76	9.10	13.98	8.82	7.66	7.30
C(4)	6.54	12.39	12.63	6.55	4.58	8.54
C(5)	5.91	10.16	10.07	2.67	0.95	6.55
C(6)	5.41	7.23	6.48	1.16	−0.55	4.06
C(7)	3.38	3.92	3.62	2.10	0.95	1.38
C(8)	3.62	4.18	3.96	1.97	1.35	1.49
C(9)	5.24	3.83	4.68	2.08	1.67	1.53
C(10)	6.57	5.28	5.38	2.30	2.69	2.23
C(11)	5.93	5.60	5.82	2.37	2.54	2.32
C(12)	5.99	6.00	5.15	0.88	1.56	1.85
C(13)	4.97	5.18	4.71	1.47	1.37	1.79
C(14)	3.70	4.48	2.73	1.65	0.43	0.97
C(15)	4.84	5.03	3.97	1.36	1.49	1.31
C(16)	5.00	6.51	4.83	0.62	1.65	0.91
C(17)	4.84	8.28	3.28	2.61	1.03	1.17
C(18)	5.14	7.54	4.15	3.91	1.44	1.24
C(19)	4.69	5.49	3.31	3.18	0.84	1.00
C(20)	3.33	4.11	2.04	0.74	0.25	1.46
C(21)	3.33	4.52	2.86	1.68	0.89	1.27
C(22)	4.57	4.86	3.98	2.23	1.30	1.39

(continued overleaf)

TABLE I. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(23)	6.99	6.59	3.66	2.51	1.88	1.92
C(24)	7.85	6.81	5.28	3.35	2.21	3.15
C(25)	8.27	4.82	5.49	2.66	2.84	2.18
C(26)	7.55	4.30	4.42	1.86	1.97	1.27
C(27)	5.94	7.62	7.00	2.19	2.37	0.10

Hydrogen atoms

Atom	x	y	z
H(2)	0.138	0.535	0.001
H(3)	0.031	0.650	−0.153
H(4)	−0.082	0.545	−0.386
H(5)	−0.097	0.323	−0.488
H(6)	−0.003	0.200	−0.335
H(9)	0.216	0.311	−0.314
H(10)	0.326	0.448	−0.437
H(11)	0.469	0.640	−0.302
H(12)	0.507	0.697	−0.042
H(13)	0.401	0.560	0.084
H(15)	0.529	0.408	0.562
H(16)	0.712	0.469	0.685
H(17)	0.783	0.300	0.781
H(18)	0.669	0.077	0.757
H(19)	0.486	0.015	0.640
H(22)	0.376	0.193	0.820
H(23)	0.383	0.072	1.027
H(24)	0.327	−0.168	0.983
H(25)	0.260	−0.289	0.738
H(26)	0.249	−0.170	0.531

TABLE II. Bond and Contact Distances (Å) with e.s.d.'s.

(a) Bond distances

Coordination polyhedron

U–O(1)	1.75(1)	U–O(3)	2.42(1)
U–O(2)	1.75(1)	U–O(4)	2.40(1)
		U–O(5)	2.38(1)
		U–O(6)	2.35(1)
		U–O(7)	2.37(1)

Ligands

O(3)–N(1)	1.39(1)	O(5)–N(2)	1.33(1)
O(4)–C(7)	1.27(1)	O(6)–C(20)	1.34(1)
N(1)–C(7)	1.32(1)	N(2)–C(20)	1.28(2)
N(1)–C(1)	1.45(2)	N(2)–C(14)	1.46(1)
C(7)–C(8)	1.47(2)	C(20)–C(21)	1.47(2)

MeOH

O(7)–C(27)	1.43(2)

TABLE II. *(continued)*

(b) Contact distances

O(3)···O(4)	2.59(1)	O(7)···O(3)	2.91(1)
O(4)···O(5)	2.95(1)	O(7)···O(6)	2.99(1)
O(5)···O(6)	2.56(1)	O(7)···O(3^{I})	2.59(1)

Symmetry code: I $\bar{x}, \bar{y}, \bar{z}$.

Bond distances and angles in the phenyl rings are normal.

The phenyl rings are inclined by *ca.* 50° to the equatorial plane. The methanol molecule of the complex can be easily replaced in CH_2Cl_2 by other, more basic monodentate ligands such as Ph_3PO, dmso, dmf, or py according to the reaction $UO_2L_2MeOH + A \rightarrow UO_2L_2A + MeOH$ (A = Ph_3PO, dmso, dmf, py). The electronic spectra in the visible region are characterized by a band near 500–520 nm and a stronger band

TABLE III. Bond Angles (°) with e.s.d. s.

Coordination polyhedron			
O(1)–U–O(2)	177.3(4)	O(3)–U–O(7)	74.8(3)
O(3)–U–O(4)	64.9(2)	O(6)–U–O(7)	78.7(3)
O(5)–U–O(6)	65.5(3)	O(4)–U–O(5)	76.1(3)
Ligands			
U–O(3)–N(1)	116(1)	U–O(5)–N(2)	119(1)
U–O(4)–C(7)	121(1)	U–O(6)–C(20)	118(1)
O(3)–N(1)–C(7)	118(1)	O(5)–N(2)–C(20)	117(1)
O(3)–N(1)–C(1)	116(1)	O(5)–N(2)–C(14)	116(1)
O(4)–C(7)–N(1)	119(1)	O(6)–C(20)–N(2)	120(1)
O(4)–C(7)–C(8)	120(1)	O(6)–C(20)–C(21)	114(1)
C(1)–N(1)–C(7)	125(1)	C(14)–N(2)–C(20)	127(1)
N(1)–C(7)–C(8)	120(1)	N(2)–C(20)–C(21)	125(1)
MeOH			
U–O(7)–C(27)	130(1)		

between 360 and 430 nm. The UV spectra are dominated by π–π^* transitions of the phenyl rings. The ir spectra show a very strong band, due to the ν_3 O–U–O, in the range 913–893 cm^{-1}, which roughly follows the basicity of the monodentate ligand, decreasing in the order MeOH > Py > dmf > Ph_3PO. It must be noted however that this tendency is not always observed in uranyl complexes. The very strong carbonyl stretch at 1636 cm^{-1} in the free N-phenylbenzoylhydroxamic acid shifted to 1537–1529 cm^{-1} upon coordination. Coordination of dmf or Ph_3PO is accompanied by a shift to lower frequencies of the νC=O and νP–O stretching (1645 and 1152 cm^{-1} respectively).

The red complex $[UO_2(L^1)_2MeOH]$ is relatively unstable in MeOH. With time it changes into a yellow powder to which a L^1/UO_2^{2+} ratio of 1:1 can be assigned on the basis of elemental analysis. The same yellow complex can be directly obtained from the ligand and $UO_2(NO_3)_2 \cdot 6H_2O$, when the solution obtained for the preparation of $[UO_2(L^1)_2MeOH]$ is

TABLE IV. Mean Planes for $[UO_2L_2MeOH]$. The equation of a plane is expressed as AX + BY + CZ = D where, X, Y and Z are the fractional coordinates of the atoms in the direct cell.

Plane 1:	O(3) to O(7) –7.26X + 8.88Y + 4.53Z = 1.02 Å [O(3) 0.05, O(4) –0.07, O(5) 0.06, O(6) –0.03, O(7) –0.01, U 0.00]
Plane 2:	O(3), O(4), C(7), N(1) –6.58X + 7.91Y + 5.81Z = 0.96 Å [O(3) –0.01, O(4) 0.02, C(7) –0.03, N(1) 0.03]
Plane 3:	O(5), O(6), C(20), N(2) –7.31X + 8.59Y + 4.94Z = 1.15 Å [O(5) 0.01, O(6) –0.01, C(20) 0.01, N(2) –0.01]
Plane 4:	C(1) to C(6) 11.42X + 1.83Y – 6.41Z = 2.55 Å
Plane 5:	C(8) to C(13) 11.20X – 8.61Y + 0.22Z = –0.32 Å
Plane 6:	C(14) to C(19) –6.80X + 2.46Y + 8.99Z = 2.45 Å
Plane 7:	C(21) to C(26) 14.23X – 3.02Y – 2.36Z = 2.83 Å

Angles (°) between the planes

Planes	Angle	Planes	Angle	Planes	Angle
1–2	10	1–4	73	1–6	43
1–3	3	1–5	41	1–7	61
2–3	7	4–5	72	6–7	63

stirred for about 2 h. The ir spectra of both the yellow and red complexes are very similar, the most important differences being in the region 3200–1800 cm^{-1} and 1050–990 cm^{-1}. The ν_3O–U–O band lies at about the same frequency.

Reactions of UO_2^{2+} salts with cupferron under a variety of conditions always yielded $NH_4[UO_2(L^2)_3]$. The high stability of the $[UO_2(L^2)_3]^-$ anion caused the failure of attempts to prepare complexes of the type $UO_2(L^3)_2A$ (A = Ph_3PO, dmf, py), starting from uranyl(VI) salts and cupferron. Only a compound of formula $UO_2(L^2)_2Ph_3PO \cdot 3H_2O$ was obtained by reacting $UO_2(NO_3)_2(Ph_3PO)_2$ with cupferron in H_2O/MeOH solution.

The presence of a molecule of water in the complex $[Th(L^2)_4(H_2O)]$, obtained by reacting $Th(NO_3)_4 \cdot 5H_2O$ with cupferron in H_2O/MeOH solution, was easily determined by thermogravimetric analysis but coordination of the water molecule to thorium was not immediately clear, even if reactions of the type:

$$Th(L^2)_4(H_2O) + A \longrightarrow Th(L^2)_4(A) + H_2O$$

(where A is a monodentate ligand containing oxygen or nitrogen as donor atoms) seem to support it. Lowering of νP=O to 1160 cm^{-1} in $[Th(L^2)_4(Ph_3PO)]$ and of νC=O to 1617 cm^{-1} in $[Th(L^2)_4dma]$ are evidence that Ph_3PO and dma are coordinated and that the most probable coordination number in these complexes is 9.

For the product obtained by reacting $Th(NO_3)_4 \cdot 5H_2O$ with an excess of cupferron in water/methanol, possibly $NH_4[Th(L^2)_5] \cdot H_2O$, a c.n. of 10 should be tentatively assumed for Th^{4+}, as was proposed for the same atom in $Li[Th(trop)_5] \cdot H_2O$ [9, 10].

A further X-ray investigation of these complexes is necessary in order to ascertain their coordination polyhedra. Attempts to grow good crystals for such an investigation were unsuccessful.

References

1 K. N. Raymond, W. L. Smith, F. L. Weith, P. W. Durbin, E. S. Jones, K. Abu-Dari, S. R. Sofen and S. R. Copper, 'Lanthanide and Actinide Chemistry and Spectroscopy', N. M. Edelstein Ed., ACS Symposium Series, 131, p. 143.
2 W. L. Smith and K. N. Raymond, *J. Inorg. Nucl. Chem., 41,* 1431 (1979).
3 A. K. De, S. M. Klopkar and R. A. Chalmers, 'Solvent Extraction of Metals', Van Nostrand Reinhold, London (1970).
4 U. Casellato, P. A. Vigato, S. Tamburini, M. Vidali and R. Graziani, *Inorg. Chim. Acta, 69,* 77 (1983).
5 D. T. Cromer and J. B. Mann, *Acta Cryst., A24,* 321 (1968).
6 International Tables for X-Ray Crystallography, Vol. IV, pp. 99–101, Birmingham, Kynoch Press (1974).
7 D. T. Cromer and Libermann, *J. Chem. Phys., 53,* 1891 (1970).
8 J. M. Stewart, F. A. Kundell and J. C. Baldwin, X-Ray System of Crystallographic Programs, University of Maryland, U.S.A.
9 E. L. Muetterties, *J. Am. Chem. Soc., 88,* 305 (1966).
10 J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem., 30,* 313 (1968).
11 W. S. Horton, *J. Am. Chem. Soc., 78,* 897 (1956).
12 P. J. Elving and E. C. Olson, *J. Am. Chem. Soc., 78,* 4206 (1956).