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Synthetic, spectroscopic, and X-ray crystallographic studies on the uranyl(VI) complexes of the β-diketophenol ligands 1-(2-hydroxyphenyl)-1,3-butanedione and 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione

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Abstract

The preparation of the mononuclear complexes $[UO_2(HL^1)_2(MeOH)]$ and $[UO_2(HL^2)_2(EtOH)]$, the heterobinuclear complexes $[UO_2Mn(L^1)_2(EtOH)] \cdot 1.5H_2O$ and $[UO_2Mn(L^2)_2(EtOH)] \cdot 2H_2O$, and the oxo-ligand adducts $[UO_2(HL^1)_2(Ph_3AsO)] \cdot 2H_2O$, $[UO_2(HL^2)_2(Ph_3PO)]$ and $[UO_2(HL^2)_2(Ph_3AsO)] \cdot (H_2L^1 = 1-(2-hydroxyphenyl)-3-butanedione and <math>H_2L^2 = 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione)$ is described. The complexes have been characterized by a variety of physicochemical techniques and the crystal structures of $[UO_2(HL^1)_2(EtOH)]$ and $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$ determined. Crystals of the former are triclinic, space group *P*1, a = 8.076(1), b = 8.131(1), c = 10.161(1) Å, $\alpha = 108.49(1), \beta = 112.26(1), \gamma = 89.89(1)^\circ$ and Z = 1. The latter is also triclinic, space group *P*1, a = 12.184(3), b = 15.578(5), c = 9.035(2) Å, $\alpha = 91.05(2), \beta = 103.20(2), \gamma = 73.21(2)^\circ$ and Z = 2. Both complexes contain seven-coordinate uranium(VI) in a pentagonal bipyramidal geometry in which the two bidentate β-diketonato ligands and the coordinated ethanol make up the equatorial pentagonal plane. For the complex $[UO_2(HL^1)_2(EtOH)]$ the HL¹ ligands are in a *trans* arrangement with respect to one another, whereas for the $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$ complex the HL² ligands adopt a *cis* arrangement. However, in solution variable temperature ¹H NMR spectra indicate that the *cis* and *trans* isomers are in equilibrium for both complexes. (1998) Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures: Uranium complexes: β-Diketophenolato complexes

1. Introduction

A variety of homobinuclear and heterobinuclear complexes of the divalent and trivalent first row transition metals with β -triketones and β -diketophenols have been studied, including an investigation of the catalytic behavior of some copper(II) complexes towards the oxidation of 3,5-di-tbutylcatechol to quinone [1-6]. For the β -diketophenol ligands, 1-(2-hydroxyphenyl)-1,3-butanedione (H₂L¹) and 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (H₂L²), mononuclear complexes of the type [M(HL¹)₂] ·xH₂O (e.g. M = Cu²⁺, x=0; M = Ni²⁺, x=2; M = UO₂²⁺, x=1) have been prepared. Interestingly, whereas heterobinuclear compounds of the type [NiCu(L¹)₂] ·2H₂O are known, none have been reported which include the $UO_2^{2^+}$ ion as one of the cations [7]. No single crystal X-ray studies have been reported for any of the above β -diketophenol compounds, but it has been proposed that the mononuclear chelates have either *cis* or *trans* structures, as shown below, with the metal ion being bound to the keto end of the ligand [6,8].

In an attempt to discover which of these two structures occurs in the solid state we obtained crystals of the complex $[Ni(HL^2)_2(H_2O)_2]$ but unfortunately they only diffracted very weakly. However suitable crystals of the two mononuclear uranyl(V1) complexes. $[UO_2(HL^1)_2(EtOH)]$ and $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$, were obtained and their X-ray crystal structures determined. For the HL¹ complex the ligands are *trans* whereas in the HL² complex they are *cis*. The ability of these two complexes to form adducts with triphenylphosphine oxide and triphenylarsine oxide has also been investigated and, as well, the synthesis and characteri-

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zation of heterobinuclear complexes with manganese(II) is reported.



2. Experimental

Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer, electronic spectra on a Hewlett-Packard 8452A diode array spectrophotometer, and ESR spectra (at 110 K) on a Varian E-104A spectrometer equipped with a Varian E-257 variable temperature accessory. Variable temperature NMR studies were carried out in CDCl₁ using a Jeol GNM-GX270 spectrometer fitted with a JDC-10 accessory. Mass spectra were obtained, by the LSI-MS method with m-nitrobenzyl alcohol or magic bullet matrices, on a VG750-250S double focusing magnetic sector mass spectrometer. Magnetic susceptibilities were measured on a Cahn 7550 millibalance with Hg[Co(SCN)4] as a standard and diamagnetic corrections were made using Pascal's constants. The molar conductances of the complexes at 10⁻¹ M were measured using a Phillips PR9509 conductivity meter and a PW 9550/ 60 cell. Microanalyses (C, H and P) were carried out at the Campbell Microanalytical Laboratory, University of Otago. Manganese was determined by AAS. Data for the complexes are summarized in Table I. The ligands, 1-(2-hydroxy-

Table I				
Analytical.	conductance	and IF	8 spectral	data

phenyl)-1,3-butanedione (H_2L^1) and 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (H_2L^2) , were purchased from Frinton Laboratories and uranyl acetate dihydrate from May and Baker.

2.1. Preparation of $[UO_2(HL^1)_2(MeOH)]$ and $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$

The method of synthesis was an adaption of the method employed by Vigato et al. [7]. To an ethanolic solution (40 cm³) of the appropriate ligand (1 mmol) was added dropwise a solution of uranyl acetete dihydrate (0.5 mmol) in ethanol (15 cm³). The resulting bright orange solution was left to stand for 48 h yielding crystals which were filtered off, washed with a small amount of ethanol followed by diethyl ether, and dried in vacuo. For the HL¹ complex, the product was washed with methanol, which resulted in a molecule of this solvent being incorporated into the complex. Yields: ~90%.

2.2. Preparation of $[UO_2Mn(L^1)_2(EtOH)] \cdot 1.5H_2O$ and $[UO_2Mn(L^2)_2(EtOH)] \cdot 2H_2O$

Manganese diacetate tetrahydrate (0.5 mmol) in ethanol (20 cm³) was added dropwise to an ethanolic solution (50 cm³) of the appropriate uranyl mononuclear complex (0.5 mmol) with gentle heating. The volume of the resulting red solution was reduced using a rotary evaporator until precipitation occurred. The solid was collected by filtration, washed with small amounts of water, ethanol and diethyl ether, and dried in vacuo. Yields: \sim 50%.

2.3. Preparation of $|UO_3(HL^1)_2(Ph_AsO)| \cdot 2H_2(),$ $|UO_3(HL^2)_2(Ph_4PO)|$ and $|UO_2(HL^2)_2(Ph_4AsO)|$

Triphenylphosphine oxide or triphenylarsine oxide (0.5 mmol) in ethanol (5 cm^3) was added to an ethanolic solution

	Analysis * (%)		Conductivity ⁴	IR ° (cm ')				
	С	н	x	(Semiaol') A	r(C∞0)	r(C⇔C)	r(O=U=O)	r(X-0)
(UO ₃ (HL ¹) ₃ (MeOH))	38.8 (38.4)	32(34)		\$ 1	1410 1896	1630		
$[UO_2(HL^2)_2(EtOH)]$	47.7 (48.5)	36(11)		19	1019,1000	1520	9(19	
UO3Mn(L1)3(E(OH)) - 1.5H.O	35.4 (35.2)	(LF) 0.0	6317314	1.0	1016, 1067	1020	914	
110 Ma(1 ²), (FIOH) 1.2H O	43 4 / 13 4		0.5 (7.5)	4.7	1010' 151A	1212	903	
	42.0 (42.2)	3.3 (3.4)	0'1 (0'3)	6.5	1620, 1590	1516	910	
1002(HL')2(Ph:ANO)1-2H2O	46.8 (46.3)	3.5 (3.8)			1617. 1585	1516	OUS	9941
[UO ₂ (HL ²) ₂ (Ph,PO)]	55.8 (56.1)	34 (36)	32(30)		1419 1697	1613	013	
UO.(HL2).(Ph.AxO)1	\$3.9/\$3.9	34 (38)			1010, 1307	1919	A12	11.54 *
	**********	20(22)			1617, 1587	1511	908	869 '

^a Calculated values in parentheses.

^h X = Mn.

" X = Phosphorus,

^J In EtOH.

* Recorded as Nujoi mulis.

' X = Ax,

 (30 cm^3) of the appropriate mononuclear complex (0.5 mmol). The solution was refluxed for 1 h and the resulting yellow-orange precipitate was filtered, washed with ethanol, and dried in vacuo. Yields: $\sim 70-90\%$.

2.4. Crystal structure of (ethanol-KO)bis/1-(2-hvdroxyphenyl)-1,3-butanedionato- $\kappa^2 O, O'$)dioxouranium(VI)] $([UO_2(HL^1)_2(EtOH)])$

Crystals were obtained by slow evaporation of an ethanol solution of $[UO_2(HL^1)_2(MeOH)]$.

2.4.1. Crystal data

 $C_{22}H_{24}O_9U$, M = 670.46, monoclinic, a = 8.076(1), b =8.131(1), c = 10.161(1) Å, $\alpha = 108.49(1)$, $\beta = 112.26(1)$, $\gamma = 89.89(1)^\circ$, $U = 580 \text{ Å}^3$ (by least squares refinement of the angular settings of 25 reflections), space group P1, Z=1, $D_{\rm c} = 1.92 \,{\rm g}\,{\rm cm}^{-3}, F(000) = 320, \,\mu({\rm Mo}\,{\rm K}\alpha) = 70.41 \,{\rm cm}^{-1}.$ Crystal size $0.28 \times 0.21 \times 0.17$ mm.

2.4.2. Data collection and processing

Enraf-Nonius CAD-4 diffractometer at 293 K, $\omega/2\theta$ scan mode with graphite monochromated Mo Ka radiation $(\lambda = 0.71069 \text{ Å})$, scan range $(0.8 + 0.34 \tan \theta)^{\circ}$, variable scan speed 0.9-8.2° min⁻¹ with a maximum scan time of 90 s, variable horizontal aperture width $(1.40 + 0.70 \tan \theta)$ mm,

Table 2 Atomic coordinates ($\times 10^4$) for (110, (HI^{+}) (E(OH))

vertical aperture width 4 mm, 7534 reflections measured $(0 \le 2\theta \le 35^\circ, +h, \pm k, \pm l)$. The intensities of three standard reflections were monitored at two hourly intervals and showed an average total loss in intensity of 2.3% during the data collection. This was compensated for by applying a linear decay correction. Empirical absorption corrections were applied, maximum and minimum transmission factors being 0.999 and 0.511, respectively. A total of 5179 unique reflections was measured (merging R = 0.014 based on intensities of observed reflections).

2.4.3. Structure analysis and refinement

The structure was solved by Fourier methods and refined by a full-matrix least-squares technique [9a]. The final refinement cycle converged to values of R1 and wR2 of 0.0297 and 0.0699, respectively, for the 298 variables and data for which $l > 2\sigma(l^2)$. R1 and wR2 were 0.0311 and 0.0728, respectively, for all data. In the refinement anisotropic thermal motion was assumed for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (C-H, 0.96 Å) with isotropic thermal parameters fixed at 0.08. Final atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3.

Table 3					
Selected bond	lengths	(Å) an	id bond	angles	(°)

Atomic coort	inates (× 10) for [0	$O_2(\mathbf{n}\mathbf{L})_2(\mathbf{E}(\mathbf{O}\mathbf{n}))$					
	X	y	.		UO ₂ (HL ¹) ₂ - (EtOH)		{UO₂(HL²)₂- (EtOH)} · EtOH
U	0	0	0		1.750(12)		1.752(7)
0(1)	- 1770(22)	- 1490(21)	- 1679(17)	U- O (2)	1.81(2)		1.759(8)
0(2)	1781(19)	1318(20)	1646(17)	U=Q(3)	2.457(5)		2.487(5)
O(3)	606(8)	- 2608(6)	744(6)	U-O(12)	2.352(5)		2.375(6)
0(11)	= 655(9)	4318(6)	- 1728(6)	U-O(13)	2.331(5)		2.298(6)
O(12)	562(9)	1541(7)	- 1427(7)	U=O(22)	2.378(5)		2.408(6)
O(13)	2138(8)	= 1235(7)	899(7)	U-O(23)	2.332(5)		2.309(5)
0(21)	- 1669(14)	2 005(10)	2998(10)	O(12) = C(11)	1.290(7)		1.269(10)
O(22)	- 1678(9)	- 22(7)	1479(6)	C(11)=C(12)	1.387(9)		1.408(12)
O(23)	- 1795(10)	2249(8)	- 37(8)	C(12) = C(13)	1.39(2)		1.385(12)
C(1)	2413(15)	2744(16)	1773(15)	C(13)=O(13)	1.28(2)		1.280(11)
C(2)	2355(28)	-4104(23)	2433(22)	O(22)-C(21)	1.298(14)		1.306(9)
C(11)	1210(8)	1288(7)	- 2446(7)	C(21) - C(22)	1.38(2)		1.392(11)
C(12)	2244(11)	-43(10)	-2712(9)	C(22) - C(23)	1.395(9)		1.397(12)
C(13)	2662(24)	- 1228(20)	- 1944(22)	C(23) = O(23)	1.262(8)		1.283(10)
C(14)	4012(12)	- 2469(12)	-2145(13)				
C(21)	-2857(18)	871(17)	1863(13)	O(1)-U-O(2)	176.1(11)		178.0(3)
C(22)	- 3644(10)	2108(11)	1250(8)	O(3)-U-O(13)	74.0(2)	O(3)-U-O(12)	73.3(2)
C(23)	- 3098(10)	2726(8)	324(7)	O(3)-U-O(22)	73.7(2)	O(3)-U-O(22)	70.8(2)
C(24)	- 4087(13)	4060(12)	- 292(11)	O(12)-U-O(13)	70.1(2)	O(12)-U-O(13)	70.0(2)
C(111)	804(9)	2518(8)	- 3279(6)	O(12)-U-O(23)	71.4(2)	O(13)-U-O(23)	76.6(2)
C(112)	- 104(9)	3966(7)	-2895(7)	O(22)-U-O(23)	71.0(2)	O(22)-U-O(23)	70.0(2)
C(113)	-517(12)	5109(8)	- 3718(8)	U-O(12)-C(11)	138.3(4)		137.2(5)
C(114)	- 50(57)	4909(48)	- 4923(41)	U-O(13)-C(13)	137.2(9)		139.9(6)
C(115)	911(12)	3468(10)	-5302(8)	O(12)-C(11)-C(12)	121.9(6)		122.4(8)
C(116)	1287(11)	2326(9)	-4518(8)	O(13)-C(13)-C(12)	124(2)		122.0(8)
C(211)	-3201(8)	562(9)	3117(7)	C(11)-C(12)-C(13)	124.2(10)		124.8(9)
C(212)	-2594(10)	851(11)	3599(8)	U-O(22)-C(21)	137.1(6)		137.1(5)
C(213)	-2912(13)	- 1073(15)	4802(11)	U-O(23)-C(23)	138.2(4)		140.6(5)
C(214)	- 3774(12)	111(17)	5531(10)	O(22)-C(21)-C(22)	123.2(10)		120.4(8)
C(215)	-4356(11)	1529(16)	5092(10)	O(23)-C(23)-C(22)	124.4(6)		122.6(7)
C(216)	- 4087(10)	1726(12)	3883(8)	C(21)-C(22)-C(23)	124.5(8)		126.4(8)

2.5. Crystal structure of (ethanol- κ O)bis[1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedionato- κ^2 O,O')dioxouranium(VI)]ethanol ($|UO_2(HL^2)_2(EtOH)] \cdot EtOH$)

Crystals were obtained by slow evaporation of an ethanol solution of the complex.

2.5.1. Crystal data

 $C_{34}H_{34}O_{10}U$, M=840.67, triclinic, a=12.184(3), b=15.578(5), c=9.035(2) Å, $\alpha=91.05(2)$, $\beta=103.20(2)$, $\gamma=73.21(2)^\circ$, U=1597 Å³ (by least squares refinement of angular settings of 25 reflections), space group $P\bar{1}$, Z=2, $D_c=1.75$ g cm⁻³, F(000) = 784, μ (Mo K α) = 48.7 cm⁻¹.

2.5.2. Data collection and processing

Enraf-Nonius CAD-4 diffractometer at 293 K, $\omega/2\theta$ scan mode with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å), scan range ($0.80 + 0.34 \tan \theta$)°, variable scan speed 0.9-8.2° min⁻¹ with the maximum scan time being 90 s, variable horizontal aperture width (2.50 + 0.80tan θ) mm, vertical aperture width 4 mm, 6625 reflections measured ($0 \le 2\theta \le 26^\circ$, $\pm h$, $\pm k$, l). The intensities of three standard reflections were monitored at two hourly intervals and showed an average total loss in intensity of 4.3% during the data collection. This loss was compensated for by applying a linear decay correction. Empirical absorption corrections were applied, maximum and minimum transmission factors being 0.999 and 0.828, respectively. A total of 5821 unique reflections was measured (merging R = 0.022 based on intensities of observed reflections).

2.5.3. Structure analysis and refinement

The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares technique [9b]. The final refinement cycle converged to values of R and R_w of 0.033 and 0.033, respectively, for the 368 variables and 3268 data for which $I > 3\sigma(I)$. The function minimized was $\Sigma w (|F_v| - |F_v|)^2$ with the weight, $w = 1.3440/[\sigma^2(F) +$ 0.000893 $(F)^2$]. In the refinement anisotropic thermal motion was assumed for all non-hydrogen atoms. The atoms of the four phenyl rings were treated as rigid groups. Hydrogen atoms were included in calculated positions (C-H, 0.96 Å) with fixed isotropic thermal parameters. Atomic scattering factors and anomalous dispersion coefficients were from Cromer and Mann [10] and Cromer and Liberman [11], respectively. Final atomic coordinates are given in Table 4 and selected bond distances and angles in Table 3.

3. Results and discussion

3.1. Mononuclear uranyl complexes

The reaction of the β -diketophenols, H_2L^1 and H_2L^2 , with uranyl(VI) acetate dihydrate in a 2:1 molar ratio affords complexes of the stoichiometry [UO₂(HL)₂(S)], where

able 4	
tom coordinates ($\times 10^4$) for [UO ₂ (HL ²) ₂ EtOH] · EtOH	

Atom	<u>x</u> /a	y/b	z/c
υ	3327.3(3)	2871.0(2)	1227.9(4)
O(1)	2335(6)	3037(5)	2411(7)
O(2)	4358(6)	2714(5)	91(7)
O(4)	5339(7)	5997(5)	4180(8)
O(3)	4681(5)	3552(4)	3012(6)
0(11)	6437(8)	1748(5)	5014(10)
O(12)	4689(5)	1686(4)	2906(7)
O(13)	2952(6)	1533(4)	580(8)
O(21)	3274(6)	5663(4)	2406(8)
O(22)	2661(5)	4476(4)	754(7)
O(23)	1874(5)	3249(4)	- 995(7)
C(3)	5653(15)	6479(11)	3115(16)
C(4)	6327(18)	7025(12)	3698(16)
C(1)	5830(8)	3580(8)	2913(12)
C(2)	5812(11)	4100(8)	1568(13)
C(11)	5055(8)	836(6)	2924(10)
C(12)	4501(8)	333(6)	1855(10)
C(13)	3468(7)	688(6)	761(10)
C(21)	1738(7)	5069(6)	- 59(9)
C(22)	1003(8)	4812(6)	-1290(9)
C(23)	1091(7)	3936(6)	- 1734(9)
C(11)	6110(4)	360(3)	4149(6)
C(112)	6736(4)	862(3)	5093(6)
C(113)	7716(4)	431(3)	6239(6)
C(114)	8070(4)	-503(3)	6441(6)
C(115)	7444(4)	-1005(3)	5497(6)
C(116)	6464(4)	- 573(3)	4351(6)
C(131)	2864(5)	120(4)	-236(6)
C(132)	3256(5)	-814(4)	-53(6)
C(133)	2659(5)	-1328(4)	-1013(6)
C(134)	1671(5)	- 908(4)	=2156(6)
C(135)	1279(5)	27(4)	- 2339(6)
C(136)	1876(5)	541(4)	= 1379(6)
C(211)	1537(5)	6013(3)	346(6)
C(212)	2313(5)	6246(3)	1564(6)
C(213)	2099(5)	7136(3)	1974(6)
C(214)	1110(5)	7793(3)	1166(6)
C(215)	334(5)	7560(3)	= 52(6)
C(216)	547(5)	6670(3)	- 462(6)
C(231)	308(5)	3740(4)	- 3174(5)
C(232)	- 706(5)	4403(4)	- 3885(5)
C(233)	- 1416(5)	1202(1)	- 5208(5)
C(234)	- 1112(5)	3347(4)	- \$760(\$)
C(235)	-98(5)	2693(1)	- \$(108(5)
C(236)	617(5)	7801(1)	- 3686(2)
	17161177	2024(4)	- 2002(2)

 $L = L^{1}$ or L^{2} and S = MeOH or EtOH. The oxo-ligand adducts $[UO_{2}(HL^{1})_{2}(Ph_{3}AsO)] \cdot 2H_{2}O, [UO_{2}(HL^{2})_{2}(Ph_{3}PO)]$ and $[UO_{2}(HL^{2})_{2}(Ph_{3}AsO)]$ are prepared by refluxing the appropriate ligand with the parent uranyl complex.

3.1.1. Physicochemical studies

The IR spectra of the complexes. $[UO_2(HL^1)_2(MeOH)]$, $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$, $[UO_2(HL^1)_2(Ph_3AsO)] \cdot$ $2H_2O$, $[UO_2(HL^2)_2(Ph_3PO)]$ and $[UO_2(HL^2)_2(Ph_3AsO)]$, show three bands in the region 1620–1510 cm⁻¹, the two highest bands being assigned as $\nu(C=O)$ stretches of the coordinated carbonyls, of which one is hydrogen bonded, and the other band as a $\nu(C=C)$ stretch [7]. The uranyl asym-



Fig. 1. Thermal ellipsoid diagram for [UO₂(HL¹)₂(EtOH)] drawn at the 50% probability level. Hydrogen atoms at an arbitrary level.

metric stretch, ν_{as} (O=U=O), appears in the region 914–908 cm⁻¹ for these complexes. For the oxo-ligand adducts, a band at 1134 cm⁻¹ is assigned [12] to a ν (P=O) stretching vibration for [UO₂(HL²)₂(Ph₃PO)], whereas [UO₂-(HL¹)₂(Ph₃AsO)] · 2H₂O and [UO₂(HL²)₂(Ph₃AsO)] have ν (As=O) stretches appearing at 884 and 869 cm⁻¹, respectively.

There are few reports on the mass spectra of uranyl(VI) B-diketonates in the literature [13–15]. The five uranyl(VI) complexes in this study all give mononuclear species in the positive ion spectra under the LSI-MS conditions employed. The parent ion is not observed in the mass spectra of the two mononuclear complexes, $[UO_2(HL^1)_2(MeOH)]$ and $[UO_2(HL^2)_2(EtOH)]$, as the coordinated alcohol ligand (ROH) is readily lost. The most intense peak is formulated as $[MH^+ - ROH]$, $(m/z = 625 (100)^+ [UO_2(HL^+)_2H]^+$ and m/z = 749 (100) [UO₂(HL²)₂H]⁺, respectively). Other significant peaks correspond to the subsequent loss of the β -diketophenol ligands (m/z = 447 (90) [UO₂- $(HL^{1})H|^{+}$, 270 (75) $[UO_{2}]^{+}$ and m/z = 509 (65) $[UO_2(HL^2)H]^+$, 270 (60) $[UO_2]^+$, respectively). Also, as observed in the electron impact mass spectra of the free ligands, a rearrangement of HL occurs as evidenced by the occurrence of the peaks m/z = 606 (75) $[UO_2(HL^1)]$ - $(L^{3})H^{+}$, 430 (70) $[UO_{2}(L^{3})]^{+}$ and m/z=714 (20) $[UO_2(L^4)_2]^+$, 492 (58) $[UO_2(L^4)]^+$, respectively.



In contrast, for the oxo-ligand adducts the parent ion is observed, owing to the stronger coordinating properties of the phosphine and arsine oxides relative to the alcohol ligands, but the peak is not the most intense peak observed. Significant peaks in the mass spectrum of the individual mononuclear oxo-ligand adducts are listed below. The most intense peak corresponds to HL loss (i.e. $[UO_2$ - $(HL^{1})(Ph_{3}AsO)]^{+}$, $[UO_{2}(HL^{2})(Ph_{3}PO)]^{+}$ and $[UO_{2}-(HL^{2})(Ph_{3}AsO)]^{+})^{2}$. Oxo-ligand migration is also observed. Under the conditions used no higher clusters were observed in any of the mass spectra as has been reported for other dioxouranium complexes [16,17].

3.1.2. Crystal structures of $|UO_2(HL^1)_2(EtOH)|$ and $|UO_2(HL^2)_2(EtOH)| \cdot EtOH$

Thermal ellipsoid drawings of the two structures, indicating the atomic numbering schemes are depicted in Figs. 1 and 2. Both complexes crystallize as seven-coordinate monomeric species with a pentagonal bipyramidal geometry about the uranium atom. The uranyl oxygens occupy the axial positions with the mean U-O(uranyl) bond distance being 1.78 Å for $|UO_2(HL^1)_2(EtOH)|$ and 1.756 Å for $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$. The angles O(uranyl)-U-O(uranyl) are 176.1(11) and 178.0(3)°, respectively. Five oxygens make up the equatorial donors (four from two bidentate B-diketophenolate ligands and the fifth from solvent ethanol acting as a ligand) to form a puckered pentagon. The mean U-O(ligand) distances are 2.370 and 2.375 Å for $[UO_2(HL^1)_2(EtOH)]$ and $[UO_2(HL^2)_2(EtOH)] \cdot EtOH$, respectively, with the U-O(3) distance being the largest of these in both complexes. The average O(ligand)-U-O(ligand) angle observed is 72.0° for the former complex and 72.1° for the latter. All these values are in accord with those observed in other similar complexes (e.g. $[UO_2(pd)_2(Ph_3PO)] \cdot C_6H_6$ and $[UO_2(3Clpd)_2(Ph_3PO)]$ where pd = 2,4-pentanedione and 3Clpd = 3-chloro-2,4-pentanedione) [18-21]. Bond distance and angle dimensions of

¹ Relative intensities are given in parentheses.

² $[UO_{2}(HL^{1})_{2}(Ph_{1}AsO)] \cdot 2H_{2}O: m/z = 1092 (13) [UO_{2}(HL^{1})(Ph_{1}AsO)_{2}]^{+}, 947 (7) [UO_{2}(HL^{1})_{2}(Ph_{1}AsO)H]^{+}, 769 (100) [UO_{2}(HL^{1})(Ph_{1}AsO)]^{+}, 592 (60) [UO_{2}(Ph_{1}AsO)H]^{-} and 270 (20) [UO_{2}]^{+}, [UO_{2}(HL^{2})_{2}(Ph_{1}PO)]; m/z = 1066 (15) [UO_{2}(HL^{2})(Ph_{1}PO)]; H]^{+}, 1028 (13) [UO_{2}(HL^{2})_{2}(Ph_{1}PO)H]^{+}, 787 (100) [UO_{2}(HL^{2})(Ph_{1}PO)]^{+}, 548 (65) ([UO_{2}(Ph_{1}PO)H]^{+}, 787 (100) [UO_{2}(HL^{2})(Ph_{1}PO)]^{+}, 548 (65) ([UO_{2}(Ph_{1}PO)H]^{+}, 787 (100) [UO_{2}(HL^{2})(Ph_{1}AsO)]^{+}, 1072 (11) [UO_{2}(HL^{2})_{2}(Ph_{1}AsO)H]^{+}, 831 (100) [UO_{2}(HL^{2})(Ph_{1}AsO)]^{+}, 592 (45) [UO_{2}(Ph_{1}AsO)H]^{+} and 270 (15) [UO_{2}]^{+}.$



Fig. 2. Thermal ellipsoid diagram for [UO₂(HL²)₂(EtOH)] · EtOH drawn at the 50% probability level. Hydrogen atoms at an arbitrary level.

the propanedione moieties of the complexes are as expected and similar to those of transition metal and uranyl B-diketonates [18-23]. The most striking feature of these two structures is that although the ligands are in a trans arrangement in $[UO_2(HL')_2(EtOH)]$ they have adopted the cis form in $|UO_2(HL^2)_2(EtOH)| \cdot EtOH$. These structures illustrate two of the three isomers that are expected to exist for uranyl(VI) complexes of unsymmetrically substituted B-diketone ligands. There are two possible cis isomers corresponding to the ethanol ligand being either near the phenolic groups (as in the crystal structure of [UO2-(HL²)₂(EtOH)] · EtOH presented here) or alternatively far from the phenolic groups. The trans isomer has the ethanol ligand near the phenolic group of one ligand and far from the phenolic group of the opposing ligand. In (UO₂(HL')₂, (EtOH)] the two propanedione fragments (O(12), O(13), C(11), C(12), C(13) and O(22), O(23), C(21), C(22), C(23)) are inclined with respect to the plane O(12), O(13), O(22) and O(23) (by 12.3 and 5.1°, respectively) to give an umbrella-like conformation to this complex. However, the phenolic ring of each ligand (atoms O(11), C(111), C(112), C(113), C(114), C(115), C(116) or O(21), C(211), C(212), C(213), C(214), C(215), C(216)) is twisted with respect to the approximate plane defined by the propanedione moiety of that ligand (O(12), O(13), C(11). C(12), C(13) (5.7°) or O(22), O(23), C(21), C(22), C(23) (19.8°), respectively) but at the same time the two phenolic rings lie approximately parallel to one another (twist angle = 1.6°). In contrast, the complex $[UO_2(HL^2)_2]$ (EtOH) · EtOH has a stepped geometry, with the propanedione moieties (numbered as above) inclined to the pentagonal coordination plane so that they are approximately parallel to one another (the angle between them being 2.0°). As above the ligand moieties in this second complex are not planar overall and within each ligand the phenol and phenyl rings are twisted in the same direction.

3.1.3. NMR spectroscopy

'H NMR spectra are difficult to interpret in detail but it is clear that in solution the molecules are fluxional and, as well, ligand dissociation occurs (as confirmed by TLC). If the three possible geometrical isomers could be observed on the NMR time scale four sets of ligand resonances could be expected, one for each of the *cis* structures and two for the trans isomer due to one phenol group being near to the ethanol ligand and the other distant from i' However it has been noted previously for others dioxouranium (VI) B-diketonate ligand complexes, e.g. [UO₂(CF₁COCHCOCH₁)₂(Me₁-SO)], that only one cis component is often observed [24,25] although recently Kannan et al. [21] were able to observe all three isomers for $|UO_2(TTA)_2(DBA)|$ (TTA = thenoyltrifluoroacetonate, DBA = dibenzylideneacetone) at -40° C. The 'H NMR spectrum of [UO₂(HL¹)₂(MeOH)] showed peaks corresponding to both coordinated and free ligands indicating the presence of ligand dissociation (Fig. 3). The methyl proton signals of the keto and enol forms of the free H_2L^1 appear at lower frequencies (2.15 and 2.30 ppm) than the singlet at 2.51 ppm observed for coordinated HL¹. Upon cooling to -30° C another singlet appears at 2.75 ppm and at -60° C there are three peaks, at 2.44, 2.68 and 2.83 ppm, associated with coordinated HL¹ and due to the existence or both cis and trans isomers. Likewise, the phenol proton signals, which at room temperature appear as one resonance at higher frequency (12.33 ppm) from the two resonances associated with the keto-enol tautomerism for free H₃L¹ (11.89 and 11.98 ppm) yield, at -60° C, three signals (12.45, 12.65 and 12.68 ppm). The 'H NMR spectrum of $[UO_2(HL^2)_2(EtOH)]$ (Fig. 4) also displays phenolic OH proton signals due to coordinated and free ligand at room temperature with two signals arising from the keto and enol tautomers of free H_2L^2 (11.94 and 12.13 ppm) and two broad signals at higher frequencies (12.47 and 12.81 ppm) from them. At a higher temperature (50°C) the signals associated



Fig. 3. Variable temperature ¹H NMR spectra for $|UO_2(HL^1)_2(MeOH)|$. (a) CH₃ resonances; (b) Ph-OH resonances; (*) peaks assigned to non-coordinated H₂L¹.



Fig. 4. Variable temperature ¹H NMR spectra for $|UO_2(HL^2)_2(EtOH)|$ showing the Ph–OH resonances; (*) peaks assigned to non-coordinated H_2L^2 .

with the coordinated HL^2 ligand coalesce into a broad peak at 12.26 ppm with a shoulder at about 12.40 ppm. At -10° C the three band pattern is again observed for the phenol OH resonances corresponding to the room temperature spectrum of the HL^1 ligand complex. Further changes occur at lower temperatures. Several intramolecular mechanisms have been proposed to describe the fluxional processes that have been observed previously for dioxouranium(VI) complexes of unsymmetrical β -diketonates of type [UO₂L₂(solvent)], where L is acetylacetonate or related ligand [24,26–29]. However, in the present study the complexes are less stable in solution with respect to ligand dissociation, indicating both inter- and as well as intramolecular exchange mechanisms need to be considered.

3.2. Heterobinuclear complexes

Previous attempts at preparing heterobinuclear complexes containing uranyl(VI) and β -diketonate ligands such as 1,5diphenyl-1,3,5-pentanetrione, 2,4,6-heptanetrione, H₂L¹ and H₂L² have been unsuccessful. As also observed by Vigato et al. [7] metal exchange is the predominant reaction. For example the addition of copper(II) acetate to [UO₂-(HL²)₂(EtOH)] in ethanol produces the copper(II) mononuclear complex [Cu(HL²)₂(H₂O)], whereas the use of nickel(II) acetate produces a mixture of the mononuclear uranyl(VI) and nickel(II) complexes.

In contrast, when manganese(II) acetate was added to an ethanolic solution of the appropriate uranyl mononuclear complex, red microcrystals were isolated that could be formulated by elemental analysis (Table 1) as $[UO_2Mn(L^1)_2]$ -(EtOH)] · 1.5H₂O and $[UO_2Mn(L^2)_2(EtOH)]$ · 2H₂O, respectively. The molar conductivity of ethanolic solutions of these two complexes give values very close to that of their parent mononuclear compounds, which are much less than values expected for 1:1 electrolytes, indicating that the manganese is coordinated. This conclusion is supported by the mass spectra of the complexes which show peaks containing both uranium and manganese. For instance, the LSI-MS spectrum of $|UO_{3}Mn(L^{1})_{2}(EtOH)| + 1.5H_{2}O$ (*m*-nitrobenzyl alcohol matrix) yielded the highest mass peak at an m/z value of 1357 (25) which is assigned to the ion $[(UO_2)_2]$ $Mn_2(L^1)_4H_3$ in line with a dimeric formulation. An intense peak corresponding to the heterodinuclear monomeric ion $[UO_2Mn(L^1)_2H]^+$ is also observed (m/z = 678)(100)). Other peaks have been assigned as follows: $[(UO_{2})_{2}Mn(L^{1})_{4}H_{4}]^{+}$ 1303 (35), $[(UO_{2})_{2}Mn(L^{1})_{3}H]^{+}$ $1124(46), [UO_2(L^1)_2H_3] + 625(90), [UO_2Mn(L^1)] + 501$ (48), $[UO_2(L^1)H]^+$ 447 (64) and $[UO_2]^+$ 270 (57). The LSI-MS spectrum of $[UO_2Mn(L^2)_2(EtOH)] \cdot 2H_2O$ also confirmed the formation of a heterodinuclear complex with the observation of the ion $[UO_2Mn(L^2)_2H_2]^+$ at m/z 803(51) (magic bullet matrix). Although higher mass peaks were observed these corresponded to flavone (L4) formation as seen in the spectrum of the mononuclear complex $[UO_2(HL^2)_2(EtOH)]$. For example $[UO_2Mn(L^2) (L^4)_2H_1^+$, 1008 (27) and $[UO_2(L^2)(L^4)_2H_2]^+$ 954 (100). Other ions observed at lower m/z values were $[UO_2(L^4)_2H_2]^+$ 716 (90), $[UO_2Mn(L^2)]^+$ 563 (30) and [UO₂] + 270 (100).

IR spectra of the complexes are very similar to those of the mononuclear chelates with the bands in the region 1620–1579 cm⁻¹ being assigned to ν (C=O) of coordinated car-

bonyls [6]. The $v_{ax}(O=U=O)$ stretching frequency is shifted down relative to the value of the corresponding mononuclear complex.

Evidence that the manganese is interacting with the Bdiketophenolate ligands also comes from electronic spectral results. The spectra of the dioxouranium(VI) mononuclear complexes in acetone exhibit two bands at 340 ($\epsilon \approx 20000$) and 388 nm ($\epsilon \approx 16\,000\,1\,\text{mol}^{-1}\,\text{cm}^{-1}$) fr [UO₂- $(HL^1)_2(MeOH)$ and at 352 ($\epsilon \approx 23\,000$) and 402 nm $(\epsilon \approx 24500 \ 1 \ \text{mol}^{-1} \ \text{cm}^{-1})$ for $[UO_2(HL^2)_2(EtOH)]$, which are assigned to ligand to metal charge transfer transitions involving π type ligand and uranium orbitals [30-33]. In both cases the lowest energy band is perturbed on complexation of the manganese with one broad band being observed at 340 ($\epsilon \approx 13\,000\,1\,\text{mol}^{-1}\,\text{cm}^{-1}$) for [UO₂- $Mn(L^{i})_{2}(EtOH)$] · 1.5H₂O and at 372 nm ($\epsilon \approx 15000$] $mol^{-1} cm^{-1}$) for $[UO_2Mn(L^2)_2(EtOH)] \cdot 2H_2O$. Similar observations have been recorded for heterobinuclear dioxouranium(VI) complexes with Schiff base ligands derived from 1,3,5-triketones [34].

Finally magnetic susceptibility and ESR data confirm the presence of manganese in the +2 oxidation state. For $[UO_2Mn(L^1)_2(EtOH)] \cdot 1.5H_2O \mu_{eff}$ has a value of 5.41 B.M. and for the L² complex the value is 5.92 B.M. consistent with a high spin 3d⁵ state [35]. In agreement with this the ESR spectra show typical six-line splitting with A values of approximately 90 G and g values close to 2.00 (for the L¹ complex g is 2.054 and for the L² complex it is 2.048) indicative of an octahedral 'MnO₆' coordination [36,37].

To date crystals of these heterodinuclear complexes suitable for X-ray analysis have not been obtained and hence the question of where the manganese(11) is coordinated cannot be categorically answered. However possible structures are given below with the dimeric formulation being favoured for the L^1 complex and the monomeric one for the L^2 complex.



Possible structures for the incorrobinuclear complexes.

4. Supplementary material

Additional information available from the Cambridge Crystallographic Data Centre comprises hydrogen atom coordinates, thermal parameters and a full listing of bond lengths and angles.

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