Inorganica Chimica Acta, 121 (1986) 103–111

Synthesis, Characterization and Crystal Structure of 2-Dimethylacetal-4-chloro-6-formylphenol and Aquabis(2-dimethylacetal-4-chloro-6-formylphenolato)-dioxouranium(VI)

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(Received May 14, 1986)

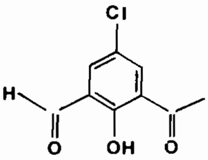
Abstract

The ligand 2-dimethylacetal-4-chloro-6-formylphenol, H(ALAC), prepared by boiling 2,6-diformyl-4-chlorophenol, H(DIAL), in methanol, was reacted with uranyl acetate to obtain the complex $[UO_2(ALAC)_2(H_2O)]$. The ligand and the uranyl complex were characterized by X-ray crystallography, infrared, ^{1}H NMR and electronic spectroscopy. Thermogravimetric and mass spectrometry data are also reported. In acid media H(ALAC) transforms easily into H(DIAL). H(ALAC) is monoclinic, $P2_1/n$, with $a = 13.951(5)$, $b = 7.902(5)$, $c = 9.465(5)$ Å, $\beta = 91.33(3)°$. The structure was refined to $R = 3.9\%$, based on 1657 observed reflexions. $[UO_2(ALAC)_2(H_2O)]$ is tetragonal, $P4_32_12$, with $a = 11.147(5)$ and $c = 19.150(4)$ Å. The structure was refined to $R = 4.0\%$, based on 2938 observed reflexions. Four ligand oxygens and one water molecule are equatorially bonded to the uranyl group in this compound. Uranium and water oxygen lie in special positions on a crystallographic twofold axis so that the two halves of this molecule are symmetrically related. Selected bond distances for $[UO_2(ALAC)_2(H_2O)]$ are: U–O (charged) 2.28(2) Å, U–O (neutral) 2.45(2) Å, U–O (uranyl) 1.77(2) Å, U–O (water) 2.44(4) Å.

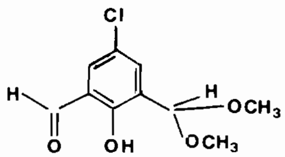
Introduction

Recently we reported various mononuclear and dinuclear complexes of copper(II), nickel(II) and dioxouranium(VI) with potentially heptadentate Schiff bases [1–4]. The complexes were generally prepared by condensation of α,ω-diamines with keto-acids, keto-phenols and formyl-phenols in the presence of the appropriate metal ion. In order to perform selective syntheses of dinuclear complexes, we thought it would be of interest to isolate the metal complexes of keto- and formyl-phenols. As a first study, we prepared and characterized the dioxouranium(VI) derivatives of 2,6-diformyl-4-chlorophenol, H(DIAL), of general formulae $[UO_2(DIAL)_2(L)]$ ($L = H_2O$ and MeOH) and $[UO_2(DIAL)_2]$ [5]. Moreover, we observed that methanolic solutions containing uranyl acetate and H(DIAL) separated in a few days into small fractions of a solid which seemed to contain acetal groups. Since the Schiff base complexes are generally prepared in methanol, the reaction of H(DIAL) with the solvent could affect the condensation intermediates.

The present paper reports synthesis, characterization and X-ray structure of the ligand 2-dimethylacetal-4-chloro-6-formylphenol, H(ALAC), and of the complex $[UO_2(ALAC)_2(H_2O)]$.



H(DIAL)



H(ALAC)

Experimental

Reagents were uranyl acetate tetrahydrate (Fluka) and 2,6-diformyl-4-chlorophenol, H(DIAL), prepared as in ref. 6. Methanol and dichloromethane (C. Erba) were purified by the usual methods [7]. Deuterated solvents were kept over molecular sieves.

Preparation of the Compounds

H(ALAC)

Crude H(DIAL) was treated with refluxing anhydrous methanol in a Soxhelet apparatus (*ca.* 2 h). Methanol was then removed under reduced pressure

0020-1693/86/$3.50

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and the oily solid was recrystallized from the minimum amount of hot benzene. The white crystals were washed with small fractions of cold diethylether. Yield, *ca.* 60%; melting point (m.p.), 87–8 °C. *Anal.* Found: C, 52.3; H, 5.0; Cl, 15.2. Calc. for $C_{10}H_{11}ClO_4$: C, 52.1; H, 4.8; Cl, 15.4%. The compound is soluble in alcohols, chlorinated hydrocarbons, benzene and diethylether and insoluble in water and n-hexane.

H(DIAL)

Good purity samples have been obtained by boiling (*ca.* 15 min) a solution of H(ALAC) (0.5 g) in methanol (30 ml) containing 5 ml of 1 M aqueous HCl. Methanol was removed in a rotavapor to obtain the pale yellow compound insoluble in water, which was filtered, washed with water and dried *in vacuo*. Yield, *ca.* 80%; m.p., 123 °C. *Anal.* Found: C, 52.3; H, 2.6; Cl, 19.4. Calc. for $C_8H_5ClO_3$: C, 52.1; H, 2.7; Cl, 19.2%.

[UO$_2$(ALAC)$_2$(H$_2$O)]

A solution of uranyl acetate (1.0 mmol) in anhydrous methanol was added to a solution of H(ALAC) (2.0 mmol) in the same solvent (total volume 25 ml). The deep red solution separated slowly into red crystals of the complex, which were washed with anhydrous methanol and dried *in vacuo. Anal.* Found: C, 32.4; H, 3.0; Cl, 9.2. Calc. for $C_{20}H_{22}Cl_2O_{11}U$: C, 32.1; H, 3.0; Cl, 9.5%. The compound is insoluble in most common solvents but easily soluble in dimethylsulfoxide (DMSO) and dimethylformamide. The compound was also obtained as side product in the reaction of uranyl acetate with H(DIAL) in methanol (molar ratio 1:2). The first reaction product was $[UO_2(DIAL)_2(MeOH)]$ [5], whereas nice crystals of $[UO_2(ALAC)_2(H_2O)]$ separated slowly when the residual methanolic solution was left standing for some days.

Measurements

Infrared spectra were recorded using a Perkin-Elmer 580B spectrophotometer (4000–400 cm^{-1}, KBr pellets). Electronic spectra were measured by a Cary 17D spectrophotometer, ^1H NMR spectra by a Varian FT 80A spectrometer. Mass spectra measurements were performed on a VG ZAB-2F instrument operating under electron impact (EI) conditions (70 eV, 200 μA; source temperature, 200 °C). Operational conditions were as reported in ref. 8. Thermogravimetric data (TG and DTA) in air were obtained using a Netzsch STA-429 thermoanalytical instrument (air flux rate, 250 ml min^{-1}; heating rate, 5 °C min^{-1}; reference material, Al_2O_3).

X-ray Data

Well-formed crystals of both compounds, $C_{10}H_{11}ClO_4$ and $C_{20}H_{22}Cl_2O_{11}U$, suitable for the X-ray work, were mounted on a glass fibre and covered with epoxy adhesive to prevent crystal air decomposition. Cell constants were determined from a least-squares refinement of the setting angles of 25 reflections, which had been carefully centered on a Philips PW 1100 diffractometer. The observed intensities were corrected for Lorentz and polarization effects, and for the uranium complex an absorption correction was applied. Scattering factors for neutral atoms were taken from ref. 9; those for H were taken from refs. 10 and 11. A correction for the anomalous dispersion effects for the uranium atom was applied. Crystal and intensity data are reported in Table I.

The structure of $C_{10}H_{11}ClO_4$ was solved by direct methods using the program included in the SHELX program package. The trial structure was refined by full-matrix least-squares to the final conventional R factor of 0.039. At convergence the maximum shift on the refined parameters was 0.2σ. The maximum electronic density on the final Fourier difference map was 0.2 e/Å^3. Positional and thermal parameters are reported in Table II, distances and angles in Table III.

The structure of $C_{20}H_{22}Cl_2O_{11}U$ was solved by the standard heavy atom techniques. The trial structure was refined by full-matrix least-squares to the final conventional R factor of 0.040. At convergence the maximum shift on the refined parameters was 0.1σ. The maximum residual electronic density on the final Fourier difference map was 3.2 e/Å^3. Positional and thermal parameters are reported in Table V, distances and angles in Table VI. The equations of selected mean planes are reported in Table VII.

Results and Discussion

The species H(ALAC) is easily obtained by refluxing a methanol solution of H(DIAL). The reaction does not require strictly anhydrous conditions and the transformation is quantitative. In the same conditions ethanol does not react to form the analogous diethylacetal, H(DIAL) being unchanged after prolonged boiling. Only one of the formyl groups is involved in the reaction, probably because the second carbonyl group is involved in hydrogen bond with the phenolic OH group.

The crystal structure of H(ALAC) is shown in Fig. 1. The molecule, apart from the H atom and the MeO groups bonded to C(8), is planar, with a maximum deviation of 0.06 Å for O(2) from the mean plane of equation $-0.188x + 0.829y - 0.527z = -5.988$ Å (where x, y, z are orthogonalized coordinates). It is noticeable that H(1) is also nearly coplanar being displaced by only 0.02 Å from the mean plane. Bond distances and angles are normal

TABLE I. Crystal and Intensity Data

Formula	$C_{10}H_{11}ClO_4$	$C_{20}H_{22}Cl_2O_{11}U$
Formula weight	230.5	747
a (Å)	13.951(5)	11.147(5)
b (Å)	7.902(5)	11.147(5)
c (Å)	9.465(5)	19.150(4)
β (deg)	91.33(3)	
V (Å^3)	1043	2379
D_c (g cm^{-3})	1.47	2.08
Z	4	4
Space group	$P2_1/n$	$P4_32_12$
System	monoclinic	tetragonal
Equivalent positions	$\pm(x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$	$x, y, z; \bar{x}, \bar{y}, \frac{1}{2}+z; \frac{1}{2}-y, \frac{1}{2}+x, \frac{3}{4}+z; \frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{4}+z; y, x, \bar{z};$ $\bar{x}, \bar{y}, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{4}-z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}-z$
Absorption coefficient		
(Mo Kα) (cm^{-1})	4.5	140.7
λ (Mo Kα) (Å)	0.7093	0.7093
Method	$\vartheta-2\vartheta$	$\vartheta-2\vartheta$
Scan speed (° min^{-1})	2	2
Standards	2 every 100 readings	2 every 100 readings
2ϑ limit	$2° < 2\vartheta < 50°$	$2° < 2\vartheta < 50°$
Number of data	3433	3924
Number of data with $I > 3\sigma(I)$	1657	2938

TABLE II. Atomic Coordinates for $C_{10}H_{11}ClO_4$

Atom	x/a	y/b	z/c
O(1)	0.89244(12)	0.20697(25)	1.01076(20)
O(2)	0.98416(13)	0.08983(25)	0.79282(19)
O(3)	0.90364(10)	0.54169(22)	1.34165(18)
O(4)	0.86288(11)	0.25439(22)	1.33733(18)
Cl(1)	1.25810(4)	0.50322(11)	1.20420(8)
C(1)	0.97807(15)	0.27128(29)	1.05402(24)
C(2)	1.06192(16)	0.24344(29)	0.97764(23)
C(3)	1.14888(16)	0.31322(32)	1.02554(25)
C(4)	1.15107(14)	0.41009(31)	1.14595(24)
C(5)	1.06817(15)	0.43789(31)	1.22097(26)
C(6)	0.98159(14)	0.36839(29)	1.17698(23)
C(7)	1.05778(19)	0.14641(34)	0.84647(26)
C(8)	0.89017(16)	0.39752(32)	1.25782(25)
C(9)	0.81711(20)	0.59781(47)	1.40629(36)
C(10)	0.93300(23)	0.20072(49)	1.44192(35)
H(1)	0.90207(205)	0.15876(406)	0.93652(312)
H(3)	1.20434(158)	0.29251(307)	0.97045(233)
H(5)	1.07093(137)	0.51098(284)	1.30098(222)
H(7)	1.11932(204)	0.13000(346)	0.80621(294)
H(8)	0.83505(139)	0.41490(260)	1.19201(215)
H(91)	0.83249(244)	0.70305(486)	1.45927(360)
H(92)	0.79698(200)	0.50930(398)	1.47716(321)
H(93)	0.77014(221)	0.61863(402)	1.33656(345)
H(101)	0.95186(235)	0.29652(435)	1.50148(349)
H(102)	0.90590(230)	0.11462(500)	1.49496(394)
H(103)	0.98841(256)	0.14897(463)	1.39847(367)

(continued)

TABLE II *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Anisotropic thermal parameters ($\times 10^4$) for $C_{10}H_{11}ClO_4$ in the form: $T = \exp[-2\pi^2 \Sigma_{ij} U_{ij} h_i h_j a_i^* a_j^*]$						
O(1)	335(9)	522(12)	436(11)	−57(10)	15(8)	−80(8)
O(2)	560(12)	581(13)	487(11)	−129(10)	−25(9)	−45(10)
O(3)	328(8)	458(11)	501(10)	−86(9)	96(7)	41(7)
O(4)	357(8)	515(12)	417(9)	71(9)	70(7)	−59(8)
Cl(1)	294(3)	796(5)	596(4)	−83(4)	0(3)	−115(3)
C(1)	300(11)	332(14)	356(12)	55(11)	8(9)	−9(10)
C(2)	348(11)	328(13)	312(12)	46(10)	29(9)	25(10)
C(3)	304(11)	413(14)	377(13)	70(12)	61(10)	48(10)
C(4)	249(10)	417(15)	422(14)	27(12)	−12(10)	−18(10)
C(5)	325(11)	375(15)	359(13)	−30(11)	9(10)	14(10)
C(6)	260(10)	344(13)	346(12)	45(11)	32(9)	8(9)
C(7)	464(14)	428(16)	403(14)	24(12)	80(12)	61(12)
C(8)	262(10)	453(15)	348(12)	19(12)	30(9)	7(10)
C(9)	416(15)	635(21)	530(18)	−53(18)	130(14)	115(15)
C(10)	566(18)	582(21)	439(16)	134(17)	64(14)	84(16)
H(1)	572(107)					
H(3)	353(63)					
H(5)	370(56)					
H(7)	449(83)					
H(8)	191(55)					
H(91)	721(120)					
H(92)	728(96)					
H(93)	748(101)					
H(101)	1158(130)					
H(102)	1131(117)					
H(103)	950(120)					

TABLE III. Distances and Angles for $C_{10}H_{11}ClO_4$

Bond distances (Å)			
C(1)–C(2)	1.406(3)	C(1)–O(1)	1.354(3)
C(2)–C(3)	1.402(3)	C(2)–C(7)	1.464(4)
C(3)–C(4)	1.370(4)	C(7)–O(2)	1.215(3)
C(4)–C(5)	1.388(3)	C(6)–C(8)	1.521(3)
C(5)–C(6)	1.384(3)	C(8)–O(3)	1.401(3)
C(6)–C(1)	1.393(3)	C(8)–O(4)	1.416(3)
C(4)–Cl	1.743(3)	O(3)–C(9)	1.434(3)
C(8)–H(8)	1.00(2)	O(4)–C(10)	1.436(4)
C(7)–H(7)	0.97(2)	O(1)–H(1)	0.81(2)
Contact distances (Å)[a]			
O(1)...O(2)	2.62		
O(1)...O(4)	3.15		
O(3)...O(4)	2.34		
O(1)...O(2^{i})	3.43		
O(2)...O(3^{i})	3.55		
O(2)...O(4^{ii})	3.69		
O(2)...H(1)	1.88		
Selected bond angles (°)			
O(1)–C(1)–C(2)	121.7(2)	C(6)–C(8)–O(3)	107.7(2)
O(1)–C(1)–C(6)	118.3(2)	C(6)–C(8)–O(4)	112.7(2)
C(2)–C(7)–O(2)	124.2(2)	C(8)–O(3)–C(9)	112.9(2)
Cl–C(4)–C(3)	120.0(2)	C(8)–O(4)–C(10)	114.7(2)
Cl–C(4)–C(5)	119.2(2)	O(3)–C(8)–O(4)	112.4(2)

[a] Symmetry code: none, x, y, z; i, $2 - x, 1 - y, 2 - z$; ii, $2 - x, \bar{y}, 2 - z$.

TABLE IV. Infrared (cm^{-1}) and ^1H NMR (ppm; $T = 27$ °C) Data

Compound	Infrared			^1H NMR					
	ν(C–O)	ν(C=C)	ν(O–CH$_3$)	Solvent	CH(ring)	CH(form)	CH(acet)	OCH$_3$	OH
H(ALAC)	1670s	1617m	1110s	$CDCl_3$	7.73, 7.51[a]	9.84	5.66	3.41	11.08
			1047s	d_6-DMSO	7.81, 7.57[a]	10.03	5.65	3.28	10.85
H(DIAL)[b]	1688vs	1584m		$CDCl_3$	7.93	10.14			11.42
	1669s								
[UO_2(ALAC)$_2$(H_2O)]	1645s[c]	1547	1110s	d_6-DMSO	7.64, 7.57[d]	10.44	6.03	3.16	3.3[e]
	1030s		1040s						

[a] Coupling constant, 2.56 Hz. [b] Ref. 5. [c] Bending mode of H_2O contributes to this absorption. [d] Unresolved signals. [e] H_2O.

TABLE V. Atomic Coordinates for $C_{20}H_{22}Cl_2O_{11}U$

Atom	*x/a*	*y/b*	*z/c*
H(1)	0.27280(200)	0.05610(200)	0.41500(200)
H(2)	−0.02070(200)	0.01850(200)	0.30510(200)
U(1)	0.16260(176)	−0.16260(177)	0.25000(0)
O(1)	0.07683(108)	−0.24135(111)	0.31275(63)
O(2)	0.00810(383)	−0.00810(382)	0.25000(0)
O(3)	0.20447(105)	−0.01119(115)	0.33945(67)
O(4)	0.33905(114)	−0.20891(93)	0.30417(55)
O(5)	0.59256(98)	−0.44386(94)	0.37616(57)
O(6)	0.59709(103)	−0.33747(116)	0.27123(51)
Cl(1)	0.63672(43)	−0.08528(46)	0.54571(23)
C(1)	0.40488(122)	−0.17866(139)	0.35760(70)
C(2)	0.38069(128)	−0.07608(128)	0.39881(76)
C(3)	0.45591(144)	−0.04595(145)	0.45596(78)
C(4)	0.54877(140)	−0.12028(150)	0.47306(73)
C(5)	0.57616(119)	−0.22045(126)	0.43352(74)
C(6)	0.50712(131)	−0.25135(136)	0.37579(81)
C(7)	0.53074(134)	−0.36228(125)	0.33218(78)
C(8)	0.71575(170)	−0.28558(202)	0.28067(99)
C(9)	0.61127(179)	−0.55771(158)	0.34253(100)
C(10)	0.28005(141)	0.00255(156)	0.38608(92)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Anisotropic thermal parameters (×10^4) for $C_{20}H_{22}Cl_2O_{11}U$ in the form: $T = \exp[-2\pi^2\Sigma_{ij}U_{ij}h_ih_ja_i^*a_j^*]$						
U(1)	312(34)	212(41)	280(4)	−34(25)	−3(25)	53(7)
O(1)	397(66)	431(69)	515(68)	90(57)	120(56)	106(51)
O(2)	365(210)	229(155)	391(76)	59(115)	−195(143)	98(165)
O(3)	390(61)	470(70)	589(76)	−197(62)	−228(56)	186(53)
O(4)	398(56)	386(54)	386(55)	−97(45)	−121(56)	139(53)
O(5)	406(58)	326(54)	329(50)	34(43)	0(45)	115(45)
O(6)	485(60)	426(57)	322(50)	32(52)	59(43)	90(58)
Cl(1)	521(27)	636(28)	420(21)	−138(20)	−192(19)	60(21)
C(1)	262(62)	350(79)	272(62)	1(58)	−15(50)	17(57)
C(2)	283(67)	269(67)	339(69)	−63(56)	−5(55)	19(55)
C(3)	366(79)	365(80)	292(69)	−82(62)	−21(61)	−29(62)
C(4)	302(74)	428(85)	307(65)	−61(63)	−16(59)	−17(57)
C(5)	202(60)	299(69)	330(67)	−19(55)	−45(52)	32(51)
C(6)	231(64)	321(72)	319(67)	40(59)	31(57)	46(56)

(continued)

TABLE V *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(7)	347(74)	256(71)	355(72)	−12(55)	−19(59)	65(53)
C(8)	324(95)	676(139)	608(109)	115(104)	34(85)	−64(75)
C(9)	652(119)	360(86)	505(103)	−61(76)	94(89)	136(80)
C(10)	320(80)	376(84)	476(91)	−144(72)	−72(69)	−2(66)

TABLE VI. Distances and Angles for $C_{20}H_{22}Cl_2O_{11}U$

Bond distances (Å)			
U–O(1)	1.77(2)	Cl–C(4)	1.75(1)
U–O(2)	2.44(4)	C(1)–C(2)	1.42(2)
U–O(3)	2.45(2)	C(2)–C(3)	1.42(2)
U–O(4)	2.28(2)	C(3)–C(4)	1.37(2)
O(3)–C(10)	1.24(2)	C(4)–C(5)	1.38(2)
O(4)–C(1)	1.30(2)	C(5)–C(6)	1.39(2)
O(5)–C(7)	1.42(2)	C(6)–C(1)	1.44(2)
O(6)–C(7)	1.41(2)	C(6)–C(7)	1.52(2)
O(5)–C(9)	1.44(2)	C(2)–C(10)	1.44(2)
O(6)–C(8)	1.45(2)	C(10)–H(1)	0.82(3)
		O(2)–H(2)	1.14(4)
Contact distances (Å)[a]			
O(2)...O(3)	2.78(3)	O(4)...O(4^{i})	2.92(2)
O(2^{ii})...O(5^{i})	2.72(2)	O(5)...O(6)	2.33(2)
O(2^{ii})...O(5^{iii})	2.72(2)	O(5)...H(2)	1.67(3)
O(3)...O(4)	2.75(2)		
Selected bond angles (°)			
O(2)–U–O(3)	69.4(3)	O(3)–C(10)–C(2)	125(2)
O(3)–U–O(4)	71.0(4)	C(6)–C(7)–O(5)	106(1)
O(4)–U–O(4^{i})	79.4(3)	C(6)–C(7)–O(6)	113(1)
U–O(3)–C(10)	136(1)	C(7)–O(5)–C(9)	112(1)
U–O(4)–C(1)	142(1)	C(7)–O(6)–C(8)	117(1)

[a] Symmetry code: none, x, y, z; i, $1 - y, 1 - x, \frac{1}{2} - z$; ii, $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{4} - z$; iii, $1 - x, 1 - y, -\frac{1}{2} + z$.

TABLE VII. Selected Mean Planes for $[UO_2(ALAC)_2(H_2O)]$ and Distances (Å) of Atoms from the Plane[a]

Plane I U, O(2), O(3), O(4)
$0.506x + 0.544y - 0.669z = 2.390$ Å
(U −0.01, O(2) 0.05, O(3) 0.00, O(4) 0.00, *C(1) −0.12, *C(2) −0.16, *C(3) −0.29, *C(4) −0.43, *C(5) −0.38, *C(6) −0.22, *C(7) −0.20, *C(10) −0.09, Cl −0.66)

Plane II C(1) to C(7), C(10), Cl
$0.593x + 0.553y - 0.585z = 4.192$ Å
[C(1) −0.01, C(2) 0.00, C(3) 0.05, C(4) 0.01, C(5) 0.02, C(6) 0.02, C(7) −0.02, C(10) −0.03, Cl 0.00)

Angle I–II = 7°

[a] Atoms with asterisk were not included in the plane calculation.

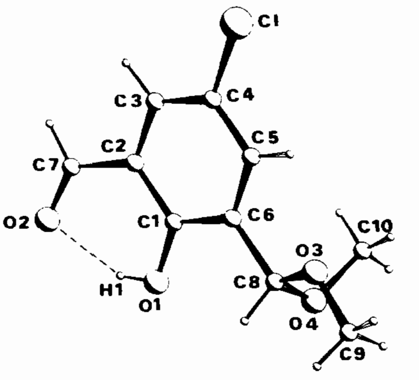

Fig. 1. The crystal structure of $C_{10}H_{11}ClO_4$.

(Table III). In particular the lengths C(8)–O(4), C(9)–O(3) and C(10)–O(4) are as found in paraffinic compounds (see for example 1.419–1.437 Å in $(C_2H_5)_2O$ [12]), the C(1)–O(1) length compares well with the values found in aromatic compounds, and the C(7)–O(2) distance is typical for aldehydes or ketones. The structure presents some intra- and intermolecular O···O contacts less than 4 Å. The O(1)···O(2) contact of 2.62 Å and the position of the hydrogen atom indicate the presence of an intramolecular hydrogen bond.

The infrared spectrum of H(ALAC) (Table IV) presents a strong absorption at 1670 cm^{-1}, belonging to the vibration of the carbonyl group. This band is observed at the same frequency of the corresponding hydrogen bonded carbonyl group in H(DIAL), which presents in addition the absorption of the free carbonyl group at 1688 cm^{-1}. The dimethylacetal moiety is clearly identified by the two strong absorptions in the 1150–1050 cm^{-1} range, assigned to the stretching of the MeO groups. In the same region, neither H(DIAL) nor its uranyl derivatives showed any absorption [5]. The ^1H NMR spectrum of H(DIAL) consists of a singlet for each group of equivalent protons, intramolecular proton exchange leading to signal averaging [13]. In the spectra of H(ALAC) the CH protons of the formyl and acetal groups give rise to distinct singlets, at 9.8 and 5.6 ppm, respectively, the O–CH_3 singlet being observed at 3.4 ppm. In the presence of two different neighboring groups, the CH ring protons are non-equivalent and show two distinct doublets, owing to reciprocal

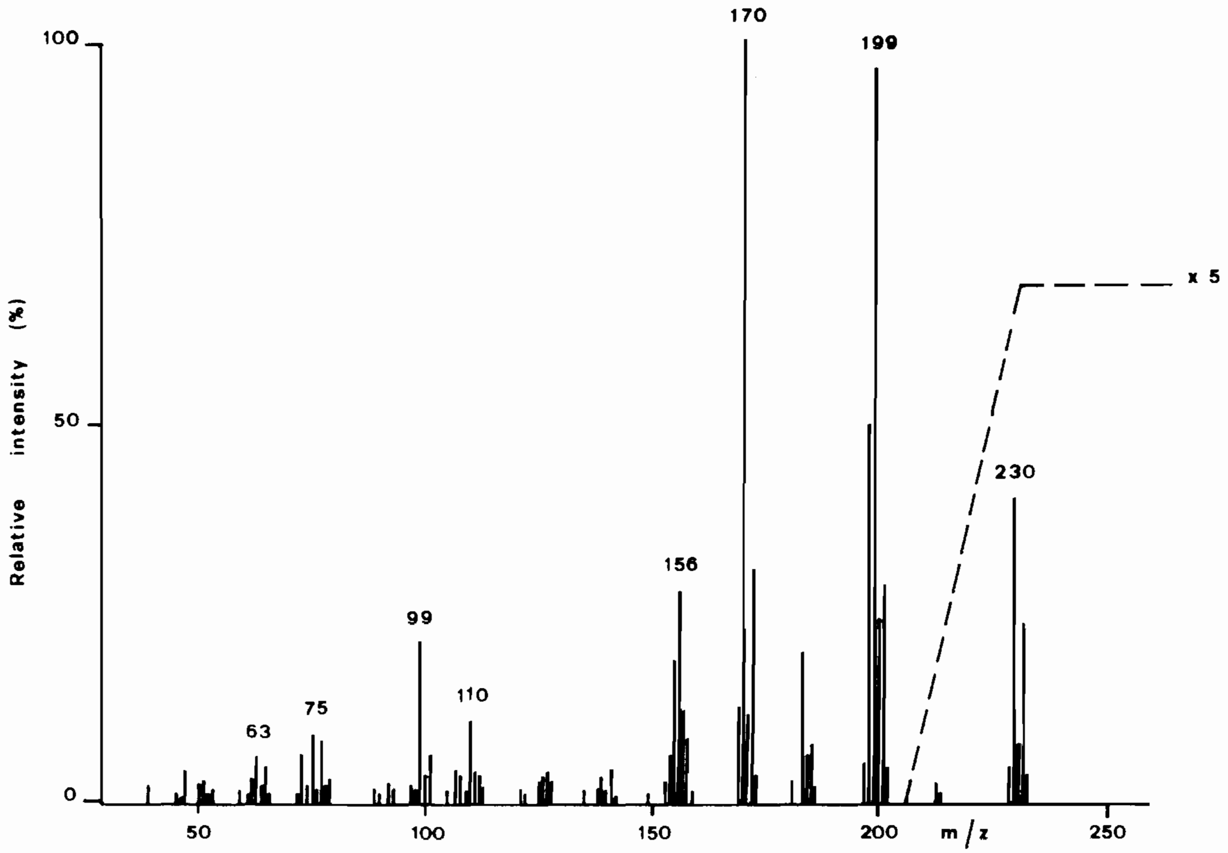

Fig. 2. 70 eV EI Mass spectrum of H(ALAC).

coupling. As in H(DIAL), the sharp OH proton resonance is observed around 11 ppm. The compound H(ALAC) transforms easily into H(DIAL) in acid media, following the usual behaviour of acetals [14, 15]. In fact, the best method to prepare H(DIAL) is to reflux MeOH/H_2O solutions of the corresponding dimethylacetal, containing hydrochloric acid. Such a reaction has been followed by electronic spectra. Apart from small solvent-dependent shifts, the intramolecular charge transfer absorption, observed for benzaldehyde below 300 nm ($\lambda_{max} \simeq 287$ nm; $\epsilon_{mol} \simeq 1100$), undergoes a red shift in 2-hydroxybenzaldehyde ($\lambda_{max} \simeq 327$ nm; $\epsilon_{mol} \simeq 3700$) [16, 17]. In the spectrum of H(ALAC) in dichloromethane, the corresponding absorption (λ_{max} = 342 nm; ϵ_{mol} = 4000) is observed at higher energy with respect to the parent one of H(DIAL) (λ_{max} = 360 nm; ϵ_{mol} = 6650). When small amounts of gaseous HCl are dissolved in a dichloromethane solution of H(ALAC), a progressive red shift of the absorption maximum is observed, and the final spectrum coincides with that of H(DIAL) at the same concentration.

The mass spectrum of H(ALAC) (Fig. 2) shows the molecular ion at m/z 230 (8%). The related fragmentation scheme is reported in Fig. 3. The initial decomposition takes place in the acetal group, yielding the primary fragments having m/z 199 (93%) and 198 (47%). The ion at m/z 170 (100%) is originated by sequential loss of one methanol and one carbonyl molecule, whereas the species at m/z 184 (6%) and 183 (20%) are the molecular H(DIAL) ion and the parent ion formed by loss of one hydrogen. At m/z values below 170 the fragmentation pattern looks like that of H(DIAL) [8], in which the most abundant decomposition species were the ions at m/z 156 (100%), 110 (25%) and 99 (30%).

The crystal structure of $[UO_2(ALAC)_2(H_2O)]$ is shown in Fig. 4. The observed systematic absences $h00$ for $h \neq 2n$ and $00l$ for $l \neq 4n$ indicate that the compound crystallizes in space group $P4_32_12$, which has eight general positions. Because only four molecules of the compound are present in the elementary cell, the uranium atom and the water oxygen atom must lie on the unique set of four special positions at $x, x, 0$; $\bar{x}, \bar{x}, \frac{1}{2}$; $\frac{1}{2} - x, \frac{1}{2} + x, \frac{3}{4}$; $\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{4}$, so that the two halves of the molecule are symmetrically related by the crystallographic twofold axis. The uranium atom is seven-coordinate in the usual pentagonal bipyramid and the atoms of the ligands up to C(7) are roughly coplanar. Nevertheless, the ligand plane is slightly inclined, by 7°, with respect

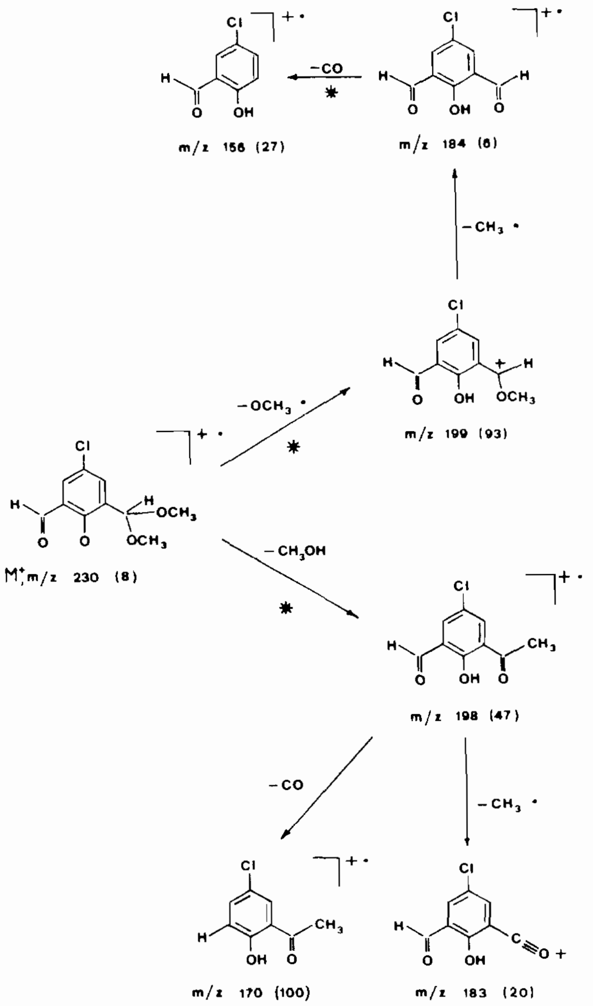

Fig. 3. EI-induced fragmentation of H(ALAC).

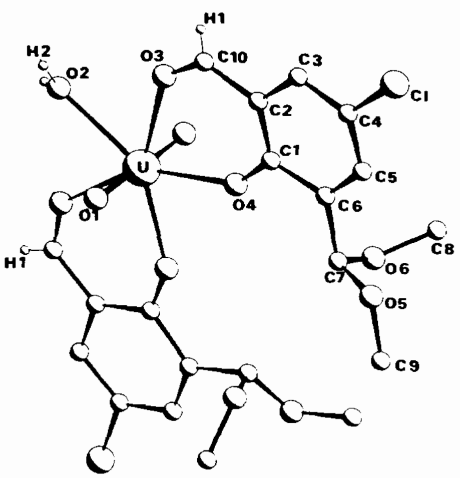

Fig. 4. The crystal structure of $C_{20}H_{22}Cl_2O_{11}U$.

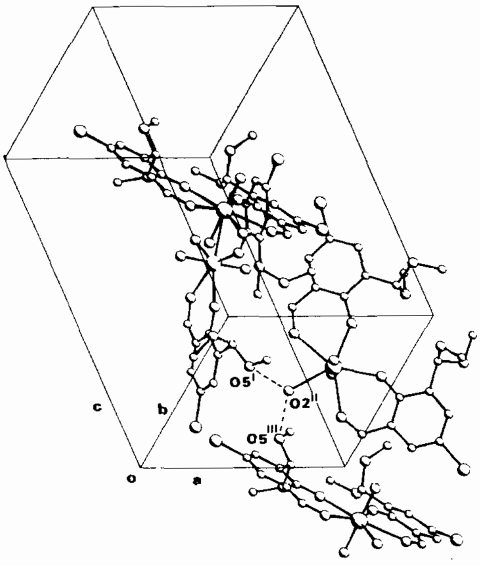

Fig. 5. Crystal packing of $[UO_2(ALAC)_2(H_2O)]$.

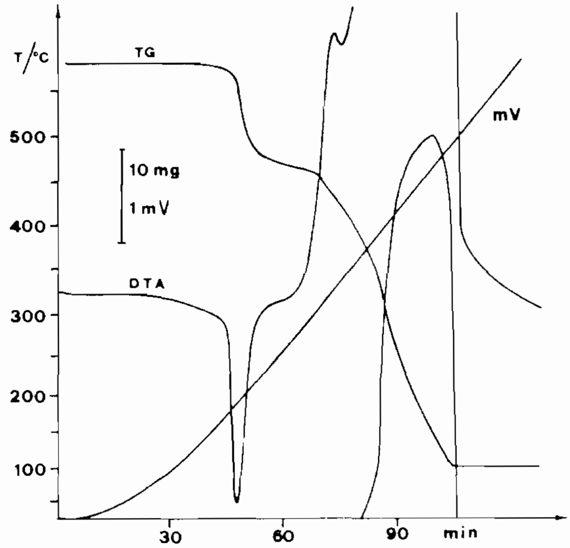

Fig. 6. Thermograms of $[UO_2(ALAC)_2(H_2O)]$ (62.8 mg).

to the equatorial plane. As expected, the U–O(4) bond distance with the charged oxygen (2.28(2) Å) is significantly shorter than the U–O distance with the neutral oxygen atoms (2.45(2) Å). Comparison with the free ligand shows few significant differences in the coordinated ligand. The most relevant feature upon coordination is that the negative charge formally attributed to the phenolato oxygen O(4) is partially redistributed over the whole metallocycle. Thus the length of 1.30(2) Å indicates that the partial double bond character of C(1)–O(4) is increased if compared with 1.354 Å in the free ligand, whereas the aldehyde C(10)–O(3) bond of 1.24(2) Å is slightly longer if compared with 1.215(5) Å in the free ligand. As shown in Table VI, the structure is characterized by the presence of some intra- and intermolecular O•••O contacts less than 4 Å. The contacts of O(2) with the symmetry-related O(3) atoms are merely due to the positions occupied by the oxygen atoms in the coordination sphere and do not necessarily imply intramolecular hydrogen bonding. On the contrary, O(2) can be reasonably considered involved in hydrogen bonding with the O(5) atoms of two neighboring molecules. Because O(2) lies on the twofold axis, the two O(2)•••O(5) distances are symmetric with respect to O(2). Thus, each molecule is directly linked to four neighboring molecules, providing a relative compactness to the crystal packing (Fig. 5).

In the infrared spectrum of [UO_2(ALAC)$_2$(H_2O)] the carbonyl stretching frequency is below the corresponding value in free ligand, as observed in the H(DIAL) complexes. The MeO stretching absorptions are unchanged with respect to free ligand and the uranyl group stretching frequency is at 920 cm^{-1}. As expected, the ^{1}H NMR spectrum of the complex in deuterated DMSO does not show the OH proton signal. The ring proton signals are scarcely affected by coordination, whereas the resonances of the aldehyde and acetal CH protons are shifted downfield with respect to the corresponding signals in H(ALAC). The thermograms of [UO_2(ALAC)$_2$(H_2O)] are shown in Fig. 6. Whereas the complex [UO_2(DIAL)$_2$(H_2O)] presented the endotherm due to release of the water molecule (170 °C) well below the decomposition temperature (300 °C) [5], the loss of water in [UO_2(ALAC)$_2$(H_2O)] takes place with decomposition of the complex. As for H(ALAC), the initial degradation process seems to involve the acetal group, with loss of two MeO and two Me moieties to give the corresponding H(DIAL) derivative. In fact, the first decomposition step yields a weight loss of *ca.* 14% (160–200 °C), a value very close to that calculated for degradation to anhydrous [UO_2(DIAL)$_2$] (14.7%). At around 200 °C massive decomposition is observed, which ends at 500 °C. As for the H(DIAL) uranyl complexes, the final pyrolysis product seems to be UO_2. The experimental total weight loss is 63.8% against a calculated value, for UO_2 as final product, of 63.9%. Attempts to prepare pure [UO_2(DIAL)$_2$] by gradual heating of [UO_2(ALAC)$_2$(H_2O)] failed. The infrared spectra of the solid heated *in vacuo* up to 170–190 °C indicated that the main species was [UO_2(DIAL)$_2$] along with unidentified decomposition products difficult to separate.

Acknowledgements

The Authors thank F. Braga and V. Corrado for technical assistance.

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