Inorganica Chimica Acta, 132 (1987) 279–288

Dioxouranium(VI) Complexes with Pentadentate Bases Containing Acetal Groups

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(Received February 6, 1987)

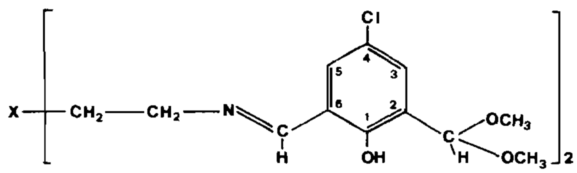
Abstract

The new ligands $[(OCH_3)_2CH-HOC_6H_2Cl-CH=N(CH_2)_2]_2NH$, $H_2(NAC)$, and $[(OCH_3)_2CH-HOC_6H_2Cl-CH=N(CH_2)_2]_2S$, $H_2(SAC)$, and the related uranyl complexes $[UO_2(NAC)]$ and $[UO_2(SAC)]$ have been prepared and characterized by infrared, ^1H and ^{13}C NMR and electronic spectroscopy. Thermogravimetric and mass spectrometry data are also reported. The crystal structures of the complexes have been determined by X-ray crystallography. $[UO_2(SAC)]$ is monoclinic, space group $P2_1/n$, with $a = 20.591(5)$, $b = 11.948(8)$, $c = 11.780(8)$ Å, $\beta = 90.11(3)°$; $D_c = 1.86$ g cm^{-3} for $Z = 4$. The structure was refined to the conventional R of 4.6%. $[UO_2(NAC)]$ is tetragonal, space group $P4_12_12$, with $a = 12.605(8)$ and $c = 17.801(5)$ Å; $D_c = 1.87$ g cm^{-3} for $Z = 4$. The structure was refined to the conventional R of 5.7%. In both compounds the pentadentate dianionic ligand binds equatorially to UO_2^{2+} leading to seven-coordinated uranium in a distorted bipyramidal coordination geometry. Selected bond distances for $[UO_2(SAC)]$ are: U–O (uranyl) 1.77 Å (mean), U–O (ligand) 2.22 Å (mean), U–N 2.61 Å (mean) and U–S 3.003(3) Å. In $[UO_2(NAC)]$ the corresponding values are: U–O (uranyl) 1.72 Å, U–O (ligand) 2.21 Å (mean), U–N 2.56 Å and U–NH 2.60 Å.

Introduction

As a part of our studies on mononuclear and dinuclear complexes of copper(II), nickel(II) and dioxouranium(VI) with Schiff bases [1–4], we recently reported dioxouranium(VI) complexes with 2,6-diformyl-4-chlorophenol, H(DIAL) [5], and 2-dimethylacetal-4-chloro-6-formylphenol, H(ALAC) [6], of general formulae $[UO_2(DIAL)_2]$, $[UO_2(DIAL)_2(L)]$ and $[UO_2(ALAC)_2(H_2O)]$ ($L = H_2O$ and MeOH). The last compound, in which two ligands are symmetrically coordinated, presents the opportune configuration to be used as an intermediate in selective synthesis of Schiff base complexes by condensation with α,ω-diamines.

We report here the synthesis of the new ligands $H_2(SAC)$ and $H_2(NAC)$ and of their dioxouranium complexes $[UO_2(SAC)]$ and $[UO_2(NAC)]$.



$H_2(NAC)$: X = NH $H_2(SAC)$: X = S

Experimental

Reagents were uranyl acetate tetrahydrate ($UO_2Ac_2 \cdot 4H_2O$; Fluka), bis(2-aminoethyl)sulphide (K and K), bis (2-aminoethyl)amine (Schuchardt) and 2-dimethylacetal-4-chloro-6-formylphenol, H(ALAC), which was prepared as reported in ref. 6. Methanol, ethanol and dichloromethane (C. Erba) were purified by the usual methods [7]. Deuterated solvents were kept over molecular sieves.

Preparation of the Compounds

$H_2(NAC)$ and $H_2(SAC)$

The ligand $H_2(NAC)$ was prepared by adding a solution of bis(2-aminoethyl)amine in anhydrous methanol (1.0 mmol in 10 cm^3) to a solution of H(ALAC) in the same solvent (2.0 mmol in 25 cm^3). The reaction was immediate, yielding a yellow solution. The solvent was removed under reduced pressure and the residual reddish oil was washed twice with cold cyclohexane (5 cm^3) in order to remove unreacted amine and H(ALAC), and finally dried *in vacuo*. Yield, *ca.* 55%.

The ligand $H_2(SAC)$ was prepared by an analogous procedure by reaction of H(ALAC) with bis(2-aminoethyl)sulphide (molar ratio 2:1) in anhydrous methanol to give a reddish orange oil, yield *ca.* 65%. The purity of both ligands was tested by ^1H NMR and infrared spectroscopy.

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[$UO_2(NAC)$]

Well formed crystals of the compound were obtained by different preparation methods. (i) A methanol solution of $UO_2Ac_2 \cdot 4H_2O$ (1.2 mmol in 10 cm^3) was added to the yellow solution containing bis(2-aminoethyl)amine (1.2 mmol) and H(ALAC) (2.4 mmol) in *ca.* 50 cm^3 of anhydrous methanol. The orange solution separated the red product (10 min), which was filtered, washed with anhydrous methanol and dried *in vacuo*. Yield, *ca.* 70%. *Anal.* Found: C, 36.5; H, 3.7; N, 5.2. Calc. for $C_{24}H_{29}Cl_2N_3O_8U$: C, 36.3; H, 3.7; N, 5.3%. (ii) A methanol solution of $UO_2Ac_2 \cdot 4H_2O$ (0.8 mmol in 8 cm^3) was added to a solution of H_2(NAC) in anhydrous methanol (0.8 mmol in 15 cm^3) to give the product in a *ca.* 70% yield. (iii) A suspension of [UO_2(ALAC)$_2$(H_2O)] (0.6 mmol) in an ethanol solution of bis(2-aminoethyl)amine (1.0 mmol in 40 cm^3) was allowed to boil until an orange solution was formed (*ca.* 30 min) which was reduced to half the volume in a rotavapor. The red crystals, which separated slowly on cooling, were washed with cold diethyl ether and dried *in vacuo*. Yield, *ca.* 60%. *Anal.* Found: C, 36.3; H, 3.6; N, 5.3%. These crystals were used in the X-ray structure determination.

[$UO_2(SAC)$]

(i) The red product separated within 1 h by addition of $UO_2Ac_2 \cdot 4H_2O$ (0.9 mmol) to a methanol solution containing bis(2-aminoethyl)sulphide (0.9 mmol) and H(ALAC) (1.8 mmol in *ca.* 50 cm^3). It was washed with anhydrous methanol and dried *in vacuo*. Yield, *ca.* 55%. *Anal.* Found: C, 34.9; H, 3.4; N, 3.4. Calc. for $C_{24}H_{28}Cl_2N_2O_8SU$: C, 35.4; H, 3.5; N, 3.4%. (ii) The compound was also obtained by reaction of H_2(SAC) and uranyl acetate (molar ratio 1:1) in methanol (yield, 60%); and (iii) by reaction of [UO_2(ALAC)$_2$(H_2O)] with bis(2-aminoethyl)sulphide in boiling ethanol (molar ratio 1:1; 2 h). Within 2 days red crystals were isolated which were used in the X-ray work. Yield, *ca.* 30%. *Anal.* Found: C, 35.4; H, 3.5; N, 3.4%.

Measurements

Infrared spectra were measured on a Perkin-Elmer 580 B spectrophotometer (4000–400 cm^{-1}; KBr pellets), ^1H and ^{13}C NMR spectra by a Jeol FX 90 Q spectrometer and electronic spectra by a Cary 17 D spectrophotometer. Thermogravimetric data (TG and DTA) in air were obtained using a Netzsch STA-429 thermoanalytical instrument (air flux rate, 250 cm^3 min^{-1}; heating rate, 5 °C min^{-1}; reference material, Al_2O_3). 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), as reported in ref. 8.

TABLE I. Infrared Data (cm^{-1})

Compound	ν(C=N)	ν(C=C)	ν(O–CH_3)	ν(O–U–O)
H_2(SAC)[a]	1640s	1592m	1119–1056s	
H_2(NAC)[a]	1639s	1592m	1119–1055s	
[UO_2(SAC)]	1623s	1560s	1117–1062s	903s
[UO_2(NAC)]	1632s	1557s	1120–1051s	897s

[a] In chloroform.

X-ray Data

Crystal and intensity data for [UO_2(SAC)] and [UO_2(NAC)] are given in Table IV. From the density value only four molecules of [UO_2(NAC)] are present in the unit cell, so that both the metal and the N(2) nitrogen atom must lie on a special position. Space group $P4_12_12$ has one set of special positions with point symmetry C_2-2. U and N(2) were located on the twofold axis at 0.2183, 0.2183, 0.0, where the x coordinate was determined from the Patterson peak. In both compounds the phenylene rings were refined as rigid bodies (C–C = 1.395 Å). Final Fourier difference maps showed no significant residuals. Atomic positional parameters are listed in Tables V and VI. Bond lengths and angles are reported in Tables VII–IX and the equations of selected mean planes in Tables X and XI.

Results and Discussion

The species H_2(NAC) and H_2(SAC) have been obtained as reddish oils by reaction of H(ALAC) with the appropriate amine $[H_2N-(CH_2)_2]_2X$ (X = NH and S). As expected, the infrared spectra of both compounds (Table I) do not show the absorption at 1670 cm^{-1}, present in H(ALAC), due to the vibration of the carbonyl group. Beyond 1600 cm^{-1} only a strong absorption is observed, belonging to the stretching of the nitrilomethylidino group, whereas the two strong bands in the 1050–1120 cm^{-1} region, assigned to the stretching of the MeO groups, are unchanged with respect to the corresponding bands in H(ALAC) (1110–1047 cm^{-1}). Moreover in the ^1H NMR spectra of both compounds (Table II) the signal of the CH formyl proton, found in H(ALAC) at 9.84 ppm, is absent, confirming the purity of the samples. The CH protons of the nitrilo groups give rise to the signal at *ca.* 8.25 ppm, and the OH proton resonance is at *ca.* 13.8 ppm, downfield with respect to the corresponding resonance in H(ALAC), found at 11.1 ppm. As in H(ALAC), the two CH ring protons are non-equivalent, owing to different neighboring groups, and show two distinct doublets, at *ca.* 7.2–7.5 ppm, the coupling constant being 2.5 Hz. As regards the ethylene

TABLE II. ^1H NMR Data (ppm, $CDCl_3$, $T = 27$ °C)

Compound	O–CH_3	CH_2–X[a]	CH_2–N=C	CH$_{(acet)}$	CH$_{(ring)}$	N=CH	OH[b]
H_2(SAC)	3.33	2.82[c]	3.74[c]	5.62	7.15–7.51[d]	8.23	13.7
H_2(NAC)	3.38	2.97[e]	3.71[e]	5.66	7.19–7.54[d]	8.29	13.9
[UO_2(SAC)]	3.52	3.80[f]	4.76[f]	6.55	7.42–7.88[g]	9.31	
[UO_2(NAC)]	3.62–3.48	3.75[e]	4.20[e]	6.58	7.30–7.89[h]	8.96	

[a]NAC, X = NH; SAC, X = S. [b]Broad signals. [c]$J = 6.6$ Hz. [d]$J = 2.5$ Hz. [e]Unresolved triplets. [f]$J \simeq 5.8$ Hz. [g]$J = 2.9$ Hz. [h]$J = 2.7$ Hz.

TABLE III. ^{13}C NMR Data (ppm, $CDCl_3$, $T = 27$ °C)

Compound	O–CH_3	CH_2–X	CH_2–N=C	CH$_{(acet)}$	CH$_{(ald)}$	Ring			N=C–H
						C^1	C^3, C^5	Other	
H(DIAL)					190.8	161.7	136.7	124.1, 125.5	
H(ALAC)	53.7			97.8	195.1	157.4	134.7, 132.5	124.5, 121.2, 128.4	
H_2(SAC)	53.6	33.1	58.8	98.2		157.4	130.7, 130.2	119.1, 122.5, 127.6	164.8
H_2(NAC)	53.9	49.6	59.3	98.4		161.2	130.7, 130.4	119.3, 123.5, 127.7	164.9
[UO_2(SAC)]	53.3	35.4	62.8	98.1		165.1	133.3, 133.0	131.2, 123.9	169.2
[UO_2(NAC)]	53.0 53.9	52.4	62.8	98.1		165.8	133.3, 133.2	131.2, 124.4, 121.5	168.2

protons, the resonance of the CH_2 moieties bound to the nitrilo groups is observed downfield (3.7 ppm) with respect to the resonance of the CH_2 groups bound to the central heteroatom (*ca.* 2.9 ppm). The signals of the acetal protons are as in H(ALAC) and are not affected by substitution of formyl group with nitrolomethylidino group in the *meta* position.

The uranyl complexes have been prepared in methanol either by reaction of uranyl acetate with the preformed ligand or by template synthesis. Moreover the complexes were obtained by using [UO_2(ALAC)$_2$(H_2O)] as starting product, and carrying out the condensation reaction with the appropriate diamine in hot ethanol. Uranyl complexes with Schiff bases are generally soluble only in donor solvents, such as DMSO and DMF, whereas in the present case the presence of acetal groups improves the solubility. In fact the complexes are slightly soluble in MeOH and EtOH and soluble in chloroform and dichloromethane, allowing spectral characterization in non-coordinating solvents. In the infrared spectra of the complex the ν(C=N) and ν(C=C) absorptions are at lower energy with respect to the free ligands (Table I) and the uranyl group stretching is as usual around 900 cm^{-1}. As expected, the ^1H NMR spectra of the complexes do not show the phenolic OH signal. A downfield shift with respect to the free ligands is observed for the resonances of the nitrilo CH and ethylene CH_2 protons, the shift being more marked for [UO_2(SAC)] ($\simeq 1$ ppm) than for [UO_2(NAC)] ($\simeq 0.6$ ppm). The downfield shift of the CH(acetal) signal is of the order of 1 ppm, larger than for [UO_2(ALAC)$_2$(H_2O)] ($\simeq 0.4$ ppm). The MeO protons originate in [UO_2(SAC)], one signal at 3.52 ppm, whereas in the corresponding NAC complex two very close signals are observed, suggesting some asymmetry in the acetal moieties. The ^{13}C NMR spectra of ligands and complexes are reported in Table III, along with the data for H(DIAL) and H(ALAC). In the last two compounds the downfield signal is due to the formyl carbon, absent in H_2(SAC) and H_2(NAC), which instead present the nitrilo carbon signal around 165 ppm. The resonance of the ring carbon bound to oxygen (*ca.* 160 ppm) is well distinct from the other ring carbon resonances. In the complex spectra a downfield shift is observed for the signals of ethylene, nitrilo and phenolic carbon atoms. The acetal carbon resonances are as in the free ligands, except for the splitting of the MeO carbon signal in [UO_2(NAC)]. The electronic spectra of the complexes in dichloromethane present an absorption around 360 nm ($\epsilon_{mol} \simeq 7000$) with two shoulders at 395 nm ($\epsilon_{mol} \simeq 6000$) and 477 nm ($\epsilon_{mol} \simeq 1200$).

The crystal structure of [UO_2(SAC)] is shown in Fig. 1. The pentadentate dianionic ligand binds equatorially to UO_2^{2+} leading to seven-coordinated uranium(VI) in a distorted bipyramidal coordination geometry. The uranyl group is essentially linear (178°) with normal U–O distances (mean 1.77 Å).

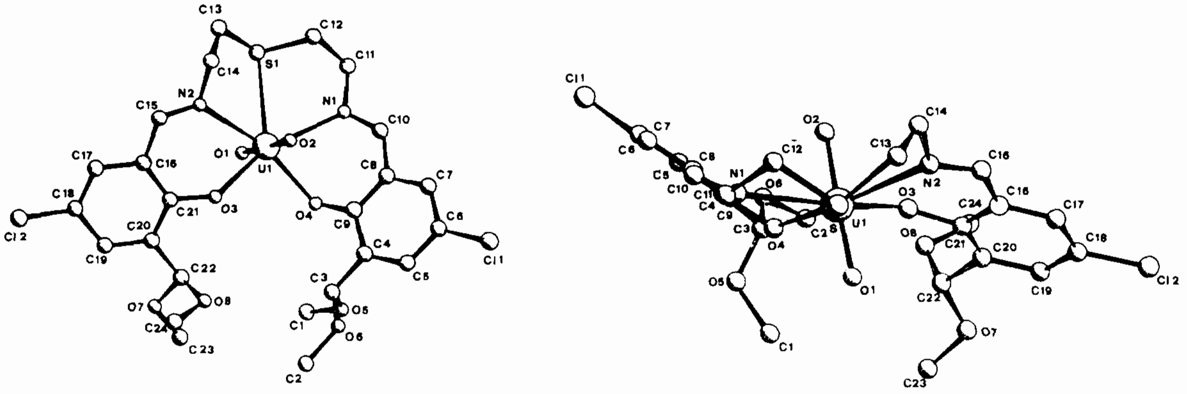

Fig. 1. The crystal structure of $[UO_2(SAC)]$ (two views).

TABLE IV. Crystal and Intensity Data

Compound	$[UO_2(SAC)]$	$[UO_2(NAC)]$
Formula	$C_{24}H_{28}Cl_2N_2O_8SU$	$C_{24}H_{29}Cl_2N_3O_8U$
Formula weight	813	796
System	monoclinic	tetragonal
Space group	$P2_1/n$	$P4_12_12$
General positions	$\pm(x, y, z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	$x, y, z; \bar{x}, \bar{y}, \frac{1}{2}+z; \frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z; \frac{1}{2}+y, \frac{1}{2}-x, \frac{3}{4}+z; y, x, \bar{z}; \bar{y}, \bar{x}, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}-z$
Cell constants	$a = 20.591(5)$ Å	$a = b = 12.605(8)$ Å
	$b = 11.948(8)$ Å	
	$c = 11.780(8)$ Å	$c = 17.801(5)$ Å
	$\beta = 90.11(3)°$	
	$V = 2898$ Å^3	$V = 2828$ Å^3
Density	$D_c = 1.86$ g cm^{-3} for $Z = 4$	$D_c = 1.87$ g cm^{-3} for $Z = 4$
Max. crystal size	0.2 mm	0.2 mm
Radiation used	Mo Kα	Mo Kα
Absorption (Mo Kα)	$\mu = 86.9$ cm^{-1}	$\mu = 86.6$ cm^{-1}
Technique and geometry	Four-circle diffractometer (Philips PW 1100) with graphite-monochromated radiation; $\vartheta/2\vartheta$ scan mode; scan rate = 2° min^{-1}	
Max. diffraction angle	$\vartheta = 25°$	$\vartheta = 25°$
Stability	No significant variation was observed on the intensities of two standard reflexions periodically recorded	
Number of recorded reflexions	$N_{tot} = 6322$	$N_{tot} = 2487$
Number of observed reflexions	$N_{obs} = 3369$	$N_{obs} = 1406$
Criterion for observed reflexions	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Corrections applied	Lp, absorption [9]	Lp, absorption [9]
Atomic scattering factors	U: ref. 10; C, N, O, Cl, S: ref. 11	
Correction for anomalous dispersion (U)	$\Delta f' = -10.67$; $\Delta f'' = 9.65$	
Solution methods	Patterson and Fourier methods	
Refinement method	Full-matrix least-squares	
Number of reflextions per parameter refined	19	14
Conventional R factor	$R = 0.046$	$R = 0.057$
Weighting scheme	$w = 1$	$w = 1$
Programs used	SHELX [12], PARST [13], PLUTO [14]	

The U–O (ligand) and U–N distances (mean 2.22 Å and 2.61 Å respectively) compare well with corresponding values in similar compounds [15–18].

The two halves of the ligand are inclined to each other by 33° and also form large dihedral angles of 45° and 18° with the equatorial plane. The U–S

TABLE V. Atomic Coordinates for [UO$_2$(SAC)]

Atom	x/a	y/b	z/c
U1	0.17533(2)	0.72266(4)	0.42039(4)
S1	0.11660(18)	0.94937(29)	0.38054(30)
Cl1	−0.01355(26)	0.20882(39)	0.27983(44)
Cl2	0.53144(20)	0.86038(36)	0.53823(52)
N1	0.04915(44)	0.71539(95)	0.39407(78)
N2	0.25010(48)	0.86471(80)	0.31734(81)
O1	0.18173(42)	0.78334(82)	0.55664(69)
O2	0.16922(40)	0.66717(76)	0.28066(68)
O3	0.27711(36)	0.66709(68)	0.43947(71)
O4	0.13853(39)	0.56250(65)	0.49371(72)
O5	0.15377(62)	0.32902(113)	0.64374(112)
O6	0.20628(66)	0.24012(121)	0.48689(115)
O7	0.38681(47)	0.56026(84)	0.71244(83)
O8	0.35101(48)	0.46881(85)	0.55155(82)
C1	0.18359(125)	0.39214(227)	0.73617(224)
C2	0.27050(120)	0.20307(215)	0.53818(206)
C3	0.17950(74)	0.34249(136)	0.53052(132)
C4	0.12237(32)	0.37173(68)	0.45433(68)
C5	0.08575(32)	0.28738(68)	0.40315(68)
C6	0.02994(32)	0.31457(68)	0.34174(68)
C7	0.01076(32)	0.42610(68)	0.33150(68)
C8	0.04739(32)	0.51044(68)	0.38267(68)
C9	0.10319(32)	0.48326(68)	0.44409(68)
C10	0.02030(61)	0.62151(112)	0.37100(109)
C11	0.01040(65)	0.81718(116)	0.37814(116)
C12	0.04682(63)	0.89917(114)	0.30058(111)
C13	0.17027(69)	1.01247(122)	0.27373(119)
C14	0.21857(66)	0.92805(119)	0.22537(117)
C15	0.31125(61)	0.87899(107)	0.33000(104)
C16	0.35218(34)	0.81557(62)	0.41142(60)
C17	0.41309(34)	0.86163(62)	0.43411(60)
C18	0.45432(34)	0.81050(62)	0.51262(60)
C19	0.43463(34)	0.71331(62)	0.56843(60)
C20	0.37372(34)	0.66725(62)	0.54574(60)
C21	0.33250(34)	0.71839(62)	0.46723(60)
C22	0.34922(62)	0.56825(112)	0.61324(110)
C23	0.35707(82)	0.48926(147)	0.79819(146)
C24	0.41495(83)	0.43462(147)	0.51699(145)

Atom[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	399(2)	349(2)	411(2)	10(3)	−24(2)	2(3)
S1	611(22)	475(19)	596(21)	20(17)	−106(17)	34(16)
Cl1	1236(38)	707(20)	1153(37)	−131(28)	−270(30)	−359(28)
Cl2	566(24)	636(26)	1916(55)	54(30)	−386(29)	−156(20)
N1	442(55)	568(64)	446(55)	57(56)	13(43)	104(56)
N2	485(59)	400(56)	442(57)	36(46)	26(46)	15(46)
O1	673(56)	640(58)	497(49)	11(51)	−78(42)	21(53)
O2	502(50)	630(56)	462(49)	−45(44)	−37(39)	−60(44)
O3	380(44)	425(46)	642(54)	101(43)	−109(39)	32(38)
O4	485(49)	344(45)	619(55)	60(41)	−19(41)	−11(38)
O5	1044(39)					
O6	1151(44)					
O7	682(27)					
O8	685(27)					
C1	1449(91)					
C2	1400(84)					
C3	701(41)					

(continued)

TABLE V. *(continued)*

Atom[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C4	541(33)					
C5	631(36)					
C6	579(35)					
C7	496(31)					
C8	461(30)					
C9	438(28)					
C10	488(31)					
C11	551(35)					
C12	547(33)					
C13	618(37)					
C14	585(36)					
C15	491(31)					
C16	418(28)					
C17	566(34)					
C18	568(35)					
C19	571(32)					
C20	486(30)					
C21	408(25)					
C22	528(33)					
C23	820(48)					
C24	837(49)					

[a]Anisotropic thermal parameters (×10^4) for $C_{24}H_{28}Cl_2N_2O_8SU$ in the form: $T = \exp[-2\pi^2\Sigma_{ij}U_{ij}h_ih_ja_i{}^*a_j{}^*]$.

TABLE VI. Atomic Coordinates for [UO_2(NAC)]

Atom	x/a	y/b	z/c
U1	0.2183(3)	0.2183(3)	0.0000
O1	0.1610(11)	0.2626(11)	0.0825(8)
O2	0.3839(9)	0.2271(13)	0.0386(7)
O3	0.6114(15)	0.3346(18)	0.0104(9)
O4	0.6160(20)	0.4302(21)	0.1229(13)
Cl1	0.6452(8)	0.1055(8)	0.2995(4)
N1	0.2692(21)	0.0451(15)	0.0709(13)
N2	0.0747(19)	0.0747(19)	0.0000
C1	0.4433(11)	0.1993(13)	0.1008(7)
C2	0.5285(11)	0.2625(13)	0.1231(7)
C3	0.5905(11)	0.2327(13)	0.1845(7)
C4	0.5673(11)	0.1396(13)	0.2235(7)
C5	0.4821(11)	0.0764(13)	0.2012(7)
C6	0.4201(11)	0.1063(13)	0.1398(7)
C7	0.3459(24)	0.0337(22)	0.1233(17)
C8	0.2041(32)	−0.0430(28)	0.0583(19)
C9	0.1221(36)	−0.0269(36)	0.0080(29)
C10	0.5532(26)	0.3619(26)	0.0764(18)
C11	0.7086(28)	0.2757(26)	0.0176(16)
C12	0.6330(33)	0.5305(34)	0.0872(22)

Atom[a]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	1089(20)	362(11)	728(6)	0(0)	0(0)	−63(8)
O1	931(102)	729(108)	1145(107)	185(88)	79(88)	−94(76)
O2	603(80)	1177(117)	916(90)	351(100)	−159(69)	−191(92)
O3	1372(150)	1609(247)	602(97)	−33(131)	197(113)	−253(155)
O4	1418(271)	1899(243)	1418(170)	454(168)	−925(179)	−1267(221)
Cl1	1797(88)	1151(99)	945(50)	37(58)	−492(58)	403(70)

(continued)

TABLE VI. *(continued)*

Atom^a	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	1397(209)	669(121)	1648(204)	−160(132)	385(182)	−451(143)
N2	929(554)	946(296)	1307(377)	0(0)	0(0)	−177(159)
C1	885(68)					
C2	897(69)					
C3	928(72)					
C4	1100(83)					
C5	1033(76)					
C6	976(76)					
C7	1122(94)					
C8	1506(120)					
C9	1208(199)					
C10	1326(111)					
C11	1674(108)					
C12	1604(167)					

^{a}Anisotropic thermal parameters ($\times 10^4$) for $C_{24}H_{29}Cl_2N_3O_8U$ in the form: $T = \exp[-2\pi^2\Sigma_{ij}U_{ij}h_ih_ja_i^*a_j^*]$.

TABLE VII. Bond and Contact Distances (Å) for $[UO_2(SAC)]^a$

Coordination			
U–O(1)	1.767(8)	U–N(1)	2.618(9)
U–O(2)	1.779(8)	U–N(2)	2.594(10)
U–O(3)	2.209(7)	U–S	3.003(3)
U–O(4)	2.233(8)		
Ligand			
S–C(12)	1.82(1)	S–C(13)	1.84(2)
C(12)–C(11)	1.54(2)	C(13)–C(14)	1.53(2)
C(11)–N(1)	1.47(2)	C(14)–N(2)	1.47(2)
N(1)–C(10)	1.30(2)	N(2)–C(15)	1.28(2)
C(10)–C(8)	1.45(2)	C(15)–C(16)	1.48(1)
O(4)–C(9)	1.33(1)	O(3)–C(21)	1.34(1)
C(4)–C(3)	1.52(2)	C(20)–C(22)	1.51(2)
C(3)–O(5)	1.44(2)	C(22)–O(7)	1.40(2)
C(3)–O(6)	1.44(2)	C(22)–O(8)	1.39(2)
O(5)–C(1)	1.46(3)	O(7)–C(23)	1.46(2)
O(6)–C(2)	1.52(2)	O(8)–C(24)	1.44(2)
C(6)–Cl(1)	1.711(9)	C(18)–Cl(2)	1.722(8)
Contacts			
O(3)···O(4)	3.18(1)	N(1)···S	3.13(1)
O(3)···N(2)	2.82(1)	N(2)···S	3.02(1)
O(4)···N(1)	2.84(1)	S···O(1)	3.17(1)
		S···O(2)	3.73(1)

^{a}Estimated standard deviations in parentheses refer to the last significant digit.

distance of 3.003(3) Å is of the same order of values found in two other determinations of the U(VI)–S (thioether) bond [18, 19]. As already observed [18], the sulphur atom, probably because of steric requirements due to the ligand geometry, is significantly out of the ideal equatorial plane. An equatorial

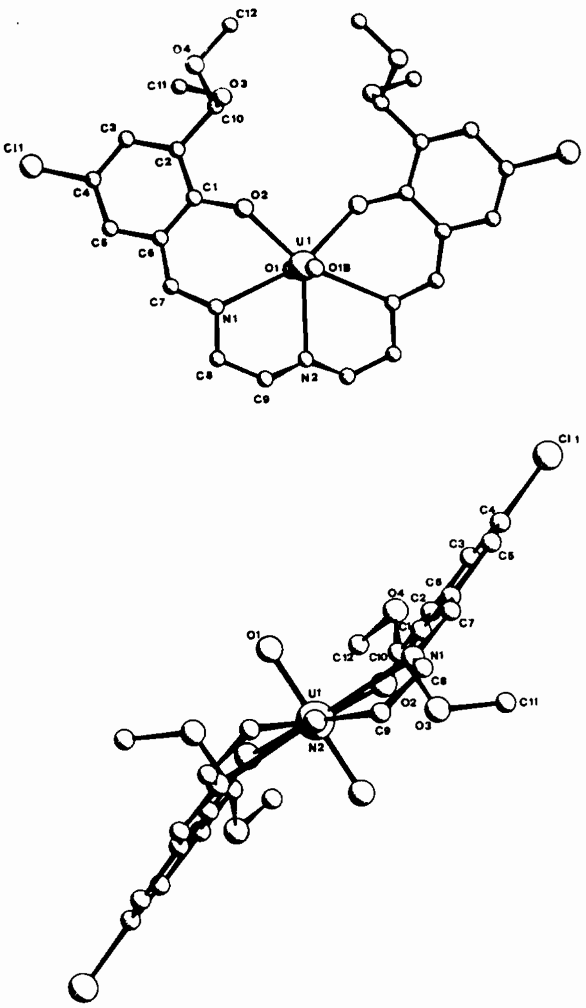

Fig. 2. The crystal structure of $[UO_2(NAC)]$ (two views).

TABLE VIII. Bond Angles (°) for $[UO_2(SAC)]^a$

Coordination		Uranium with ligand	
O(1)–U–O(2)	177.6(4)	U–O(3)–C(21)	134.2(6)
O(3)–U–O(4)	91.5(3)	U–O(4)–C(9)	128.8(6)
O(3)–U–N(2)	71.4(3)	U–N(1)–C(10)	120.5(8)
O(4)–U–N(1)	71.3(3)	U–N(1)–C(11)	121.8(8)
S–U–N(1)	67.2(3)	U–N(2)–C(15)	128.1(8)
S–U–N(2)	64.9(2)	U–N(2)–C(14)	114.8(8)
N(1)–U–N(2)	123.8(3)	U–S–C(12)	95.8(5)
		U–S–C(13)	103.6(5)
Ligand			
C(12)–S–(13)	104.8(6)		
S–C(12)–C(11)	106.8(9)	S–C(13)–C(14)	112.2(10)
C(12)–C(11)–N(1)	110(1)	C(13)–C(14)–N(2)	111(1)
C(11)–N(1)–C(10)	116(1)	C(14)–N(2)–C(15)	117(1)
N(1)–C(10)–C(8)	127(1)	N(2)–C(15)–C(16)	124(1)
C(4)–C(3)–O(5)	107(1)	C(20)–C(22)–O(7)	108(1)
C(4)–C(3)–O(6)	106(1)	C(20)–C(22)–O(8)	113(1)
O(5)–C(3)–O(6)	112(1)	O(7)–C(22)–O(8)	111(1)
C(3)–O(5)–C(11)	118(2)	C(22)–O(7)–C(23)	113(1)
C(3)–O(6)–C(2)	116(2)	C(22)–O(8)–C(24)	115(1)

[a] Estimated standard deviations in parentheses refer to the last significant digit.

TABLE IX. Bond Distances and Angles for $[UO_2(NAC)]^a$

(a) Bond distances (Å)			
Coordination			
U–O(1)	1.72(1)	U–N(1)	2.60(2)
U–O(2)	2.21(1)	U–N(2)	2.56(2)
Ligand			
N(2)–C(9)	1.38(4)	C(4)–Cl(1)	1.72(1)
C(9)–C(8)	1.53(6)	C(2)–C(10)	1.54(3)
C(8)–N(1)	1.40(4)	C(10)–O(3)	1.43(3)
N(1)–C(7)	1.35(3)	C(10)–O(4)	1.44(3)
C(7)–C(6)	1.34(3)	O(3)–C(11)	1.44(3)
O(2)–C(1)	1.38(1)	O(4)–C(12)	1.43(4)
(b) Bond angles (°)			
O(2)–U–O(2^I)	133.6(4)	N(2)–C(9)–C(8)	131(5)
O(2)–U–N(1)	69.5(7)	C(9)–C(8)–N(1)	114(4)
N(1)–U–N(2)	65.2(6)	N(1)–C(7)–C(6)	125(2)
U–N(2)–C(9)	113(2)	C(2)–C(10)–O(3)	111(2)
U–N(1)–C(8)	116(2)	C(2)–C(10)–O(4)	107(2)
U–N(1)–C(7)	127(2)	C(10)–O(3)–C(11)	119(2)
U–O(2)–C(1)	139(1)	C(10)–O(4)–C(12)	111(2)
		O(3)–C(10)–O(4)	110(3)

[a] Estimated standard deviations in parentheses refer to the last significant digit.

TABLE X. Selected Mean Planes for $[UO_2(SAC)]$, X, Y and Z are Orthogonal Coordinates^a

Plane 1: O(3), O(4), N(1), N(2)
$0.034X - 0.515Y - 0.857Z = -8.343$
[O(3) 0.00, O(4) 0.00, N(1) 0.00, N(2) 0.00, S −1.25, U − 0.22]

Plane 2: N(1), C(10), C(8), C(9), O(4)
$0.546X + 0.050Y - 0.836Z = -2.950$
[N(1) 0.04, C(10) − 0.11, C(8) 0.01, C(9) 0.02, O(4) − 0.02, U 1.21]

Plane 3: N(2), C(15), C(16), C(21), O(3)
$0.346X - 0.484Y - 0.804Z = -6.125$
[N(2) − 0.09, C(15) 0.14, C(16) 0.03, C(21) − 0.08, O(3) 0.08, U − 0.78]

Angles (°) between the planes

1–2	44.8
1–3	18.3
2–3	33.2

[a] Distances (Å) of atoms from the planes are in parentheses.

plane has been then calculated as the best plane through the ligand oxygen and nitrogen atoms, which are perfectly coplanar (see Table X), while the sulphur atom is displaced by 1.25 Å from this plane towards O(1). Angles in the range 96–107°, and in particular the C–S–C angle of 107°, show that the S atom can be considered to be sp^3 hybridized. It is likely that the pronounced displacement of S from the base plane allows a better arrangement of the other coordinated atoms in the plane. The fact that the N–U–N angles (124° in the actual compound and 126° in the mentioned thia compound [18]) are relatively small if compared with corresponding values in oxa and aza analogues seems to be evidence of this.

TABLE XI. Selected Mean Planes for [UO_2(NAC)], *X*, *Y* and *Z* are Orthogonal Coordinates[a]

Plane 1: O(2), N(1), N(2), $N(1^I)^b$, $O(2^I)^b$
$0.341X - 0.341Y - 0.876Z = 0$
[O(2) 0.07, N(1) – 0.14, N(2) 0.00, $N(1^I)$ 0.14, $O(2^I)$ – 0.07, U 0.00]

Plane 2: O(2), C(1), C(6), C(7), N(1)
$0.613X - 0.516Y - 0.599Z = 1.067$
[O(2) 0.01, C(1) – 0.01, C(6) 0.00, C(7) 0.07, N(1) – 0.04]

Plane 3: C(1), C(2), C(3), C(4), C(5), C(6)
$0.605X - 0.512Y - 0.610Z = 1.00$

Angles (°) between the planes

1–2	24.6
1–3	23.8
2–3	0.8

[a] Distances (Å) of atoms from the planes are in parentheses. [b] (*I*) = *Y*, *X*, –*Z*.

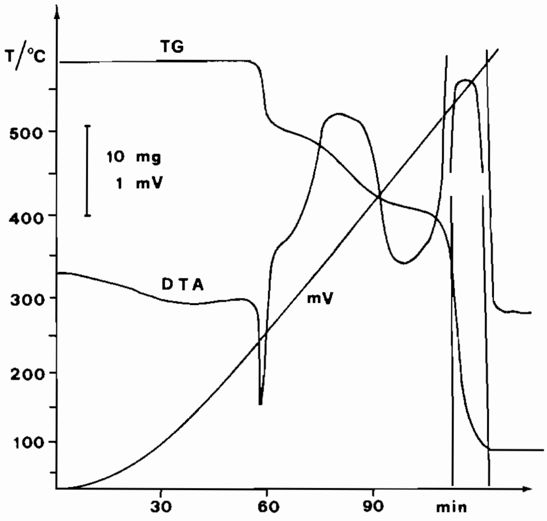

Fig. 3. Thermograms of [UO_2(NAC)] (68.17 mg).

Figure 2 shows perspective views of the molecular structure of [UO_2(NAC)]. The ligand is pentadentate in the equatorial plane of the uranyl ion and the five-coordinated atoms form a rather puckered pentagon. Because the U–N(2) line coincides with the crystallographic twofold axis, the two halves of the ligand are symmetrically related and the wings are in the chair configuration with respect to the equatorial moiety of the molecule with which they form dihedral angles of 24° (see Table XI). Because, on the contrary, an 'umbrella' or boat configuration was adopted by a very similar compound [20], we may conclude that the choice between the two configurations is independent of the molecular structure, being largely determined by packing forces in the crystal. Bond distances and other structural details agree with the values found in a number of parent compounds [15–17, 21]. Nevertheless, the numerous reflexions of low intensity (about 45% of the recorded reflexions had $I < 3\sigma(I)$), and the fact that the temperature factors are generally high suggest that the compound has a limited degree of crystallinity and cause the e.s.d.s on atomic coordinates and therefore on the calculated bond distances and angles to be relatively large. Similar circumstances were observed in the crystal structure of the analogous compound $UO_2[o\text{-}C_6H_4\text{–}C(CH_3)\text{=}N\text{-}(CH_2)_2]_2NH$ [20]. Thermograms of [UO_2(NAC)] (Fig. 3) show that the degradation begins at *ca.* 200 °C. The first decomposition step, with the related endothermal peak at 245 °C, seems to involve the acetal groups, as previously observed for [$UO_2(ALAC)_2(H_2O)$]. In fact the experimental weight loss (11.5%) is in accordance with the calculated value for the loss of 2OMe + 2Me groups (11.6%). The degradation process ends at *ca.* 650 °C, the final product being probably UO_2 (total weight loss, 66.0%; calc. weight loss to UO_2, 66.1%). The complex [$UO_2(SAC)_2$] behaves in an analogous way, the experimental weight loss being in the first step *ca.* 12% (calc., 11.3%) and in the complete degradation *ca.* 66.7% (calc. 66.8%).

In the mass spectra of both complexes the higher mass species is the protonated molecular ion $[M + H]^+$, at *m*/*z* 797 for [UO_2(NAC)] and 814 for [UO_2(SAC)]. Similar behaviour was observed in macrocyclic sulphur containing Schiff bases [22] as well as in crown ethers [23], and was ascribed to the 'trapping' ability of large molecules with respect to H. The fragmentation path way confirms the cleavage of the acetal groups, the corresponding fragments having *m*/*z* 766, 750, 720 for [UO_2(NAC)] and *m*/*z* 783, 767, 737 for [UO_2(SAC)].

Acknowledgements

The authors thank V. Corrado and A. Zaghini for technical assistance.

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