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The Preparation and Crystal Structure of a Dioxouranium(VI) and of an Oxovanadium(IV) Complex with a Hexadentate, Compartmental Schiff Base Ligand

N. A. BAILEY, D. E. FENTON*, C. A. PHILLIPS

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

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

Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Padua, 35100, Italy

and R. GRAZIANI

Istituto di Chimica Generale, Università di Padua, Via Loredan, Padua, 35100, Italy

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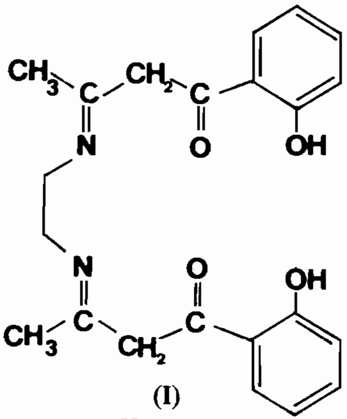
Abstract

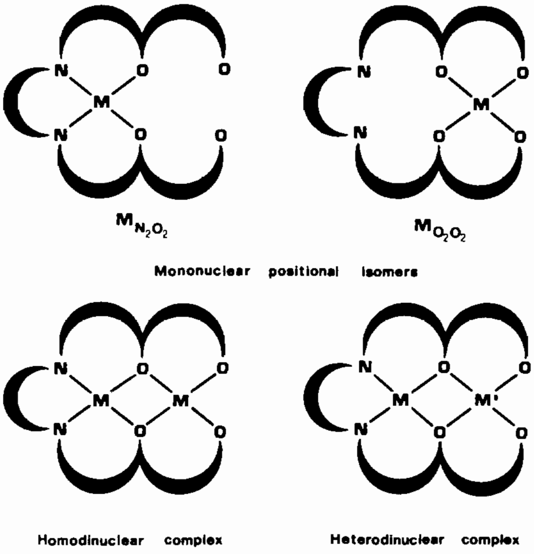
The title compounds were prepared by reacting the compartmental Schiff base ligand, H_4-aapen, obtained by condensation of *o*-acetoacetylphenol and ethylenediamine, and oxovanadium(IV) or dioxouranium(VI) salts in alcoholic media and their crystal structures were determined by X-ray crystallography, $VO(H_2\text{-aapen})$, 0.5 $CHCl_3$, $0.5H_2O$ is monoclinic $P2_1/a$, a = 15.04(3), b =14.37(3), c = 11.20(2) Å, and β = 96.43(3)°; D_c = 1.42 g cm^{-3} for Z = 4. $UO_2(H_2\text{-aapen})(dmf)$ is monoclinic, $P2_1/n$, a = 22.20(3), b = 8.70(1), c = 13.86(2) Å and β = 97.90(3)°; D_c = 1.80 g cm^{-3} for Z = 4. The oxovanadium(IV) and dioxouranium(VI) units occupy the outer (O_2O_2) compartment of the potentially binucleating ligand. Relevant distances are: V–O (ligand), 1.916–1.992 Å; V–O (oxovanadium), 1.585 Å; U–O (ligand), 2.28–2.47 Å; U–O (dmf), 2.45 Å; U–O (dioxouranium), 1.66 Å (mean).

Introduction

During the last few years we have studied the interaction of the compartmental ligand H_4-aapen (I) with a series of transition metal salts [1–3]. This ligand provides adjacent, dissimilar donor sets capable of forming mononuclear positional isomers, homodinuclear, and heterodinuclear complexes (II). In the mononuclear species nickel(II) has been found to occupy the inner-N_2O_2 chamber, whereas oxovanadium(IV) and dioxouranium(VI) were found to occupy the outer-O_2O_2 chamber. Copper(II) provided an example of positional iso-



(I)
H_4-aapen



(II)

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*Author to whom correspondence should be addressed.

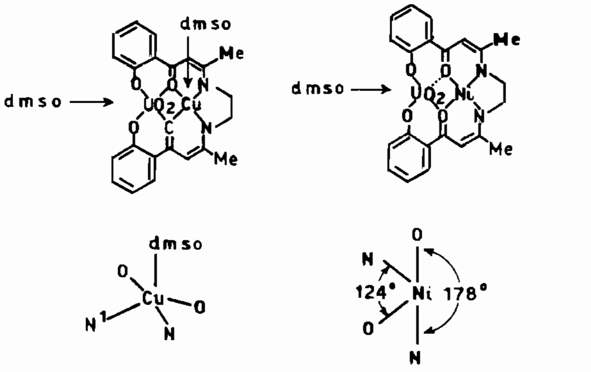

Fig. 1. Metal coordination in $CuUO_2$(aapen)(dmso)$_2$ and $NiUO_2$(aapen)(dmso).

merism by occupying either chamber depending upon reaction conditions [4].

The structures of the heterodinuclear complexes UO_2Cu(aapen)(dmso)$_2$ [5] and UO_2Ni(aapen)(dmso) [6] show that the dioxouranium(VI) lies in the -O_2O_2 chamber and that it is further bound to a molecule of solvent (Fig. 1). The copper(II) atom is in a distorted square pyramidal geometry, and the nickel(II) atom is in an unusual geometry which may be considered as either distorted tetrahedral, or trigonal bipyramidal with an empty equatorial site. From these structures it appeared that the presence of the large dioxouranium(VI) induces some distortion in the coordination geometry of the second metal ion in the heterodinuclear complex. In order to further investigate the influence of the metal ion on ligand conformation and site geometry the structure of the mononuclear nickel(II) complex was determined and showed a square coplanar environment around the metal [7]. We report here the crystal structure of the mononuclear dioxouranium(VI) complex, [UO_2(H_2aapen)(dmf)] (dmf = dimethylformamide), and, in order to compare the influence of 'hard' ions with different ionic radii on the conformation of the ligand we report also the structure of the analogous oxovanadium(IV) complex.

Experimental

The ligand H_4aapen was obtained by condensation of *o*-acetoacetylphenol, prepared by the Wittig method [8], and ethylenediamine in methanol [9].

[UO_2(H_2aapen)(H_2O)] was prepared, as already reported, by the reaction of H_4aapen and UO_2-(CH_3COO)$_2$, 2H_2O in methanol [4, 9].

[UO_2(H_2aapen)(dmf)] was prepared by dissolving UO_2(H_2aapen)(H_2O) in the minimum quantity of dimethylformamide, followed by addition of diethylether. Well formed orange-red crystals were obtained by recrystallization from a dimethylformamide/diethylether solution. Analysis: [UO_2(H_2aapen)-(dmf)]. Calcd. for $C_{25}H_{27}N_3O_7U$: C = 41.72; H = 3.75; N = 5.84%; found: C = 41.54; H = 3.82; N = 5.79%. The strong IR band at 1643 cm^{-1} can be ascribed to C=O of the coordinated dimethylformamide and the strong band at 907 cm^{-1} is due to the ν_3 of the O–U–O group.

[VO(H_2aapen)] was prepared by the reaction of H_4aapen (0.001 mol) dissolved in chloroform (50 cm^3) with VO(CH_3COO)$_2$ (0.004 mol) suspended in hot EtOH (50 cm^3). The suspension was refluxed for 6 h and excess VO(CH_3COO)$_2$ removed by filtration. The solution was allowed to cool and gave a light green amorphous powder. The supernatant then was stood overnight and gave olive green needles and dark green chunky crystals, having the same IR spectra. As analytical data showed the presence of halogen the samples were dried for several days at 80 °C *in vacuo*. Analysis. (i) Light green amorphous solid. Found: C = 50.36; H = 4.18; N = 5.37; Cl = 15.75. Calcd. for VO(H_2-aapen), 0.8 $CHCl_3$ [$C_{22.8}H_{22.8}Cl_{2.4}N_2O_5V$], C = 50.61; H = 4.21; N = 5.17; Cl = 15.76%. (ii) Light green solid after drying. Found: C = 59.97; H = 4.07; N = 5.47; Cl = 8.00%. Calcd. for VO(H_2-$H_{22}N_2O_5V$], C = 59.32; H = 4.94; N = 6.29%. (iii) Olive green needles. Found: C = 54.55; H = 4.07; N = 5.47; Cl = 8.00%. Calcd. for VO(H_2-aapen), 0.4 $CHCl_3$, [$C_{22.4}H_{22.4}Cl_{1.2}N_2O_5V$], C = 54.54; H = 4.54; N = 5.68; Cl = 8.64%. (iv) Green chunks. Found before drying: C = 54.70; H = 3.91; N = 5.36; Cl = 8.83%. Found after drying: C = 54.38; H = 3.74; N = 5.35; Cl = 8.34%.

In the infrared spectrum of [VO(H_2aapen)] the strong band at 980 cm^{-1} is assigned to the stretching of the V–O group.

X-ray Crystallography

Crystal and Intensity Data for [VO(H_2aapen)]-0.5 $CHCl_3$·0.5H_2O

$C_{22.5}H_{23.5}Cl_{1.5}N_2O_{5.5}V$; M = 514.06; crystallises from $CHCl_3$ as green needles; crystal dimensions 0.35 × 0.11 × 0.12 mm. Monoclinc, a = 15.04(3), b = 14.37(3), c = 11.20(2) Å, β = 96.43(3)°, U = 2404(10) Å^3, D_m = 1.45, D_c = 1.42 g cm^{-3}, Z = 4; space group $P2_1/a$, MoK_α radiation (λ = 0.71069 Å), μ(MoK_α) = 6.03 cm^{-1}, F(000) = 1060.

Three-dimensional X-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method. 1544 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarization effects. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms of the complex and of a chloroform of solvation (see below) were placed in calculated

TABLE I. Atomic Positional Parameters with e.s.d.s for $[(VO)(H_2aapen)] 0.5CHCl_3 0.5H_2O$.

	x	*y*	*z*
V(1)	0.20183(10)	0.37028(11)	0.16780(14)
Cl(1)	0.5256(5)	0.3008(7)	0.3387(9)
Cl(2)	0.4275(9)	0.2601(9)	0.5156(12)
Cl(3)	0.4858(8)	0.4290(10)	0.5066(16)
O(1)	0.1406(4)	0.2533(4)	0.1499(6)
O(2)	0.1615(4)	0.3902(4)	−0.0058(5)
O(3)	0.1727(4)	0.5047(4)	0.1735(5)
O(4)	0.1759(4)	0.3697(5)	0.3341(5)
O(5)	0.3066(4)	0.3553(4)	0.1722(6)
O(6)	0.0426(17)	0.2694(17)	0.4632(27)
N(1)	0.1337(5)	0.5277(5)	−0.1605(7)
N(2)	0.1137(5)	0.6445(5)	0.0347(7)
C(1)	0.1291(6)	0.1992(6)	0.0521(9)
C(2)	0.1176(6)	0.1040(6)	0.0688(10)
C(3)	0.1095(7)	0.0458(6)	−0.0302(12)
C(4)	0.1092(7)	0.0768(7)	−0.1455(11)
C(5)	0.1163(6)	0.1703(6)	−0.1638(10)
C(6)	0.1257(5)	0.2341(6)	−0.0665(9)
C(7)	0.1264(5)	0.3349(6)	−0.0910(8)
C(8)	0.0898(6)	0.3709(7)	−0.2015(7)
C(9)	0.0885(6)	0.4649(7)	−0.2313(8)
C(10)	0.0365(7)	0.4959(7)	−0.3467(9)
C(11)	0.1352(6)	0.6290(7)	−0.1757(8)
C(12)	0.0816(7)	0.6748(6)	−0.0887(9)
C(13)	0.1212(7)	0.7994(6)	0.1227(10)
C(14)	0.1325(6)	0.6956(6)	0.1310(9)
C(15)	0.1632(6)	0.6560(6)	0.2440(9)
C(16)	0.1836(5)	0.5620(6)	0.2635(8)
C(17)	0.2153(5)	0.5285(6)	0.3839(7)
C(18)	0.2512(6)	0.5900(7)	0.4738(9)
C(19)	0.2773(7)	0.5631(9)	0.5894(10)
C(20)	0.2666(7)	0.4710(9)	0.6185(9)
C(21)	0.2319(7)	0.4070(8)	0.5367(9)
C(22)	0.2084(6)	0.4343(7)	0.4134(9)
C(23)	0.4582(15)	0.3310(15)	0.4275(17)

Atoms Cl(1)–Cl(3) and C(23) comprise the half-occupancy chloroform molecule: atom O(6) is the oxygen atom of the half-occupancy water molecule.

positions (C–H 0.95, N–H 0.92 Å, C–C–H(methyl) 110°); their contributions were included in structure factor calculations (B = 8.0 $Å^2$) but no refinement of positional parameters was permitted. A molecule of chloroform of crystallisation was detected close to the inversion centre at (0.5, 0.5, 0.5) and was therefore inserted with 50% occupancy. A water molecule was also detected in a position which was consistent with its occurrence, also at 50% occupancy, on the opposite side of the inversion centre to the chloroform. Refinement converged at *R* 0.0611 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of vanadium and chlorine. Table I lists the atomic positional parameters with estimated standard deviations. Tables of anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters and observed structure amplitudes and calculated structure factors are available from the authors. Scattering factors were taken from ref. 10; unit weights were used throughout the refinement; computer programs used were SHELX [11] and those of the Sheffield X-ray system.

Crystal and Intensity Data for [$UO_2(H_2aapen)(dmf)$]

$C_{25}H_{27}N_3O_7U$; FW = 719; approximate crystal dimensions 0.10 × 0.12 × 0.15 mm. Monoclinic, a = 22.20(3), b = 8.70(1), c = 13.86(2) Å, β = 97.90(3)°, U = 2650 $Å^3$, D_m = 1.82, D_c = 1.80 g cm^{-3} for Z = 4; space group $P2_1/n$, general positions (x, y, z; ½ + x, ½ − y, ½ + z), MoK_α radiation (λ = 0.71069 Å), $\mu(MoK_\alpha)$ = 91.4 cm^{-1}, F(000) = 1384.

Three-dimensional diffraction data were collected in the range $4 < 2\theta < 50°$ on a Philips 1100 diffractometer by the θ–2θ scan method. The 4144 measured intensities were corrected for Lorentz, polarization, and for absorption effects [12], and 2775 reflections for which $I/\sigma(I) > 3.0$ were used in subsequent calculations. The structure was solved by standard Patterson and Fourier techniques and refined to *R* 0.070 by full-matrix least-squares using unit weights. The largest parameter shift in the last cycle was 0.2σ.

The two phenylene rings were treated as rigid bodies. Allowance was made for anisotropic thermal motion of all non-carbon atoms and of the carbon atoms of dmf.

A final difference Fourier map showed no significant features. Scattering factors for C, N, O were supplied internally by SHELX and for U were those of ref. 13. A correction for the anomalous dispersion of U was also applied [14].

Computer programs used were SHELX [11] and X-ray [15].

Table II lists the atomic positional parameters with estimated standard deviations.

Tables of thermal parameters and observed and calculated structure factors are available from the authors.

Results and Discussion

The reaction of $VO(OAc)_2$ and H_4-aapen, when carried out in equimolar quantities in ethanol–$CHCl_3$, gave a dark green crystalline product the mass spectrum of which indicated the presence of two compounds [4]. A low temperature spectrum showed P^+ at m/e = 445 ($VO(H_2aapen)$) and a high temperature run showed this peak and a further peak at m/e = 510 ($(VO)_2aapen$) corresponding to the oxo-vanadium(IV) complex. The C, H, N analysis

TABLE II. Atomic Positional Parameters with e.s.d.s for $[UO_2(H_2aapen)(dmf)]$.

Atom	*x*	*y*	*z*
U	0.2873(0)	0.3022(1)	0.5048(1)
O(1)	0.2641(7)	0.2546(19)	0.6103(14)
O(2)	0.3112(8)	0.3487(16)	0.4020(15)
O(3)	0.1886(7)	0.3849(16)	0.4540(11)
O(4)	0.2241(7)	0.0831(16)	0.4372(11)
O(5)	0.3532(8)	0.0851(19)	0.4980(11)
O(6)	0.3827(8)	0.3676(20)	0.5766(14)
O(7)	0.2801(10)	0.5709(22)	0.5550(13)
N(1)	0.2284(8)	−0.1787(20)	0.3452(12)
N(2)	0.3573(10)	−0.1494(27)	0.3833(15)
N(3)	0.2840(13)	0.7746(25)	0.6562(17)
C(1)	0.1420(9)	0.3215(14)	0.4876(14)
C(2)	0.1038(9)	0.4228(14)	0.5283(14)
C(3)	0.0546(9)	0.3662(14)	0.5704(14)
C(4)	0.0437(9)	0.2083(14)	0.5717(14)
C(5)	0.0820(9)	0.1070(14)	0.5310(14)
C(6)	0.1311(9)	0.1636(14)	0.4889(14)
C(7)	0.1666(11)	0.0600(28)	0.4381(18)
C(8)	0.1371(12)	−0.0718(31)	0.3879(19)
C(9)	0.1689(12)	−0.1809(31)	0.3457(18)
C(10)	0.1342(13)	−0.3228(40)	0.2969(21)
C(11)	0.2662(12)	−0.2983(37)	0.3105(19)
C(12)	0.3277(12)	−0.2408(32)	0.2941(20)
C(13)	0.4041(11)	−0.1999(35)	0.4460(19)
C(14)	0.4335(12)	−0.3528(31)	0.4342(19)
C(15)	0.4305(12)	−0.1013(32)	0.5260(19)
C(16)	0.4054(12)	0.0346(30)	0.5468(19)
C(17)	0.4350(9)	0.1315(17)	0.6318(19)
C(18)	0.4197(9)	0.2852(17)	0.6438(19)
C(19)	0.4486(9)	0.3688(17)	0.7228(15)
C(20)	0.4928(9)	0.2986(17)	0.7899(15)
C(21)	0.5080(9)	0.1449(17)	0.7779(15)
C(22)	0.4791(9)	0.0613(17)	0.6989(15)
C(23)	0.3073(22)	0.6620(41)	0.6199(24)
C(24)	0.2220(16)	0.8182(46)	0.6382(22)
C(25)	0.3250(16)	0.8642(42)	0.7269(22)

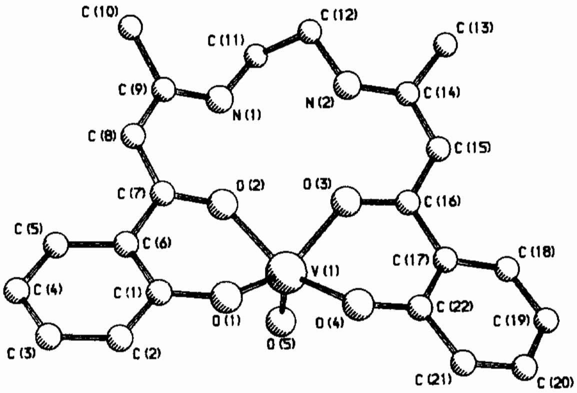

Fig. 2. The molecular structure of $VO(H_2aapen)$ with atom labelling.

gave values which corresponded well with the analysis of a mixture of $(VO)_2$aapen:$VO(H_2aapen)$ in a 2:1 ratio; it was not possible to separate the components from the mixture.

When an excess of $VO(OAc)_2$ was used in this reaction a dark green solid was first recovered; the C, H, N analyses on different batches varied from one agreeing with the above result to one suggesting that only $(VO)_2$aapen was present but the mass spectrum indicated only $VO(H_2aapen)$. A halogen analysis showed Cl to be present and the analyses were acceptable if up to one mole of $CHCl_3$ was present in the bulk sample, based on $VO(H_2aapen)$ only. The supernatant gave two crystalline products, light green chunks and light green needles. These both gave analyses corresponding to $VO(H_2aapen)$, ~0.5 $CHCl_3$. The IR spectra were similar for all three products. The samples were pumped on *in vacuo* at 80° for several days and this led to a loss of $CHCl_3$ from the bulk product leaving $VO(H_2$-aapen), but the crystals were essentially unaffected and analysed as $VO(H_2aapen) \sim 0.4\ CHCl_3$.

The X-ray structure of the green needles was solved. The structure of the vanadium complex is illustrated in Fig. 2 with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables III and IV.

The vanadyl unit occupies the outer (O_2O_2) compartment of this potentially binucleating ligand. The structure is very similar to that previously reported [16] for the related complex $(VO)(H_2daaen)$, for which two crystalline forms were found, in both of which there was evidence for co-crystallisation of the bimetallic species $(VO)_2$(daaen). No such evidence was found here. Bond lengths show the chelates defining the inner (empty) compartment to be delocalised and the bond linking the β-keto-imine fragment to the phenol residue to be single. The carbon-carbon torsion angle for the di-imino-ethane fragment is close to a normal free-ligand value (54.6°). The vanadium is displaced by 0.60 Å from the plane of the four coordinating oxygen atoms of the acyclic ligand.

The half-occupancy water molecule is hydrogen bonded to the phenolic oxygen O(4) (although hydrogen atoms were not positioned on this water). The position and orientation of the half-occupancy chloroform of crystallisation is such that the C–H bond is directed towards the vanadyl oxygen atom O(5) and, although the distance is not short, some dipolar interaction may be postulated here too. Since these intermolecular contacts occur on opposite sides of the vanadium complex, any one molecule may experience both such interactions: however, it is statistically more likely that each molecule makes one or other such contact.

TABLE III. Bond Lengths (Å) and Angles (°) with e.s.d.s for Molecule [(VO)(H_2aapen)] 0.5$CHCl_3$0.5H_2O.

V(1)–O(1)	1.916(6)	N(2)–C(12)	1.478(12)
V(1)–O(2)	1.992(6)	N(2)–C(14)	1.310(12)
V(1)–O(3)	1.983(6)	C(13)–C(14)	1.502(13)
V(1)–O(4)	1.946(6)	C(14)–C(15)	1.417(13)
V(1)–O(5)	1.585(6)	C(15)–C(16)	1.396(12)
O(1)–C(1)	1.338(11)	O(3)–C(16)	1.298(10)
C(1)–C(2)	1.394(14)	C(16)–C(17)	1.461(12)
C(2)–C(3)	1.384(15)	C(17)–C(22)	1.400(13)
C(3)–C(4)	1.367(15)	C(17)–C(18)	1.401(13)
C(4)–C(5)	1.364(15)	C(18)–C(19)	1.366(15)
C(5)–C(6)	1.419(13)	C(19)–C(20)	1.377(16)
C(6)–C(1)	1.416(13)	C(20)–C(21)	1.360(15)
C(6)–C(7)	1.474(12)	C(21)–C(22)	1.442(14)
O(2)–C(7)	1.308(10)	O(4)–C(22)	1.339(11)
C(7)–C(8)	1.397(12)	C(23)–Cl(1)	1.56(2)
C(8)–C(9)	1.391(13)	C(23)–Cl(2)	1.53(2)
C(9)–C(10)	1.501(14)	C(23)–Cl(3)	1.69(3)
N(1)–C(9)	1.336(12)	O(4)···O(6)	2.97(3)
N(1)–C(11)	1.466(12)	O(5)···C(23)	3.47(2)
C(11)–C(12)	1.486(14)	O(5)···H(23)	2.54
O(1)–V(1)–O(2)	86.19(25)	N(1)–C(9)–C(8)	121.4(8)
O(1)–V(1)–O(3)	138.78(26)	N(1)–C(9)–C(10)	119.4(8)
O(1)–V(1)–O(4)	87.19(27)	C(8)–C(9)–C(10)	119.1(8)
O(1)–V(1)–O(5)	110.40(30)	C(9)–N(1)–C(11)	128.0(8)
O(2)–V(1)–O(3)	81.21(24)	N(1)–C(11)–C(12)	110.3(8)
O(2)–V(1)–O(4)	149.73(26)	N(2)–C(12)–C(11)	109.8(8)
O(2)–V(1)–O(5)	104.05(29)	C(12)–N(2)–C(14)	128.6(8)
O(3)–V(1)–O(4)	84.53(25)	N(2)–C(14)–C(13)	119.5(8)
O(3)–V(1)–O(5)	110.72(29)	N(2)–C(14)–C(15)	121.9(8)
O(4)–V(1)–O(5)	105.94(30)	C(13)–C(14)–C(15)	118.5(8)
V(1)–O(1)–C(1)	127.7(6)	C(14)–C(15)–C(16)	124.9(8)
V(1)–O(2)–C(7)	132.8(5)	O(3)–C(16)–C(15)	119.0(8)
V(1)–O(3)–C(16)	129.3(5)	O(3)–C(16)–C(17)	120.6(7)
V(1)–O(4)–C(22)	122.3(6)	C(15)–C(16)–C(17)	120.4(8)
O(1)–C(1)–C(2)	117.8(8)	C(16)–C(17)–C(18)	121.1(8)
O(1)–C(1)–C(6)	123.4(8)	C(16)–C(17)–C(22)	120.7(8)
C(6)–C(1)–C(2)	118.8(9)	C(22)–C(17)–C(18)	118.2(8)
C(1)–C(2)–C(3)	119.1(9)	C(17)–C(18)–C(19)	123.3(9)
C(2)–C(3)–C(4)	123.5(10)	C(18)–C(19)–C(20)	117.9(10)
C(3)–C(4)–C(5)	118.1(10)	C(19)–C(20)–C(21)	122.4(10)
C(4)–C(5)–C(6)	121.5(9)	C(20)–C(21)–C(22)	119.8(10)
C(5)–C(6)–C(1)	118.9(8)	O(4)–C(22)–C(17)	123.0(8)
C(1)–C(6)–C(7)	121.5(8)	O(4)–C(22)–C(21)	118.7(8)
C(5)–C(6)–C(7)	119.5(8)	C(21)–C(22)–C(17)	118.2(9)
O(2)–C(7)–C(6)	118.1(7)	Cl(1)–C(23)–Cl(2)	119.5(15)
O(2)–C(7)–C(8)	120.6(8)	Cl(1)–C(23)–Cl(3)	115.3(14)
C(6)–C(7)–C(8)	121.3(8)	Cl(2)–C(23)–Cl(3)	106.9(14)
C(7)–C(8)–C(9)	124.5(8)	V(1)–O(5)···H(23)	122
		C(23)–H(23)···O(5)	163

The structure of the uranyl complex is illustrated in Fig. 3 with the atom labelling used in the corresponding Tables. Bond lengths and angles (together with estimated standard deviations) and details of planar fragments are given in Tables V and VI. The molecular structure consists of uranyl groups five coordinated by H_2aapen ions and by one dmf molecule giving approximately pentagonal bipyramidal geometry about the uranium.

The pentagonal girdle carries the O(phenolic)···O(dmf) and the O(ketonic)···O(ketonic) contact distances (mean 2.85 Å) which are slightly greater, and the two O(phenolic)···O(ketonic) contact distances (mean 2.74 Å) which are slightly shorter than the van der Waals diameter (2.80 Å). Very similar values were found in the binuclear complexes [Ni-UO_2(aapen)(dmso)] [5] and [CuUO_2(aapen)-(dmso)$_2$] [4]. In these complexes however the

TABLE IV. Details of Planar Fragments of [VO(H_2aapen)]. Equations of Least-squares Planes are of the Form: $pX + qY + rZ = d$, where p, q and r are Direction Cosines Referred to Orthogonal Crystal Axes a, b, c^*. Deviations of Atoms from the Mean Planes (Å) are given in Parentheses.

	p	*q*	*r*	*d*
Plane A	[O(1)–O(4)]			r.m.s. deviation 0.088 Å
	0.9907	−0.1284	0.0447	1.6018
	[O(1) −0.086, O(2) 0.089, O(3) −0.090, O(4) 0.087, V(1) 0.597, O(5) 2.181, O(6) −1.810, N(1) −0.465, N(2) −1.123, C(1) −0.085, C(6) −0.112, C(7) −0.268, C(16) −0.100, C(17) 0.345, C(22) 0.394]			
Plane B	[C(1)–C(6)]			r.m.s. deviation 0.014 Å
	0.9929	−0.1008	0.0625	1.5860
	[C(1) 0.024, C(2) −0.018, C(3) −0.000, C(4) 0.013, C(5) −0.006, C(6) −0.012, O(1) 0.064, C(7) −0.133]			
Plane C	[C(17)–C(22)]			r.m.s. deviation 0.017 Å
	0.9554	−0.1884	−0.2276	0.2477
	[C(17) −0.017, C(18) −0.004, C(19) 0.013, C(20) 0.000, C(21) −0.021, C(22) 0.029, O(4) 0.032, C(16) −0.114]			
Plane D	[O(2), N(1), C(7)–C(9)]			r.m.s. deviation 0.045 Å
	0.9193	−0.1605	−0.3592	1.4065
	[O(2) −0.044, N(1) 0.051, C(7) 0.038, C(8) 0.017, C(9) −0.063, C(6) 0.134, C(10) −0.259, C(11) −0.083]			
Plane E	[O(3), N(2), C(14)–C(16)]			r.m.s. deviation 0.020 Å
	0.9644	0.1636	−0.2079	3.0635
	[O(3) 0.015, N(2) −0.023, C(14) 0.031, C(15) −0.015, C(16) −0.009, C(12) 0.018, C(13) 0.141, C(17) −0.051]			
Plane F	[O(2), O(3), N(1), N(2)]			r.m.s. deviation 0.119 Å
	0.9771	0.2114	−0.0227	3.6900
	[O(2) −0.123, O(3) 0.123, N(1) 0.114, N(2) −0.114, V(1) 0.152, O(1) −1.077, O(4) −0.477, C(11) 0.466, C(12) −0.311]			

Selected angles between planes (°)				
	A–B	1.9	B–D	25.0
	A–C	16.2	C–E	20.3
	A–F	20.0	D–F	29.2
	B–C	17.6	E–F	11.0

Torsion angle (°) N(1)–C(11)–C(12)–N(2) +54.6

TABLE V. Bond Lengths (Å) and Angles (°) with e.s.d.s for Molecule [UO_2(H_2aapen)(dmf)].

(a) Bond Lengths

U–O(1)	1.68(2)	U–O(5)	2.40(2)
U–O(2)	1.64(2)	U–O(6)	2.28(2)
U–O(3)	2.32(1)	U–O(7)	2.45(2)
U–O(4)	2.47(2)		
O(3)–C(1)	1.31(2)	O(6)–C(18)	1.36(2)
C(6)–C(7)	1.44(3)	C(17)–C(16)	1.52(3)
C(7)–O(4)	1.29(3)	C(16)–O(5)	1.33(3)
C(7)–C(8)	1.45(3)	C(16)–C(15)	1.36(3)
C(8)–C(9)	1.36(3)	C(15)–C(13)	1.46(4)
C(9)–C(10)	1.56(4)	C(13)–C(14)	1.50(4)
C(9)–N(1)	1.32(3)	C(13)–N(2)	1.33(3)
N(1)–C(11)	1.46(3)	N(2)–C(12)	1.54(3)
C(11)–C(12)	1.50(4)		

(continued on facing page)

TABLE V. *(continued)*

O(7)–C(23)	1.28(4)	N(3)–C(24)	1.42(4)
C(23)–N(3)	1.24(4)	N(3)–C(25)	1.47(4)
(b) Contact Distances			
N(1)···N(2)	2.85	O(3)···O(4)	2.76
N(1)···O(4)	2.62	O(5)···O(6)	2.73
N(2)···O(5)	2.60	O(3)···O(7)	2.82
O(4)···O(5)	2.87	O(6)···O(7)	2.86
(c) Bond Angles			
O(1)–U–O(2)	179.1(9)	O(4)–U–O(5)	72.3(5)
O(3)–U–O(4)	70.2(5)	O(5)–U–O(6)	71.3(6)
O(3)–U–O(7)	72.2(6)	O(6)–U–O(7)	74.4(6)
U–O(3)–C(1)	121(1)	U–O(6)–C(18)	127(1)
U–O(4)–C(7)	129(1)	U–O(5)–C(16)	137(1)
O(3)–C(1)–C(6)	124(1)	O(6)–C(18)–C(17)	124(1)
O(4)–C(7)–C(6)	121(2)	O(5)–C(16)–C(17)	118(2)
C(1)–C(6)–C(7)	120(2)	C(16)–C(17)–C(18)	122(2)
C(6)–C(7)–C(8)	119(2)	C(15)–C(16)–C(17)	120(2)
O(4)–C(7)–C(8)	120(2)	O(5)–C(16)–C(15)	122(2)
C(7)–C(8)–C(9)	122(2)	C(13)–C(15)–C(16)	123(2)
C(8)–C(9)–C(10)	119(2)	C(14)–C(13)–C(15)	118(2)
C(8)–C(9)–N(1)	125(2)	C(15)–C(13)–N(2)	120(2)
C(10)–C(9)–N(1)	116(2)	C(14)–C(13)–N(2)	122(2)
C(9)–N(1)–C(11)	128(2)	C(12)–N(2)–C(13)	124(2)
N(1)–C(11)–C(12)	113(2)	N(2)–C(12)–C(11)	110(2)
U–O(7)–C(23)	138(2)	C(23)–N(3)–C(24)	126(3)
O(7)–C(23)–N(3)	126(4)	C(23)–N(3)–C(25)	116(4)
		C(24)–N(3)–C(25)	118(3)

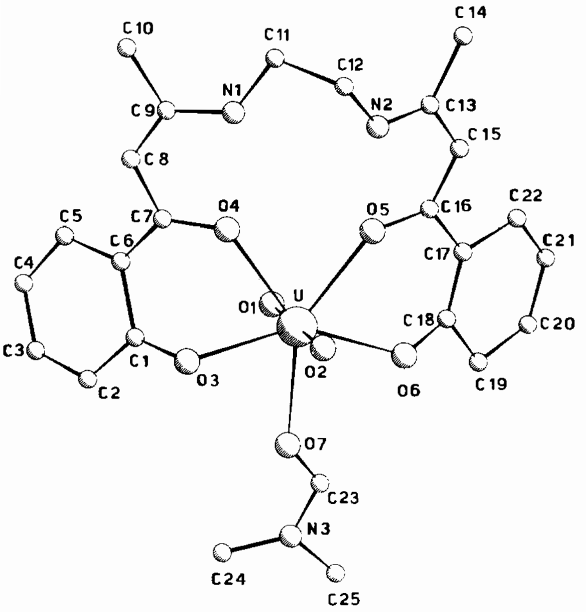

Fig. 3. The molecular structure of $UO_2(H_2aapen)(dmf)$ with atom labelling.

TABLE VI. Least-squares Planes. Deviations (Å) of Atoms from the Planes are given in Square Brackets; *X*, *Y* and *Z* are Fractional Coordinates in the Direct Cell. Atoms not used in the Plane Calculation are marked with an Asterisk.

Plane 1: O(3) to O(7)
$-7.730X - 2.409Y + 12.954Z = 3.594$
[O(3) −0.12, O(4) 0.13, O(5) −0.09, O(6) 0.026, O(7) 0.05, U^* 0.00]

Plane 2: O(4), O(5), N(1), N(2)
$-3.884X - 4.835Y + 11.486Z = 3.833$
[O(4) −0.09, O(5) 0.09, N(1) 0.09, N(2) −0.09]

The angle (°) between planes 1–2 is 19.5.

O(4)···O(5) contact is shorter [2.64 and 2.61 Å] since these oxygen atoms are also associated with the nickel and copper coordination.

Contact values in the N_2O_2 compartment are strongly asymmetric, the N···O distances being significantly shorter [mean 2.61 Å] than the N···N and O···O distances [mean 2.86 Å]. This apparently makes it difficult to accommodate a second metal ion, having square planar coordination geometry, in this compartment. It is noteworthy that the presence of both nickel(II) and uranium(VI) atoms in [$NiUO_2$(aapen)(dmso)] results in an unusual coordination mode for nickel(II), and that the copper(II) atom in [$CuUO_2$(aapen)$(dmso)_2$] is pentacoordinated in a distorted square pyramidal arrangement [5, 6].

The U–O equatorial bonds in the mononuclear dioxouranium(VI) complex are not chemically equivalent, the U–O (phenolic) distances being significantly shorter than U–O distances with neutral oxygen atoms. The five equatorial oxygens are coplanar within 0.12 Å and the uranium atom lies in the mean plane. It is suggested that it is the presence, and influence, of the dioxouranium(VI) ion that is instrumental in producing the unusual geometries at the second metal in the heterodinuclear complexes.

Other structural details of the ligand are basically similar to those found in the vanadium complex. In both complexes the plane of the N_2O_2 compartment is inclined by *ca.* 20° to the equatorial (or basal) plane of the metal coordination polyhedron.

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