Crystal and Molecular Structure of [*NN'*-Ethylenebis(salicylideneiminato)](methanol)dioxouranium

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The crystal and molecular structure of the title compound has been determined by three-dimensional *X*-ray methods. Crystals are monoclinic, space group $P2_1/n$ with cell dimensions: $a = 18{\cdot}695(15)$, $b = 9{\cdot}012(9)$, $c = 10{\cdot}652(10)$ Å, $\gamma = 97{\cdot}52°(5)$, and $Z = 4$. The structure was solved by the heavy-atom method from 2239 reflections collected by counter, and refined by least-squares methods to R 0·055.

Four atoms of the Schiff base and the oxygen of the methanol are co-ordinated in a plane, forming a slightly irregular pentagon, with the uranyl group perpendicular to this plane. Equatorial U–O(3) and U–O(4) distances are 2·25(2) and 2·33(3) Å, while U–O(MeOH) is 2·45(3) Å; U–N(1) and U–N(2) are 2·57(2) and 2·54(5) Å. The only short intermolecular distance, O(4) · · · O(5) of two neighbouring molecules 2·58 Å, suggests the presence of a hydrogen bond. The N(1)–CH_2–CH_2–N(2) group is in a near-gauche conformation (torsion angle 51·8°) and the complex exhibits an overall ' stepped ' geometry. The stereochemistry and chemical properties of 3*d* transition-metal compounds of such ligands are compared.

As an extension of our studies [1,2] of ligands selective for MO_2^{2+} cations of the actinides, we have investigated the molecular structure and reactivity of the complexes of uranyl salts with *NN'*-ethylenebis(salicylideneimine) (H_2ensal), a quadridentate condensed Schiff base.

This structure was determined in order to ascertain (i) the co-ordination number in the equatorial plane of the uranyl group, and in particular whether a molecule of solvent (MeOH) is co-ordinated in the ' inner core ' as in [*NN'*-*o*-phenylenebis(salicylideneiminato)(UO_2)(EtOH)][1] and [(H_2O)(glyoxal)(2-hydroxyanil)$_2UO_2$],[2] even though the i.r. spectrum does not reveal any ν(OH) stretching band in the range 3500—3200 cm^{-1}; (ii) to compare the stereochemistry [3-12] and chemical properties [13,14] of well known 3*d* transition metal compounds of such ligands; and (iii) to investigate the U–N distance which has already been shown to be considerably longer than U–O in similar compounds.[1,2,15,16] Preliminary reports of the structure have already been published.[17]

EXPERIMENTAL

The compound was obtained from the reaction of $UO_2Cl_2,3H_2O$ or $UO_2(NO_3)_2,6H_2O$ with stoicheiometric amounts of H_2ensal,[14] by condensation of salicylaldehyde with ethylenediamine in presence of uranyl salts, or by reaction of a freshly prepared solution of the complex [UO_2-salicylaldehyde)$_2$(H_2O)] with the stoicheiometric quantity of ethylenediamine. These reactions occur at room temperature with methanol as solvent. I.r. spectra, elemental analysis, and molecular weights are identical for the products of all three reactions. Crystals from methanol, are red-yellow plates elongated along *c*. A single crystal (0·10 × 0·04 × 0·12 mm) was mounted with the *c* axis near the ϕ axis of the goniometer and data were collected on a Siemens AED-automated four-circle diffractometer with nickel-filtered Cu-K_α radiation and a Na(Tl)I scintilation counter. Accurate lattice and orientation parameters were obtained by least-squares treatment.[18] In these calculations the cell was assumed to be triclinic and the angles $\alpha = 90{\cdot}05°$, $\beta = 90{\cdot}02°$, and $\gamma = 97{\cdot}52°$ were derived and used in all orientation calculations.

Crystal Data.—$C_{17}H_{18}N_2O_5U$, $M = 568{\cdot}4$, Monoclinic, $a = 18{\cdot}695(15)$, $b = 9{\cdot}012(9)$, $c = 10{\cdot}652(10)$ Å; $\gamma = 97{\cdot}52°(5)$, $U = 1779{\cdot}2$ Å^3, $D_m = 2{\cdot}13$ (by flotation), $Z = 4$, $D_c = 2{\cdot}12$ g cm^{-3}, $F(000) = 1064$. λ(Cu-K_α) = 1·54178 Å; μ(Cu-K_α) = 359·3 cm^{-1}. Space group $P2_1/n$ (a non-standard orientation of $P2_1/b$) from systematic absences: $hk0$ for $h + k$ odd and $00l$ for l odd with equivalent positions $\pm(x,y,z)$; $\pm(1/2 + x,\ 1/2 + y;\ 1/2 - z)$. There were no systematic absences in the general set hkl; however, reflections with $h + k = 2n$ were generally stronger than those with $h + k = 2n + 1$ indicating that the heavy atoms are related by a translation of *ca.* $(a + b)/2$.

Intensity data were measured by use of the θ—2θ scan method.[19] A general reflection was remeasured every twenty reflections as a monitor of crystal stability and to normalize the intensities to a common basis. The normalization factor was essentially constant with time, with an overall variation of 3% in intensity. The usual 1/Lp corrections were applied to the intensities.

In the reciprocal space corresponding to $2\theta_{\max.}$ of 110° there are 2239 non-equivalent lattice sites excluding those prohibited by the space group, of which 1768 were considered

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observed having $I > 2\sigma(I)$.[19] Also, all reflections were remeasured with the same tube-current setting; the $|F_0|$ data were the best least-squares values derived from the two sets of measurements, using the method of Hamilton, Rollett, and Sparks.[20] The scale of the $|F_0|$ data and the overall temperature factor were estimated from a Wilson plot.

Solution and Refinement of the Structure.—The position of the uranium atom was determined from a three-dimensional Patterson synthesis and confirmed by least-squares refinement to R 0·23. A difference electron-density synthesis based upon the uranium signs, revealed the positions for all 25 non-hydrogen atoms and four least-squares cycles, computed with the anisotropic temperature factor of uranium, gave R 0·12. When anisotropic temperature factors were assigned to the atoms of the ' inner core,' the R decreased to 0·105, but this value was practically constant with any further weighting scheme in the least-squares procedure.

An absorption correction was then applied according to the method of Huber and Köpfmann.[21] Thirty reflections were measured, each in all possible positions arising for rotation of 10° around the corresponding reciprocal vector. We are able to measure 520 values of which 503 were used. The acentric half of the transmission surface was represented by 105 grid points, the number of variables being in this case 135 in 503 equations. The choice of this experimental absorption was justified since measurements of the geometrical shape of the crystal were not good, and the present maximum μR is 4·3 and it has been shown that the approximations in this model calculation are satisfactory for $\mu R \leqslant 4{\cdot}5$; also, the machine-time both on the four-circle diffractometer and on the computer is surprisingly short.

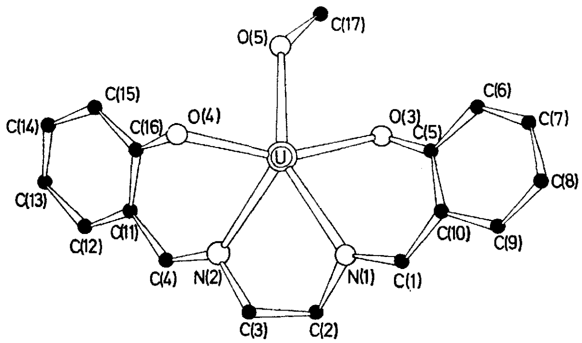

FIGURE 1 Projection of the molecule on to the mean plane of the co-ordination pentagon. The 0(1) and 0(2) atoms, indicated by the inner circle, overlap the uranium atom

The final parameters were obtained after five cycles of full-matrix least-squares refinement. The weighting scheme was $w = \{1 + [(|F_o| - b)/a]^2\}^{-1}$, where a and b were derived from a quadratic curve of best fit for $\langle|F_o| - |F_c|\rangle$ as a function of $|F_o|$; a was 36, and b 55. Zero weights were given to the seven reflections of highest intensity, apparently effected by extinction, and also to the unobserved reflections. The final R was 0·055.

A difference-Fourier map computed at this stage showed two peaks up to a maximum of 2 eÅ^{-3} in the vicinity of the uranium atom position, whilst elsewhere peaks were <0·6 eÅ^{-3}, occurring in some cases at the expected positions of the hydrogen atoms. However for the location of all hydrogen atoms some additional stereochemical considerations were needed. Scattering-factor curves were taken from ref. 22 and values of $\Delta f'$ and $\Delta f''$ used to correct for anomalous dispersion in the scattering factor of uranium were taken from ref. 23. Observed and calculated structure factors from the last cycle of refinement are listed in Supple-

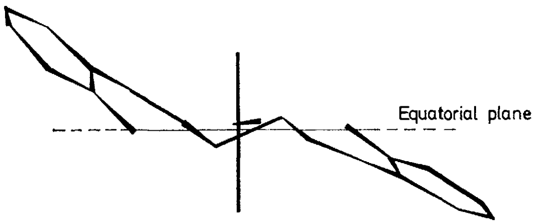

FIGURE 2 The ' stepped ' conformation of the molecule

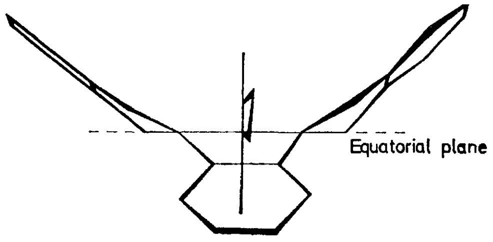

FIGURE 3 The ' boat ' conformation of [NN'-o-phenylenebis(salicylideneiminato)(UO_2)(EtOH)]

TABLE 1

Final fractional co-ordinates (× 10^4) and thermal parameters with standard deviations in parentheses

	x	y	z	$B/\text{Å}^2$
U	671(0)	5930(1)	2428(1)	*
O(1)	−53(7)	6032(14)	3472(11)	3·45(24)
O(2)	1392(8)	5779(15)	1376(12)	4·19(27)
O(3)	952(8)	8427(15)	2528(10)	4·07(25)
O(4)	95(7)	3676(14)	1633(11)	3·69(24)
O(5)	−88(7)	6757(15)	764(12)	4·10(26)
N(1)	1631(8)	6686(15)	4120(13)	3·09(27)
N(2)	940(7)	3769(14)	3807(11)	2·45(24)
C(1)	2100(9)	7921(19)	4148(15)	2·94(32)
C(2)	1689(11)	5621(22)	5144(17)	3·81(37)
C(3)	1602(11)	4015(22)	4578(18)	3·96(38)
C(4)	453(10)	2594(19)	4089(15)	3·07(33)
C(5)	1515(10)	9423(21)	2563(15)	3·09(33)
C(6)	1544(11)	1 0781(22)	1883(17)	3·82(37)
C(7)	2134(12)	1 1833(24)	1974(20)	4·68(42)
C(8)	2745(12)	1 1623(24)	2708(18)	4·00(40)
C(9)	2701(11)	1 0304(22)	3422(17)	3·99(38)
C(10)	2105(10)	9151(20)	3328(15)	2·77(32)
C(11)	−199(11)	2152(22)	3440(17)	3·75(37)
C(12)	−680(11)	1065(22)	4074(17)	3·91(39)
C(13)	−1338(11)	511(23)	3518(18)	4·09(40)
C(14)	−1458(14)	992(29)	2306(21)	5·48(49)
C(15)	−997(12)	2099(24)	1680(19)	4·33(43)
C(16)	−356(10)	2673(20)	2243(16)	3·10(33)
C(17)	−497(14)	8013(28)	938(22)	5·70(53)

* Anisotropic parameters for uranium in the form: $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + 2hka^*b^*B_{12} +$ *etc.*$)]$ with coefficients (× 10^3):

	B_{11}	B_{22}	B_{33}
U	2388(36)	2729(36)	2708(35)
	B_{12}	B_{13}	B_{23}
	−646(22)	−70(22)	291(22)

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mentary Publication No. SUP 20799 (3 pp., 1 microfiche).* Positional and thermal parameters are given in Table 1. The atom numbering system used and the configuration of the molecule are illustrated in Figures 1 and 2, while bond lengths and bond angles with their estimated standard deviations are listed in Table 2 (uncorrected for thermal motion). Equations of the principal planes and the deviations of atoms therefrom are given in Table 3.

TABLE 2

Bond lengths (Å) and angles (°), with standard deviations * in parentheses

(*a*) Distances

U–O(1)	1·763(13)	C(1)–C(10)	1·41(4)
U–O(2)	1·772(15)	C(4)–C(11)	1·41(3)
U–O(3)	2·245(14)	C(2)–C(3)	1·56(4)
U–O(4)	2·330(32)	C(5)–C(6)	1·42(4)
U–O(5)	2·447(25)	C(5)–C(10)	1·42(3)
U–N(1)	2·572(24)	C(6)–C(7)	1·36(3)
U–N(2)	2·542(47)	C(7)–C(8)	1·42(3)
O(3)–C(5)	1·29(2)	C(8)–C(9)	1·40(4)
O(4)–C(16)	1·32(3)	C(9)–C(10)	1·42(3)
O(5)–C(17)	1·46(3)	C(11)–C(12)	1·41(3)
N(1)–C(1)	1·32(2)	C(11)–C(16)	1·40(3)
N(2)–C(4)	1·34(2)	C(12)–C(13)	1·40(3)
N(1)–C(2)	1·47(4)	C(13)–C(14)	1·39(3)
N(2)–C(3)	1·48(2)	C(14)–C(15)	1·40(4)
		C(15)–C(16)	1·38(3)

(*b*) Angles

O(1)–U–O(2)	178·6(0·6)	O(3)–C(5)–C(6)	121·4(1·7)
O(3)–U–O(5)	78·3(0·4)	O(3)–C(5)–C(10)	118·6(1·6)
O(4)–U–O(5)	77·4(0·4)	C(6)–C(5)–C(10)	120·0(1·6)
O(3)–U–N(1)	68·8(0·5)	C(5)–C(6)–C(7)	120·1(1·9)
O(4)–U–N(2)	70·0(0·4)	C(6)–C(7)–C(8)	122·7(2·0)
N(1)–U–N(2)	66·2(0·4)	C(7)–C(8)–C(9)	116·9(1·8)
U–O(3)–C(5)	139·5(1·3)	C(8)–C(9)–C(10)	122·2(1·8)
U–O(4)–C(16)	126·7(1·0)	C(1)–C(10)–C(5)	124·5(1·6)
U–O(5)–C(17)	121·9(1·1)	C(1)–C(10)–C(9)	117·0(1·6)
U–N(1)–C(1)	126·9(1·1)	C(5)–C(10)–C(9)	117·8(1·6)
U–N(1)–C(2)	117·2(1·0)	C(4)–C(11)–C(12)	114·2(1·7)
C(1)–N(1)–C(2)	115·8(1·4)	C(4)–C(11)–C(16)	124·1(1·6)
U–N(2)–C(3)	116·9(1·0)	C(12)–C(11)–C(16)	121·7(1·7)
U–N(2)–C(4)	123·6(1·1)	C(11)–C(12)–C(13)	119·7(1·7)
C(3)–N(2)–C(4)	117·7(1·4)	C(12)–C(13)–C(14)	116·9(1·9)
N(1)–C(1)–C(10)	125·6(1·5)	C(13)–C(14)–C(15)	123·8(2·1)
N(2)–C(4)–C(11)	125·9(1·6)	C(14)–C(15)–C(16)	119·0(1·9)
N(1)–C(2)–C(3)	108·2(1·4)	O(4)–C(16)–C(11)	122·2(1·6)
N(2)–C(3)–C(2)	109·8(1·6)	O(4)–C(16)–C(15)	119·2(1·6)
		C(11)–C(16)–C(15)	118·6(1·7)

* Taking into account the accuracy of cell parameters.

The solution and refinement of the structure were carried out by use of the Crystal Structure Calculations System '*X*-Ray '70,'[24] integrated with the *ABSORP* program of Dr. G. Kopfmann. Calculations were done on the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), CDC 6600 computer.

DISCUSSION

The uranyl group is surrounded equatorially by a slightly irregular pentagon comprised of two oxygen and two nitrogen atoms of ensal and the oxygen atom of methanol. With respect to the equatorial plane these five atoms are in a slightly puckered arrangement [Table 3, plane (1)] similar to that in other compounds of this type.[1,2,16] This puckering is greater for six- than for five-co-ordinate uranyl complexes.† Consequently, in the present case the angles between a uranyl U–O bond and an equatorial bond are close to 90° (84·6—94·5°) and the angle between the normal to the equatorial plane and the line O(1)–U–O(2) is 1·7°.

TABLE 3

(*a*) Least-squares planes with the deviations (Å) of relevant atoms in square brackets. The equation of a plane *in direct* space is given by $PX + QY + RZ = S$

	P	*Q*	*R*	*S*
Plane (1):				
U, O(3), O(4), N(1), N(2)	14·5256	−1·7461	−6·6323	−1·6743
[U 0·003, O(3) − 0·091, 0(4) 0·087, N(1) 0·143, N(2) − 0·143, O(5) −0·140, C(2) − 0·265, C(3) 0·264]				
Plane (2):				
C(5)—(10), O(3), C(1)	8·9646	−4·5195	−8·0717	−4·9947
[C(5), 0·03, C(6) − 0·01, C(7) − 0·03, C(8) 0·02, C(9) 0·0, C(10) 0·06, O(3) 0·0, C(1) − 0·05, N(1) 0·11, U O·96]				
Plane (3):				
C(11)—(16), 0(4), C(4)	10·0962	−7·1611	−4·4575	−3·2569
[C(11) − 0·02, C(12) − 0·01, C(13) − 0·03, C(14) 0·05, C(15) 0·0, C(16), − 0·02, O(4) − 0·01, C(4) 0·03, N(2) − 0·19, U 1·39]				
Plane (4):				
U, C(3), C(4), N(2)	9·0769	−4·5315	−8·0274	−4·0062
[U 0·02, C(3) − 0·03, C(4) − 0·04, N(2) 0·09]				
Plane (5):				
U, C(1), C(2), N(1)	13·5215	−4·8415	−5·6123	−3·3296
[U 0·0, C(1) 0·01, C(2) 0·01, N(1) − 0·01]				

* The equation of least-squares line (L) defined by O(1), U, 0(2) in parametric form in direct space is:

$$X = 0{\cdot}0670 + 0{\cdot}0409\,T,$$
$$Y = 0{\cdot}5914 - 0{\cdot}0072\,T,$$
$$Z = 0{\cdot}2425 - 0{\cdot}0593\,T$$

[U 0·01, 0(1) 0·01, 0(2) 0·01]

(*b*) Angles (deg.) between the mean planes and between plane (1) and the line *L* (for a plane and a line, the angle is to the normal of the plane)

(1)–(2)	27·7	(2)–(3)	25·9
(1)–(3)	41·6	(2)–(5)	19·3
(1)–(4)	27·4	(3)–(4)	25·7
(1)–(5)	21·3	(1)–(*L*)	1·7

Comparison of the U–O distances in this and other compounds indicates that the U–O(1) (1·76) and U–O(2) (1·77 Å) apical distances, are consistent with values found previously.[25–27] It is our opinion that the number and nature of the equatorial ligands has little effect upon the apical bond length. Zachariasen[28,29] has suggested that the uranyl U–O distance varies as a function of its bond strength. However, if the uranyl oxygen atoms are attached to only one uranium atom, bond lengths are in the range 1·72—1·82 Å, and more accurate determinations reduce this range further.

On the other hand, if the U–O distance variation is real, though exaggerated by experimental error, it is not possible to find a generally applicable relationship between the apical bond length and the equatorial field.

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* See note about Supplementary Publications in Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are supplied as full size copies.)

† See ref. 29.

[24] '*X*-ray '70,' System of Programs, University of Maryland Technical Report, TR 646.

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[27] G. A. Barclay, T. M. Sabine, and J. C. Taylor, *Acta Cryst.*, 1965, **19**, 205.

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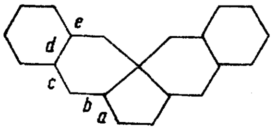
[29] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 526.

The $5f$ atomic orbitals (those with $m = 0$ and $m = \pm 1$) used by the uranium atom in UO_2^{2+} molecular orbitals are poorly involved in bond formation with the equatorial ligands.[30] In the equatorial plane these could be either covalent bonds between uranium and the atoms surrounding it (with orbitals having $m = \pm 2$ and $m = \pm 3$ playing the most important role), or bonds having a large electrostatic component. (In this case the electronic distribution of UO_2^{2+} is not appreciably influenced by the field of the equatorial ligands, since these are too far away).

TABLE 4

Comparison of bond distances (Å) in ensal complexes



	a	*b*	*c*	*d*	*e*
Present work	1·48	1·33	1·41	1·41	1·31
Ref. 4	1·455	1·310	1·440	1·405	1·330
Ref. 5	1·490	1·280	1·435	1·405	1·325
Ref. 6	1·476	1·315	1·441	1·416	1·347
Ref. 7	1·507	1·283	1·442	1·403	1·344
Ref. 8	1·467	1·288	1·445	1·412	1·332
Ref. 9	1·485	1·255	1·470	1·370	1·315
Ref. 10	1·455	1·325	1·410	1·397	1·345
Ref. 11	1·487	1·283	1·413	1·422	1·322
Ref. 12	1·476	1·295	1·443	1·413	1·340
Mean (excluding present work)	1·477	1·292	1·437	1·404	1·333

Accordingly, the electronic configuration of UO_2^{2+} can be depicted, in the limiting case, as having triple bonds between the uranium and each of the apical oxygens.[30] This configuration gives a very high stability to this molecule-ion, and is reflected in the absence of any measurable proton affinity for the uranyl oxygen atoms.[31]

The U–O(3) and U–O(4) equatorial distances (2·25 and 2·33 Å) are in the expected range for similar five-co-ordinate uranyl complexes with a set of O_3N_2 [1,2,15] or O_2N_3 [16] equatorial donors and are shorter than those in six-co-ordinate systems [25-27] This shortening could be expected on the basis of the bond length *vs.* bond strength curve for U^{VI}–O bonds,[29] although the empirical rules governing this variation in bond length are merely qualitative.

The U–O(3) distance (2·25 Å) is in agreement with the sum of the Pauling crystal radii (0·83 + 1·40 Å) [32] and of the Shannon crystal radii (0·87 + 1·40 Å),[33] as expected.[34]

The lengthening of the U–O(4) distance can be ascribed to the existence of a short hydrogen bond (2·58 Å) between O(4) and the methanol oxygen of a neighbouring molecule (Table 5), and may also account for the asymmetry in the U–O(3)–C(5) (139°) and U–O(4)–C(16) (127°) angles. Similar asymmetries also occur [1] in [*NN'*-*o*-phenylenebis(salicylideneiminato)(UO_2)(EtOH)] and can be ascribed to the partial polar contribution in the U–O equatorial bond, as well as to the hydrogen bond. This idea is consistent with the results in [(H_2O)(glyoxa)-(2-hydroxyanil)$_2(UO_2)$],[2] in which both ligand oxygen atoms are involved in hydrogen bonds, with U–O 2·33 and 2·36 Å, and U–O–C angles near to 120° (124·7 and 124·6°).

The U–O(5) distance (2·45 Å) corresponding to the neutral unidentate ligand, is in agreement with values found in this type of compound, irrespective of the equatorial c.n. The larger value for this U–O distance, in comparison with that of the negative multidentate ligand, may be explained by the decrease in the partial polar nature of this bond, as mentioned earlier.

The U–N(1) and U–N(2) distances (2·57 and 2·54 Å) are consistent with those reported previously.[1,2,15,16] U–N Distances are always remarkably longer than U–O equatorial distances and much greater than suggested by the difference in covalent radii.[32] In ensal complexes with $3d$ metals of known structure, there are two types of bonding to the metal. In the complexes [3-5] of Cu^{II} and of [10,11] Co^{II} the metal–nitrogen and –oxygen distances are roughly equivalent, while with titanium(IV) [34] and iron(III) [6-9] the metal–oxygen bonds are much shorter than metal–nitrogen bonds. This behaviour was tentatively explained by Pearson's [35] 'hard' and 'soft' acid–base concept.[36] Nitrogen would be expected to be bonded less strongly to a 'hard' acid (UO_2^{2+}), because oxygen has a relatively higher base-strength towards such an acid. This conclusion fits the observed data on 8-quinolinolate–metal complexes,[37-43] but in ensal complexes there are some deviations.[12,44]

TABLE 5

Geometry of the hydrogen-bond system (primed atoms refers to the molecule at $\bar{x}, 1 - y, \bar{z}$)

O(4) · · · O(5')	2·58 Å
U–O(4)–C(16)	126·7°
U–O(4) · · · O(5')	118·9°
C(16)–O(4) · · · O(5')	113·1°
C(17')–O(5') · · · O(4)	104·5°

The mean bond distances for our complex and for other ensal complexes with $3d$ transition-metals (Table 4) confirm Lingafelter's statement that the ligand molecule is

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relatively insensitive to the nature of the metal ion, even though the present work shows a small lengthening in *b* distance and a shortening in *c* and *e* distances.

The chelating ligands are bent away in opposite directions (' stepped ' conformation) with respect to the equatorial plane, the N(1) and N(2) imine atoms lying 0·11 and 0·19 Å out of planes (2) and (3) (Table 3), with the trigonal nature of the bonds at these atoms being preserved (Table 2).

The N(1)–C(2)–C(3)–N(2) group is in a near-gauche conformation, as observed in most compounds of this type [4,10,12] and its torsion angle is 51·8°. This conformation and the maintenance of the trigonal nature of the nitrogen cause the salicylaldehyde groups to adopt a ' stepped ' geometry.

In fact, in the analogous compound,[1] where a *cis*-conformation for the N–C–C–N group is fixed, a ' boat ' geometry is required (Figure 3). The deviation of the bridge carbons C(2) and C(3) from the equatorial plane is symmetrical (±0·26 Å), despite the unsymmetrical nature of the molecular step, shown by the different angles between the two halves of the ensal ligand and the equatorial plane (41·6 *vs.* 27·7°), and by the distance of the uranium atom from these planes (−1·39 *vs.* 0·96Å). Since this unsymmetrical arrangement of the ' stepped ' configuration is not linked to any asymmetry of the N(1)–C(2)–C(3)–N(2) group, we suggest that a principal role must be ascribed to the hydrogen bond at O(4) and to crystal packing contacts (Table 6). None of the intermolecular distances is sufficiently short to suggest any significant deviation from normal van der Waals interactions, the shortest being O(1) ··· C(4$^{\mathrm{I}}$) 3·01 Å.

TABLE 6

Intermolecular distances (Å) <3·5 Å

N(2) ··· O(1$^{\mathrm{I}}$)	3·36	O(1) ··· C(4$^{\mathrm{I}}$)	3·01
C(1) ··· C(13$^{\mathrm{I}}$)	3·28	O(4) ··· O(5$^{\mathrm{II}}$)	2·58
C(12) ··· N(1$^{\mathrm{I}}$)	3·45	C(15) ··· O(5$^{\mathrm{II}}$)	3·38
C(12) ··· C(1$^{\mathrm{I}}$)	3·48	C(16) ··· O(5$^{\mathrm{II}}$)	3·33
		O(4) ··· C(17$^{\mathrm{II}}$)	3·27

Roman numerals as superscripts refer to atoms in the equivalent positions, relative to the reference molecule at x, y, z: I $\bar{x}, 1 - y, 1 - z$; II $\bar{x}, 1 - y, \bar{z}$

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