# PREPARATION, CRYSTAL AND MOLECULAR STRUCTURE OF |UO₂(o-OC₆H₄-CH=N(CH₂)₂NH(CH₂)₂N(CH₃)₂)NO₃|·CH₂Cl₂

$$|UO_2(o-OC_6H_4-CH=N(CH_2)_2NH(CH_2)_2N(CH_3)_2)NO_3|\cdot CH_2Cl_2$$

G. BANDOLI* and D. A. CLEMENTE

Laboratorio di Chimica e Tecnologia dei Radioelementi C.N.R.-Via Vigonovese 52, 35100 Padova, Italy

and

M. BIAGINI CINGI

Istituto di Chimica Generale-Università di Parma, Italy

**Abstract**—The crystal and molecular structure of $|UO_2(o-OC_6H_4-CH=N(CH_2)_2NH(CH_2)_2N(CH_3)_2)NO_3|\cdot CH_2Cl_2$ has been determined from 3-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final conventional $R$ factor of 8·2 per cent. The material crystallizes in space group $Pbc2_1$ of the orthorhombic system, with four molecules in a cell of dimensions $a = 9·298(6)$, $b = 20·541(9)$ and $c = 10·925(8)$Å. The crystal consists of discrete monomeric molecules interspersed with $CH_2Cl_2$ molecules which do not interact with the "inner core" of the complex. The coordination around uranium is approximately pentagonal bipyramidal with uranyl oxygens in axial positions; four equatorial sites are occupied by the tetradentate Schiff base, nitrate group occupying the fifth site. The bond distances and angles reveal no surprises when compared with other analogous uranyl-Schiff bases complexes.

## INTRODUCTION

THE determination of the structure of $|UO_2(o-OC_6H_4-CH=N(CH_2)_2NH(CH_2)_2N(CH_3)_2)NO_3|\cdot CH_2Cl_2$ is part of a long-range series of studies[1] in this laboratory on the synthesis and characterization of uranyl complexes containing various multidentate Schiff bases. In order to gain more insight into the stereochemistry and to examine the planarity of the "inner core" of the complex, its bond lengths and valence angles and their dependence on the ligand, the detailed structure was undertaken.

## EXPERIMENTAL

*Preparation.* To 2 mmole of salicylaldehyde dissolved in 50 ml of absolute ethanol, 2 mmole of N-dimethyldiethylentriamine were added. To the yellow resulting solution 2 mmole of sodium hydroxide were added. The solution was stirred for 1 hr at room temperature and then poured into stoicheiometric ethanolic solution of uranyl nitrate hexahydrate (2 mmole). The resulting red solution was stirred for 2 hr; the solvent was evaporated at reduced pressure and the residue extracted with dichloromethane. The solution was then reduced at small volume and cooled at 0°C. The product, crystallized as red crystals, was filtered, washed with cold $CH_2Cl_2$ and dried under vacuum. A satisfactory elemental analysis has been obtained. A single crystal ($0·14 \times 0·10 \times 0·39$ mm) was mounted with the $c$ axis nearly coincident with the $\phi$ axis of the goniometer and data were collected on a Siemens AED-automated four-circle diffractometer with nickel-filtered Cu $K_\alpha$ radiation and a Na(Tl)I scintillation counter. Accurate lattice and orientation parameters were obtained by least-squares treatment[2].

*Crystal data.* $C_{13}H_{20}N_4O_5U\cdot CH_2Cl_2$, $M = 635·3$, Orthorhombic, $a = 9·298(6)$, $b = 20·541(9)$, $c = 10·925(8)$Å, $U = 2086·6$ Å³; $D_m = 2·09$ (by flotation in $CCl_4/BrCH_2CH_2Br$), $Z = 4$, $D_c = 2·07$ g cm⁻³, $F(000) = 1200$. $\lambda(Cu-K\alpha) = 1·54178$ Å; $\mu(Cu \ K_\alpha) =$

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*To whom correspondence should be addressed.

$338·5$ cm⁻¹. Space group $Pbc2_1$ or $Pbcm$ from systematic absences: $h0l$ for $l$ odd and $0kl$ for $k$ odd.

The crystals were brittle and tended to powder on prolonged exposure to X-ray and they were also prone to splitting under X-rays. Attempts to recrystallize the original crystal from a number of solvents under a variety of conditions failed to produce any more suitable single crystal.

Intensity data were measured by use of the $\theta$–$2\theta$ scan method and the intensities of 1395 independent reflections, accessible within the sphere bounded by $\sin \theta/\lambda \leq 0·5313$, were measured. Using the criterion $I \leq 2\sigma(I)$, 131 reflections were rejected as statistically insignificant and were treated as unobserved. Only the 1264 independent reflections were used in the structure solution and refinement.

The 432 reflection was used as a reference every twenty reflections as a monitor of crystal stability, and to normalize the intensities to a common basis; unfortunately, the net count of this reflection fell uniformly by about 20 per cent over the collection period (approx. 4 days) indicating slow radiation damage rather than random instability of the X-ray equipment. Although there was the possibility of radiation damage causing errors in the data, it was decided to collect all the data from the one crystal because of the difficulty in obtaining more suitable crystals for the diffractometer.

The data were scaled using the reference reflection and Lorentz and polarization corrections were applied. To avoid the risk of invalid correction, we report the data uncorrected for absorption. In fact, the measurements of the geometrical shape of the crystal were not good.

*Structure analysis.* With four formula weights in the unit cell either a mirror plane, a 2-fold axis, or a center of symmetry is imposed if the centrosymmetric space group $Pbcm$ is correct, but no symmetry is imposed if the space group is the noncentrosymmetric $Pbc2_1$. Indeed, from the inspection of the known part of the molecule and from the structure of analogous complexes[1], no crystallographic symmetry can be imposed to the molecule; hence the noncentric space group $Pbc2_1$ was assumed. The uranium atom was located from a 3-dimensional Patterson

function. The fractional $z$ coordinate of the uranium atom was set at 1/4 to fix the origin of the unit cell. Three cycles of least-squares refinement of scale factor and uranium $x$ and $y$ coordinates yielded the discrepancy conventional $R$ factor of 0·25. In this and succeeding refinement the function minimized was $\sum w(K|F_0| - |F_c|)^2$. In all calculations of $|F_c|$ the usual tabulation of the atomic scattering factors was used[3]; the values of $\Delta f'$ and $\Delta f''$ for U and Cl were those given by Cromer[4]. Subsequent difference Fourier maps, interspersed with least-squares refinements, led to positions of all remaining non-hydrogen atoms. It soon became apparent that a molecule of dichloro-methane of solvation was also present in the crystal. With all of the non-hydrogen atoms in the calculation, refinement of positional and isotropic thermal parameters led to $R = 0·119$.

A difference Fourier map calculated at this point revealed pronounced anisotropy in the motions of the heavy atom and the benzene carbons and the presence of some disorder in the solvent molecule. Refinement was therefore continued with introduction of anisotropic thermal parameters only for the uranium atom and the benzene ring. After seven more cycles the refinement gives the discrepancy factor $R = 0·082$. A final electron density difference map at this stage showed two peaks up to a maximum of 2 e.$\text{Å}^{-3}$ in the vicinity of the uranium atom position, whilst many of the smaller peaks were near the solvent molecule and the two $-CH_2-CH_2-$ bridging groups. Unfortunately, the $R$ value was practically constant with any further weighting scheme in the least-squares procedure and therefore the refinement was not pursued any further. Consequently, it was evident that no further information could be gained from the original data, certainly in error due to their poor quality.

In fact, the combined effects of crystal decomposition and the lack of absorption correction for the rather larger crystal ultimately prevented satisfactory refinement even though all the nonhydrogen atoms were easily located. Finally, there were two possible structure to consider: the enantiomorph A, the structure as hitherto assumed, and enantiomorph B, the mirror image of A

Table 1. Final fractional co-ordinates and thermal parameters with standard deviations in parentheses

|       | $\underline{x}$ | $\underline{y}$ | $\underline{z}$ | $U \ (\times 10^2)$ |
|-------|-----------------|-----------------|-----------------|---------------------|
| U     | .0573(1)        | .0504(1)        | .2500(0)        | ♦ |
| O(1)  | .0258(26)       | .0331(12)       | .4074(23)       | 4.54(55) |
| O(2)  | .0877(25)       | .0649(12)       | .0939(23)       | 3.88(59) |
| O(3)  | .0409(19)       | .1583(10)       | .2795(21)       | 4.39(57) |
| O(4)  | .3053(24)       | .0665(11)       | .2973(20)       | 5.41(59) |
| O(5)  | .4510(60)       | .0598(29)       | .4491(72)       | 15.44(252) |
| O(6)  | .2762(52)       | .1189(26)       | .4685(52)       | 13.54(164) |
| N(1)  | -.2057(23)      | .0835(11)       | .2375(25)       | 3.77(62) |
| N(2)  | -.1218(32)      | -.0416(13)      | .1987(27)       | 3.71(66) |
| N(3)  | .1871(42)       | -.0661(19)      | .2213(30)       | 4.18(112) |
| N(4)  | .3449(38)       | .0839(18)       | .4021(35)       | 6.65(91) |
| C(1)  | -.2606(38)      | .1309(18)       | .3057(34)       | 5.42(96) |
| C(2)  | -.1811(32)      | .1829(13)       | .3678(29)       | ♦ |
| C(3)  | -.2662(58)      | .2202(18)       | .4507(33)       | ♦ |
| C(4)  | -.1865(52)      | .2692(17)       | .5096(54)       | ♦ |
| C(5)  | -.0429(36)      | .2777(16)       | .4966(38)       | ♦ |
| C(6)  | .0358(50)       | .2429(17)       | .4146(32)       | ♦ |
| C(7)  | -.0385(33)      | .1933(14)       | .3476(35)       | ♦ |
| C(8)  | -.3144(42)      | .0369(19)       | .1845(36)       | 5.35(93) |
| C(9)  | -.2733(34)      | -.0313(16)      | .2317(28)       | 4.39(89) |
| C(10) | -.0736(60)      | -.1074(38)      | .2128(91)       | 13.33(233) |
| C(11) | .0828(41)       | -.1161(21)      | .1791(38)       | 4.73(96) |
| C(12) | .3067(51)       | .0584(22)       | .1329(47)       | 7.11(123) |
| C(13) | .2509(60)       | -.0863(30)      | .3411(57)       | 8.49(164) |
| C(14) | .3206(63)       | .2173(31)       | .1321(63)       | 12.22(183) |
| Cl(1) | .4142(21)       | .1648(11)       | .0322(22)       | 15.09(71) |
| Cl(2) | .4437(16)       | .2620(10)       | .2235(23)       | 14.69(79) |

♦Anisotropic thermal parameters $(\times 10^2)$. These values were obtained from $\beta_{ij} = 2\pi b_i b_j U_{ij}$, where $\beta_{ij}$'s appear as a temperature effect through $\exp-[(\beta_{11}h^2 + 2\beta_{12}hk + \cdots)]$ in the structure-factor expression and $b_i$ are the reciprocal lattice vectors.

|       | $\underline{U}_{11}$ | $\underline{U}_{22}$ | $\underline{U}_{33}$ | $\underline{U}_{12}$ | $\underline{U}_{13}$ | $\underline{U}_{23}$ |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| U     | 372(7)    | 259(6)    | 415(7)    | -51(7)    | -4(12)    | -32(9)    |
| C(2)  | 582(208)  | 300(139)  | 572(178)  | 259(136)  | -83(162)  | 206(144)  |
| C(3)  | 1432(362) | 248(201)  | 352(195)  | 383(215)  | -43(219)  | -174(167) |
| C(4)  | 1543(385) | 602(269)  | 618(333)  | 558(226)  | -410(355) | -65(297)  |
| C(5)  | 905(231)  | 253(156)  | 649(209)  | -56(132)  | 40(194)   | -228(200) |
| C(6)  | 1418(403) | 162(167)  | 403(203)  | 212(216)  | 40(218)   | 76(176)   |
| C(7)  | 611(192)  | 276(174)  | 446(219)  | 41(136)   | 116(156)  | 244(166)  |

Table 2.

reflected across a plane at $z = 1/4$. Two cycles of least-squares refinement with $(\bar{h}\bar{k}\bar{l})$ assumed in place of $(hkl)$ gave a higher discrepancy factor $R = 0.094$.

Hence our original arbitrary choice of enantiomorph A is correct, also by an assessment of the relative stereochemical plausibilities of the two structure (expecially the geometry of the equatorial co-ordination plane (1)).

The positional and thermal parameters of enantiomorph A obtained from the last cycle of least-squares refinement are listed in Table 1 together with their associated standard deviations as estimated from the inverse least-squares matrix.

Observed and calculated structure factors from the last cycle of refinement are in Table 2.

The solution and refinement of the structure were carried out using the Crystal Structure Calculations System X-Ray '70

described by J. M. Stewart in the University of Maryland Technical Report TR 646. The calculations were carried out on the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), CDC 6600 computer.

## RESULTS AND DISCUSSION

The $^1$H NMR spectra indicated that the Schiff base acts as quadridentate ligand, while the i.r. data were not a good guide to distinguish, by means of the selection rules alone, between unidentate or bidentate coordination mode for the nitrate ion. Therefore, an X-ray investigation was necessary to elucidate the exact coordination geometry.

The structure consists of discrete, monomeric molecules of uranyl-Schiff base complex interspersed

Table 3. Distances (Å) and angles (°), with standard deviations in parentheses

**a) Bond lengths**

| | | | | | |
|---|---|---|---|---|---|
| U | - O(1) | 1.78(2) | N(3) | - C(13) | 1.50(6) |
| U | - O(2) | 1.75(2) | N(4) | - O(5) | 1.22(6) |
| U | - O(3) | 2.26(2) | N(4) | - O(6) | 1.21(6) |
| U | - O(4) | 2.39(2) | C(1) | - C(2) | 1.47(4) |
| U | - N(1) | 2.54(2) | C(2) | - C(3) | 1.43(5) |
| U | - N(2) | 2.58(3) | C(2) | - C(7) | 1.36(4) |
| U | - N(3) | 2.70(4) | C(3) | - C(4) | 1.41(5) |
| O(3) | - C(7) | 1.27(4) | C(4) | - C(5) | 1.35(5) |
| O(4) | - N(4) | 1.26(4) | C(5) | - C(6) | 1.36(4) |
| N(1) | - C(1) | 1.33(4) | C(6) | - C(7) | 1.43(4) |
| N(1) | - C(8) | 1.51(4) | C(8) | - C(9) | 1.54(4) |
| N(2) | - C(9) | 1.47(4) | C(10) | - C(11) | 1.51(6) |
| N(2) | - C(10) | 1.43(6) | C1(1) | - C(14) | 1.77(5) |
| N(3) | - C(11) | 1.49(5) | C1(2) | - C(14) | 1.77(5) |
| N(3) | - C(12) | 1.48(5) | | | |

**b) Angles**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| O(1) | - U | - O(2) | 178.2 (1.1) | C(12) | - N(3) | - C(13) | 107.6 (3.0) |
| O(3) | - U | - N(1) | 71.3 (0.7) | O(4) | - N(4) | - O(5) | 120.5 (3.6) |
| N(1) | - U | - N(2) | 64.1 (0.8) | O(4) | - N(4) | - O(6) | 124.3 (3.2) |
| N(2) | - U | - N(3) | 67.3 (1.0) | O(5) | - N(4) | - O(6) | 114.7 (3.9) |
| N(3) | - U | - O(4) | 73.5 (1.0) | N(1) | - C(1) | - C(2) | 126.9 (2.7) |
| O(4) | - U | - O(3) | 84.1 (0.7) | C(1) | - C(2) | - C(3) | 113.9 (2.7) |
| U | - O(3) | - C(7) | 132.6 (1.9) | C(1) | - C(2) | - C(7) | 122.0 (2.5) |
| U | - O(4) | - N(4) | 121.4 (2.1) | C(3) | - C(2) | - C(7) | 124.0 (2.6) |
| U | - N(1) | - C(1) | 122.4 (2.0) | C(2) | - C(3) | - C(4) | 112.5 (3.5) |
| U | - N(1) | - C(8) | 119.7 (1.9) | C(3) | - C(4) | - C(5) | 124.3 (3.4) |
| C(1) | - N(1) | - C(8) | 115.0 (2.2) | C(4) | - C(5) | - C(6) | 122.1 (3.3) |
| U | - N(2) | - C(9) | 117.4 (1.9) | C(6) | - C(7) | - C(2) | 119.9 (2.8) |
| U | - N(2) | - C(10) | 117.8 (2.5) | O(3) | - C(7) | - C(6) | 114.7 (2.6) |
| C(9) | - N(2) | - C(10) | 114.2 (2.9) | O(3) | - C(7) | - C(2) | 125.2 (2.5) |
| U | - N(3) | - C(11) | 110.9 (2.3) | N(1) | - C(8) | - C(9) | 106.4 (2.4) |
| U | - N(3) | - C(12) | 108.5 (2.3) | C(8) | - C(9) | - N(2) | 106.7 (2.4) |
| U | - N(3) | - C(13) | 108.8 (2.6) | N(2) | - C(10) | - C(11) | 112.7 (3.7) |
| C(11) | - N(3) | - C(12) | 111.2 (2.7) | C(10) | - C(11) | - N(3) | 118.1 (3.5) |
| C(11) | - N(3) | - C(13) | 109.8 (3.0) | C1(1) | - C(14) | - C1(2) | 110.2 (2.2) |

*Taking into account the accuracy of cell parameters.

**c) 'Bite' distances and contacts distances within the 'inner core'**

| | | | | | | |
|---|---|---|---|---|---|---|
| N(1) | - N(2) | 2.72 | O(1) | - N(2) | 3.07 |
| N(2) | - N(3) | 2.93 | O(1) | - N(3) | 3.25 |
| N(3) | - O(4) | 3.05 | O(2) | - O(3) | 2.83 |
| O(4) | - O(3) | 3.11 | O(2) | - O(4) | 3.00 |
| O(3) | - N(1) | 2.80 | O(2) | - N(1) | 3.17 |
| O(1) | - O(3) | 2.94 | O(2) | - N(2) | 3.15 |
| O(1) | - O(4) | 2.95 | O(2) | - N(3) | 3.17 |
| O(1) | - N(1) | 3.03 | | | |

with solvent molecules of dichloromethane. Projection of the molecule on to the mean plane of the coordination pentagon is given in Fig. 1 and the projection down a direction perpendicular to the uranyl group in Fig. 2.

Table 3 gives the most significant distances and angles with their standard deviations which have been estimated using the diagonal approximation. Equations of the

principal planes and the deviations of atoms therefrom are given in Table 4.

From Fig. 1 it is clear that the coordination about uranium is that of a pentagonal bipyramid with uranyl oxygens in axial positions, four equatorial sites occupied by the quadridentate Schiff base, nitrate group occupying the fifth site.

Table 4.

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 $\underline{P}\underline{X} + \underline{Q}\underline{Y} + \underline{R}\underline{Z} = \underline{S}$

| | $\underline{P}$ | $\underline{Q}$ | $\underline{R}$ | $\underline{S}$ |
|---|---|---|---|---|

Plane (1):
U,O(3),O(4),N(1),N(2),N(3)    -1.301    -3.736    10.634    2.417
[U -0.02;O(3) -0.09;O(4) 0.10;N(1) 0.06;N(2) 0.01; N(3) -0.0;O(1) 1.76; O(2) -1.77;C(3) -0.18;C(9) 0.52; C(10) 0.34;C(11) -0.19]

Plane (2):
C(2)—(7), C(1), O(3)    -1.919    13.185    -8.068    -0.221
[C(2) 0.01;C(3) 0.0;C(4) 0.02;C(5) -0.04;C(6) 0.01;C(7) 0.04;C(1) -0.02; O(3) -0.02 ;N(1) -0.20]

Plane (3):
U, N(2), C(10), C(11), N(3)    -0.406    -3.444    10.760    2.468
[U 0.02;N(2) -0.14;C(10) 0.22;C(11) -0.17; N(3) 0.06]

Plane (4):
U, N(1), C(8), C(9), N(2)    -1.081    -1.631    10.816    2.538
[U 0.02;N(1) 0.12;C(8) -0.26;C(9) 0.31;N(2) -0.19]

Plane (5):
U, N(1), C(1), C(2), C(7), O(3)    0.474    -8.291    9.980    1.822
[U 0.28;N(1) -0.24;C(1) 0.02;C(2) 0.25;C(7) 0.03;O(3) -0.33]

Plane (6):
O(4), N(4), O(5), O(6)    4.891    15.774    -3.993    1.368
[O(4) -0.01;N(4) 0.03;O(5) -0.01;O(6) -0.01]

Plane (7):
U , C(1), C(8), N(1)    1.251    10.964    -9.121    -1.629
[U -0.03 ;C(1) -0.05 ; C(8) -0.04 ; N(1) 0.12]

Plane (8):
N(1), C(8), C(9)    -5.428    2.763    8.747    3.423

Plane (9):
C(8), C(9), N(2)    2.632    8.196    9.528    1.232

Plane (10):
N(2), C(10), C(11)    2.445    3.997    10.324    1.587

Plane (11):
C(10), C(11), N(3)    -1.396    10.683    -9.188    -3.001

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

$$\underline{X} = 0.0569 - 0.0175 \, T$$
$$\underline{Y} = 0.0493 - 0.0090 \, T$$
$$\underline{Z} = 0.2504 + 0.0887 \, T$$

[U 0.02, O(1) 0.01, O(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)

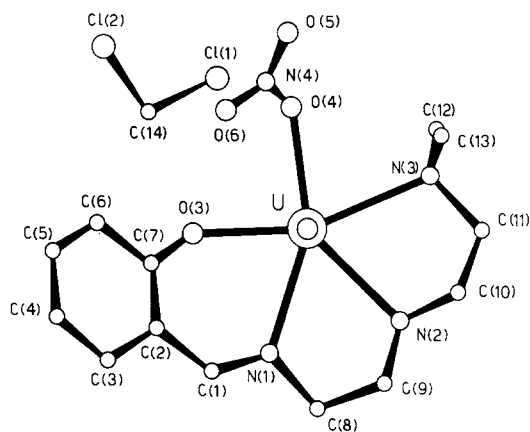| | | | | | |
|---|---|---|---|---|---|
| (1) - (2) | 36.2 | | (3) - (4) | 6.9 |
| (1) - (3) | 6.0 | | (3) - (5) | 15.3 |
| (1) - (4) | 6.2 | | (4) - (5) | 21.5 |
| (1) - (5) | 17.2 | | (9) - (10) | 12.5 |
| (1) - (6) | 55.3 | | (8) - (9) | 54.1 |
| (2) - (3) | 34.4 | | (10) - (11) | 42.9 |
| (2) - (4) | 40.7 | | (1) - (L) | 1.3 |
| (2) - (5) | 19.2 | | | |

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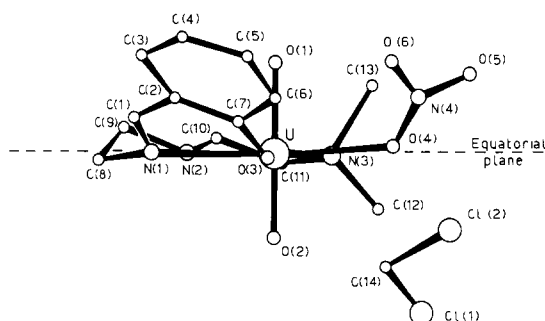


Fig. 2. Projection of the molecule down a direction perpendicular to the uranyl group.

The dichloromethane molecule does not interact with the "inner core" of the complex neither with its external portion, being the shortest Cl---C separation 3·67 Å. The rather high temperature factor of the solvent atoms may be due truly to a high rigid body motion or to some disorder of the molecule, but this question has not been analysed, as beyond our aims. The C–Cl distances are equal and compare well with tabulated values[5].

Although the deviations of the donor atoms from the least-squares equatorial mean plane are of the same order as the e.s.d.'s, their regularly alternating disposition (N(2) + 0·01, N(3) −0·06, 0(4) +0·10, 0(3) −0·09 and N(1) +0·06 Å) suggests a slightly puckered arrangement similar to that in other compounds of this type[1, 6]. The uranyl group is nearly perpendicular to the coordination pentagon (Table 4).

The bond distances and angles reveal no surprises when compared with other analogous uranyl-Schiff bases complexes[1]. In fact, as expected on the ground of the previous uranyl structure determinations, the apical U–O

distances are as assumed and are, as usual, considerably shorter than the equatorial U–O bonds.

The U–O(3) (2·26(2)Å) is in agreement with the sum of the Pauling crystal radii (0·83 + 1·40 Å)[7] and of the Shannon crystal radii (0·87 + 1·40 Å)[8], as expected ([9], Table 7 of [1c]). The U–O(4) distance (2·39(2) Å) are significantly shorter than in uranyl nitrates[10], probably because of the different bonding mode of nitrate groups. The U–N bond lengths are considerably longer than the U–O distances: U–N(1) 2·54, U–N(2) 2·58 and U–N(3) 2·70 Å.

The U–N(1) and U–N(3) distances are as expected (Table 7 of [1c]), being N(1) in $sp^2$ hybridization (Table 3 and plane (7) of Table 4) and N(3) in $sp^3$ hybridization. The U–N(2) distance calls for some comment, being shorter than the expected value for U–N($sp^3$) with the angles involving N(2) atom nearest to 120°. It may be qualitatively accounted for in terms of changes in the hybridization of nitrogen.

Finally, the molecules are packed together mainly by van der Waals forces and there is no abnormal feature in the packing. (Since none of the contacts is substantially shorter than normal van der Waals contacts, any contacts table is reported).

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