# PREPARATION, CRYSTAL AND MOLECULAR STRUCTURE OF |UO<sub>2</sub>(*o*-OC<sub>6</sub>H<sub>4</sub>-CH=N(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)NO<sub>3</sub>|·CH<sub>2</sub>Cl<sub>2</sub>

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Abstract—The crystal and molecular structure of  $|UO_2(o-OC_6H_4-CH=N(CH_2)_2NH(CH_3)_2)NO_3|-CH_2CI_2$ 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  $Pbc_2$ , of the orthorhombic system, with four molecules in a cell of dimensions  $a = 9\cdot298(6)$ ,  $b = 20\cdot541(9)$  and  $c = 10\cdot925(8)$ Å. The crystal consists of discrete monomeric molecules interspersed with CH<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub> and dried under vacuum. A satisfactory elemental analysis has been obtained. A single crystal  $(0{\cdot}14{\times}0{\cdot}10{\times}$ 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.  $C_{13}H_{20}N_4O_5U \cdot CH_2Cl_2$ ,  $M = 635 \cdot 3$ , Orthorhombic,  $a = 9 \cdot 298(6)$ ,  $b = 20 \cdot 541(9)$ ,  $c = 10 \cdot 925(8)$ Å,  $U = 2086 \cdot 6$ Å<sup>3</sup>;  $D_m = 2 \cdot 09$  (by flotation in CCl<sub>4</sub>/BrCH<sub>2</sub>CH<sub>2</sub>Br), Z = 4,  $D_c = 2 \cdot 07$  g cm<sup>-3</sup>, F(000) = 1200.  $\lambda$  (Cu-K $\alpha$ ) = 1 · 54178 Å;  $\mu$  (Cu K $_{\alpha}$ ) = 338.5 cm<sup>-1</sup>. Space group Pbc2, 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  $\theta/\lambda \le 0.5313$ , were measured. Using the criterion  $I \le 2\sigma(I)$ , 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. The uranium atom was located from a 3-dimensional Patterson

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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 isotopic 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.Å<sup>-3</sup> 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

	×	Y	1	U (x10 <sup>2</sup> )	
U	.0573(1)	.0504(1)	. 2500(0)	•	
0(1)	.0258(26)	.0331(12)	.4074(23)	4.54(55)	
0(2)	.0877(25)	.0649(12)	.0939(23)	3.88(59)	
0(3)	.0409(19)	.1588(10)	.2795(21)	4.39(57)	
0(4)	.3053(24)	.0665(11)	.2973(20)	5.41(59)	
0(5)	.4510(60)	.0598(29)	.4491(72)	15.44(252)	
0(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)	1151(21)	.1791(38)	4.73(96)	
C(12)	.3067(51)	.0584(22)	.1329(47)	7.11(123)	
C(13)	.2509(60)	0863(30)	.3:11(57)	8.49(164)	
C(14)	. 3206 (63)	.2178(31)	.1321(63)	12.22(153)	
C1(1)	.4142(21)	.1648(11)	.0322(22)	15.09(71)	
C1(2)	.4437(16)	.2620(10)	.2235(23)	14.69(79)	

•Anisotropic thermal parameters  $(x10^2)$ . These values were obtained from  $\beta_{ij}=2u\underline{b}_i\underline{b}_j\underline{U}_{ij}$ , where  $\beta_{ij}$ 's appear as a temperature effect through  $\exp-[(\beta_{11}h^2+2\beta_{12}hk+\beta_{11})]$  the structure-factor expression and  $b_i$  are the reciprocal lattice vectors.

	<u>U</u> 11	<u>U</u> 22	<u>U</u> 33	<u>U</u> 12	<u>U</u> 13	<u>U</u> 23
υ	372(7)	259(6)	415(7)	-51(?)	-4(12)	-32(9)
C(2)	582(208)	300(139)	572(178)	259(136)	-83(162)	20ú(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)	3418(403)	162(167)	403 (203)	212(216)	40(218)	76(176)
C(7)	611(192)	276(174)	446(219)	41(136)	116(156)	Z44(166)

Table 2.

"+1010 1 2220 J34 981 2 1995 23_7 972 3 1834 20_4 983 4 744 744 983 5 347 61 978	5 553 546 919 6 653 687 946 7 634 686 953 8 482 714 955 **13.0	5 452 546 927 5 757 847 946 7 1260 1264 956 A 1253 1214 952 9 950 930 959 	L 247 J26 969 2 545 952 953 Higiz 6 3543 3963 969 L 2367 3268 997	0 1784 1644 955 1 1644 1460 965 2 1302 1137 983 3 449 685 959 4 184 86 804 5 390 481 943 5 433 594 971	2 1715 1548 969 3 1081 1996 961 4 144 100 943 5 479 518 945 6 754 595 945 7 1073 1103 955 7 1073 1103 955	71.14 0 992V 340 440 1 175V 6110 405 2 1544 68 403 3 715 64 978 4 304 41 492	۰۷۵۵۰۰ ۲ ۲۰۰۵ ۲۵۵۰ ۲۵۵۰ ۲۰۰۵ ۲۵۵۱ ۲۵۵ ۲۰۰۵ ۲۵۱۵ ۲۵۵ ۲۰۰۹ ۲۵۵۵ ۲۰۰۵	4 357 207924 n 42. 416923 7 66n 316927 9 4-2 53.936 H446	-1410 5 857 /93 462 1 263 258 464 2 445 522 464 3 241 376 464 4 621 179 453	44,2,7 1 1170 1104 7 1 1140 1251 977 2 445 342 470 3 413 347 945 4 144 51 114
6 1227 1151 959 7 1241 1447 955 4 1374 1447 955 4 1314 1447 958 4 1141 1447 958 4 1141 1447 958	) 514 503 043 > 1319 [14] 043 3 1330 [263 445 • 1254 [312 042 5 1022 [124 040 6 605 014 040 7 528 556 057	1 1157 4×4 041 > 4×9 904 920 3 971 904 940 4 1436 1561 950 5 840 1013 941 4 699 717 986	2 1442 1816 467 3 1845 1876 31 4 794 786 141 5 778 777 454 6 940 183 4936 7 1303 1257 958 8 1922 1316 939	7 765 747 953 8 477 707 952 441342 1 475 508 968 2 1914 1013 969	9 694 852 961 4,7,3 1 642 463 993 2 819 899 936 3 787 969 696	5 243 2424 6 1205 9495 7.1144 142.465 H 1264 142.465 9 1035 9470 milite	4 721 820 420 7 554 522 471 -1114.4 1 750 303 472	1 1045 872 473 2 1374 1195 417 3 1737 1544 847 4 1544 3414 908 5 1344 3404 908 5 1344 3404 908 5 1344 3404 909 5 000 1078 921 7 550 664 920	5 1018 106 469 5 317 316 476 7 318 226 406 6 405 433 476 7 4940	5 125- 151 972 A 174 363 966 7 445 571 995 
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1 982 614 978 2 286 258 926 3 285 274 859 8 232 245 87 6 218 286 868	2 1101 1082 945 3 531 581 941 H+21+0 1 192 236 978 2 307 307 948	8 5)7 540 046 H+13+1 1 JA1 169 906 2 716 704 950 3 043 914 902	8 344 337 4 9 159+ 79 944 	H.20,2 0 1264 1302 961 1 1223 1212 969 2 993 966 977 3 513 569 967 H.21,2	* 272 337 927 7 141 444 542 H,13,3 2 445 437 928 3 932 445 437 928 4 444 759 447	6 1108 13 889 1 935 72- 979 2 558 53- 878 3 118 8- 24 2 24 24 5 212 21 858	- 112 272 044 - 2354 1832 7 1 1324 1162 14 7 429 1000 044 3 600 658 446		7 736 784 964 H.11+0 1 210 154 78 2 365 321 990 3 472 507 939 5 430 449 967	1 624 503 * 2 1122 1463 979 3 1265 1396 963 4 1323 1276 976 5 1316 1059 965 5 415 809 959
8 520 430 068 9 214 254 949 Hu7.0 1 1162 1043 977 2 19(3 1766 977	H.L.) 1 1208 (235 6 2 1335 (770 944 3 2164 2651 943 4 2373 2597 942 5 1959 2063 973	8 463 743 901 5 731 820 009 6 547 622 957 7 742 274 911 H+18+1 0 2320 1764 979	2 034 032 010 3 273 158 157 4 147* 34 917 5 151* 51 956 6 299 262 950 7 320 342 934 8 48* 431 940 9 27* 288 499	1 212 105 3+ 2 199 180 955 ++1+3 1 405 236 26	5 402 701 941 6 453 553 955 7 267 264 957 1 344 352 964 2 485 637 962 3 432 964 4 455 637 962 4 455 752 957	6 157 12- 430 7 3×1 33 4×3 8 +32 3× 4×4 × 7×4 1 1300 40. 11	<ul> <li>⇒ 219</li> <li>≥16</li> <li>≈ 273</li> <li>≥74</li> <li>≥74</li> <li>≥74</li> <li>≥74</li> <li>≥74</li> <li>≥74</li> <li>≥74</li> <li>≈ 510</li> <li>≈ 510</li></ul>	17+5 1 149 333 972 2 443 517 945 3 543 565 945 4 543 614 949	5 392 396 968 5 260 327 956 *+12+0 0 1132 1089 968 1 1115 1083 962	-+14,7 0 323 317 428 1 167* 193 233 2 169 173 65 3 167* 25 679 4 173 121 910
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4 206 2/c 970 5 470 41 971 6 840 4/3 955 7 883 905 985 6 1199 1007 981 941140	4 058 942 944 7 1720 1247 945 9 126 196 942 9 958 907 943 *.5.1	5 An5 764 980 1 Tao 704 970 2 An2 611 975 3 133 317 987 4 1408 38 885 4 143 175 978	0 2491 2595 957 1 2430 2116 979 3 1714 1535 483 3 1462 1035 980 4 257 252 44 5 447 513 940	2 130 1510 114 3 1023 1033 083 4 323 344 930 5 483 348 94 6 854 850 7 1052 1050 954 6 1214 1139 957 9 952	4 633 (13 75) 5 587 693 953 H,18,3 0 666 673 951 1 798 766 977 2 613 566 8	5 241 2 475 6 66 0, 473 7 614 5, 405 8 434 4, 404 	3 -24 - 144 - 424 4 -27 - 307 -40 5 -33 -335 -5 4 -75 - 724 -27 7 -46 - 920 -460 - 412 -904 -265 - 412 -904 -265	4+2+5 1 51+4 (435 9)( 1 140( 1853 922 2 15+4 1197 922 1 682 3+1 93 1 682 3+1 93	9 121 943 424 9 221 324 925 9 121 324 925 9 121 424 9 121 424	1 52 244 2 91 750 3 84 764 4
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1 101 14- 05 2 174 179 963 3 304 309 970 4 592 4-7 991 5 469 30 993 6 349 2 - 25 7 185 1 - 72		4 922 937 967 4 745 dij 974 4 69 dij 974 4 69 dij 974 1 115 ji66 91 1 115 ji66 94	) 174* 40 12) 2 277 243 946 3 371 408 931 4 297 336 918 5 204 J25 928	2 465 656 982 H,1,9 1 462 387 976 2 668 737 989 3 951 964 965	0 007 1010 076 1 1120 1135 762 2 036 105 776 3 406 305 776 4 1710 70 6 5 104 167 761	H.84.4 0 724 5d 17 1 858 5d 994 2 537 44 972 2 54 2.4 1 4 1574 7, 849 1 6, 64 45 1 574 7, 849	: 558 547 -45 2 .79 44. 943 1 .71 278 445 1 .1349 1 .747 253 361	1 313 324 408 4 370 122 934 ~.3410 1 252 225 991 2 418 495 996		-+++++++ 0 425 511 972 1 515 527 970 2 399 412 950 3 213 195 950 +3412
H+2+8 0 1034 (1)34 VSH 1 1124 (124 VS) 3 815 024 VS 3 470 524 3 4 350 144 14	H:5:8 1 ale aja qen 2 432 Hin ves 1 112 jine 4ai 1 111 Lidz gao 5 i:41 1005 ves	2 715 804 949 1 440 464 9/7 4 214 177 906 4 143 131 997 6 349 414 948 H1946	U 826 837 950 1 464 853 963 2 722 733 963 3 391 438 961 4 158 82 980	- 107070 418 472 5 1015 A49 966 6 703 507 960 	H,5,7 1 157+ 59 239 2 149+ 62 790 3 147+ 62 132 4 144+ 45 757 5 145+ 113 844	3 104- 133 470 	2 167 365 274 Hr0,10 2 902 956 366 1 776 843 966 2 721 694 873 3 425 649 957	3 kij 651 954 4 741 723 949 H44410 0 248 305 921 1 146 244 919 2 14 174 94	0 den 428 962 1 /92 /41 961 2 508 608 662 3 350 362 666 509,10	1 144 174 973 2 153 357 943 
1 444 11 479	- +03 707 444 +,6,8 r 478 546 919 1 427 458 919 2 330 304 911 2 326 106 97	1 244 300 942 2 244 223 9 3 241 224 44 4 310 2471040 5 326 272 943 	H:13:8 1 327 344 954 2 002 613 941 3 550 727 934 4 005 746 948 H:14:4	2 523 584 955 3 219 209 974 4 1699 56 17 5 1599 74 857 6. 350 288 928 H:3,9	H:6.9 0 1124 1110 765 1 1086 1571 950 2 810 797 953 3 355 390 749 4 104.0 40 793	H-1014 0 1674 0 12 1 1684 12 894 3 1954 1-4 922 3 1644 34 977	4 194 199 958 4 143 123 9 ~41410 1 1814 55 339 2 195 191 970	1 172* 151 939 1 173* 151 939 1 173* 15 850 	1 145 189 955 2 CD4 149 972 H+1D+16	2 542 ADD 950 M-5411 1 1AU 66 ADJ 2 1574 48 232
5 942 944 954	4 152 77 914 5 1760 24 181 6 190 188 805	5 1242 1361 976 1 1231 1317 975 2 962 965 975	u Juv 231 46 1 240 178 67 2 140 95 75	1 253 297 962 2 459 552 954 3 537 635 945 4 622 611 948	- 1/3- 174 449 H17,8 3 1704 136 947	Artifed F 484 - 471 480 F 848 - 0-5 484	• 104 276 943 • 287 236 445	4 772 827 932 4 7k0 834 940 4,4,10	1 /60 /68 951 2 06/ 634 960 Helets	-4,6,11 0 797 324 945 1 754 783 965

reflected across a plane at z = 1/4. Two cycles of least-squares refinement with (hkl) 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 <sup>1</sup>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

-									and the second se		
a)	Bond	length	s								
	U	- 0()	.)	1.78(	2)	N(3)	- C(13)	1.	50(6)		
	U	- 0(2	5	1.75(	2)	N(4)	- 0(5)	1.	22(6)		
	U	- 0(3	0	2.26(	2)	N(4)	- 0(6)	1.	21(6)		
	U	- 0(-	1)	2.39(	2)	C(1)	- C(2)	1.	47(4)		
	U	- N()	)	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	5)	2.70(	4)	C(3)	- C(4)	1.	41(5)		
	0(3)	- C(3	')	1.27(	4)	C(4)	- C(5)	1.	35(5)		
	0(4)	- N(4	()	1.26(	4)	C(5)	- C(6)	1.	36(4)		
	N(1)	- C()	1)	1.33(	4)	C(%)	- C(7)	1.	43(4)		
	N(1)	- C(	3)	1.51(	4)	C(8)	- C(9)	1.	54(4)		
	N(2)	- c(	<b>)</b> )	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)	Angle	<b>\$</b>									
	0(1)	- U	-	0(2)	178.2	(1.1)	C(12)	- N(3)	- C(13)	107.6	(3.0)
	0(3)	- ប	-	N(1)	71.3	(0.7)	0(4)	- N(4)	- 0(5)	_120.5	(3.6)
	N(1)	- U	-	N(Z)	64.1	(0.8)	0(4)	- N(4)	- 0(6)	124.3	(3.2)
	N(2)	- U	-	N(3)	67.3	(1.0)	0(5)	- N(4)	- 0(6)	114.7	(5.9)
	N(3)	- U	-	0(4)	73.5	(1.0)	N(1)	- C(1)	- C(2)	126.9	(2.7)
	0(4)	- U	-	0(3)	84.1	(0.7)	C(1)	- C(2)	- C(3)	113.9	(2.7)
	U	- 0(	3) -	C(7)	132.6	(1.9)	C(1)	- C(2)	- C(7)	122.0	(2.5)
	U	- 0(	4} -	N(4)	121.4	(2.1)	C(3)	- C(2)	- C(7)	124.0	(2.6)
	U	- N (	1) -	C(1)	127.4	(2.0)	C(2)	- C(3)	- C(4)	112.5	(3.5)
	U	- N(	1} -	£(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)	0(3)	- C(7)	- C(6)	114.7	(2.6)
	C(9)	- N (	2) -	C(10)	114.2	(2.9)	0(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(1+	) - C1(2)	110.2	(2.2)
						_					
€Ta	aking	into a	ccou	int the	accurac	y of cel	ll param	eters.			
c)	'Bite	' dist	ance	es and	contacts	distan	ces with	in the	'inner co	re'	

0(1) - N(2)N(1) - N(2)2.72 3.07 0(1) - N(3)3.25 N(2) - N(3) 2.93 N(3) - 0(4) 3.05 0(2) - 0(3) 2.83 0(2) - 0(4) 3.00 0(4) - 0(3) 3.11 0(3) - N(1) 0(2) - N(1)2.80 3.17 3.15 0(1) - 0(3) 2.94 0(2) - N(2) 0(1) - 0(4) 2.95 O(2) - N(3)3.17 0(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-square planes with the deviations (A) of relevant atoms in square brackets. The equation of a plane in direct space is given by PX + QV +<u>RZ = S</u> Plane (1): P 9 R s -3.736 10.634 Z.417  $U_0(3)_0(4)_N(1)_N(2)_N(3)$ -1.301 [U -0.02;0(3) -0.09;0(4) 0.10;N(1) 0.06;N(2) 0.01; N(3) -0.00;0(1) 1.76; 0(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; 0(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): -1.081 U, N(1), C(8), C(9), N(2) -1.631 10.816 2.538  $\begin{bmatrix} U & 0.02; N(1) & 0.12; C(8) & -0.26; C(9) & 0.31; N(2) & -0.19 \end{bmatrix}$ 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 -3.9931.368 [0(4) - 0.01; x(4) 0.03; 0(5) - 0.01; 0(6) - 0.01]Plane (7): U, C(1), C(8), N(1) [u -0.03; C(1) -0.05; C(3)-0.04; N(1) 0.12] Plane (8): 1.251 10.964 +9.121 -1.629N(1), C(\$), C(9) 2.763 8.747 3.423 -5.428 Plane (9): C(8), C(9), N(2) 2.632 8.196 9.528 1.232 Plane (10): N(2), C(10), C(11) 2.415 3.997 10.324 1.587 Plane (11): -1.396 10.683 -9.188 -3.001 C(10), C(11), N(3) \*The equation of least-squares line (1.) defined by O(1), U, O(2) in parametric form in direct space is: X = 0.0569 - 0.0175 T y = 0.0495 - 0.0090 Tz = 0.2504 + 0.0887 T  $\begin{bmatrix} U & 0.02, 0(1) & 0.01, 0(2) & 0.01 \end{bmatrix}$ 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) (3) - (5) 6.0 15.3 (1) - (4)6.2 (4) - (5) 21.5 (1) - (5) 17.2 (9) - (10**)** 12.5 (1) - (6)(2) - (3)55.3 (8) - (9) \$4.1 34.4 (10) - (11) 42.9 (2) - (4)  $(1) \cdot (L)$ 40.7 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)  $(2\cdot26(2)\text{\AA})$  is in agreement with the sum of the Pauling crystal radii  $(0\cdot83 + 1\cdot40\text{\AA})[7]$  and of the Shannon crystal radii  $(0\cdot87 + 1\cdot40\text{\AA})[8]$ , as expected ([9], Table 7 of [1c]). The U-O(4) distance  $(2\cdot39(2)\text{\AA})$  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)  $2\cdot54$ , U-N(2)  $2\cdot58$  and U-N(3)  $2\cdot70\text{\AA}$ .

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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