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Synthesis and Crystal Structure of (N-2-oxyphenylsalicylaldiminato) Bis(dimethylsulphoxide)dioxouranium(VI)

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Two compounds, $UO_2A \cdot 2dmso$ and $UO_2A \cdot dmso \cdot H_2O$ (A = N-2-oxyphenylsalicylaldiminato) have been synthesized and characterized, and the X-ray crystal structure of the former has been determined from diffractometer data. The substance crystallizes in the monoclinic system, space group $P2_1/n$, *with* a = *20.76(2),* b = *8.10(2),* c = *12.98(2) Å, and* β = *96.84(4)°,* Z = *4. The final conventional* R *was 0.073. In this compound the* U *atom is at the centre of a distorted pentagonal bipyramid whose apexs are occupied by the O atoms of the linear uranyl group. The ligand has a chair-like configuration. The U–O(A) bond distances (2.20 and 2.19 Å) are shorter than the U–O(dmso) ones (2.43 Å); whereas the nitrogen atom, which is significantly displaced from the equatorial plane, makes with the metal atom a rather long bond (2.73 Å). The structure is partially disordered.*

Introduction

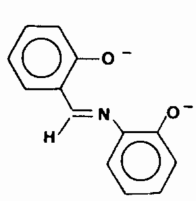
An interesting series of adducts of the UO_2T moiety with a number of monodentate and bidentate oxygen and nitrogen donors were recently reported [1]: $UO_2T \cdot D$, $UO_2T \cdot D \cdot H_2O$ and $UO_2T \cdot$D–D (T = tridentate dianionic Schiff base ligand, D = monodentate ligand and D–D = bidentate ligand). Herein, we describe an example belonging to the new type $UO_2T \cdot 2D$ *viz.* (N-2-oxyphenylsalicylaldiminato) bis(dimethylsulphoxide)dioxouranium(VI). The complex has been fully characterized using physicochemical techniques and its detailed structure has been worked out using three dimensional X-ray crystallography. The results are reported in this paper.

Experimental

Synthesis

The starting material $UO_2A \cdot 2H_2O \cdot CH_3OH$ is obtained by reacting $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ with the Schiff base (H_2A), salicylaldehyde-2-hydroxyanil in 1:1 ratio in hot methanol as described elsewhere [1].

A =



The reaction of this compound with dmso produces either $UO_2A \cdot 2dmso$ or $UO_2A \cdot dmso \cdot H_2O$ depending on the preparative method.

$UO_2A \cdot 2dmso$

$UO_2A \cdot 2H_2O \cdot CH_3OH$ (≅800 mg) was dissolved in dry dmso. The resulting reddish brown solution, on standing overnight at room temperature, deposited reddish brown crystals which were filtered, washed with a small amount of carbon tetrachloride and then dried over anhydrous calcium chloride. Yield, 60%. *Anal.* Calcd. for $UO_2A \cdot 2dmso$: C, 32.07; H, 3.03; N, 2.02; U, 37.42. Found: C, 31.91; H, 3.22; N, 2.04; U, 37.14%.

$UO_2A \cdot dmso \cdot H_2O$

$UO_2A \cdot 2H_2O \cdot CH_3OH$ (≅800 mg) was dissolved in dmso to form a nearly saturated solution. To this, water was added in drops till a turbidity appeared and then redissolved by warming the solution. On keeping this solution over a period of 1–2 days,

TABLE I. Table of Data.

IR data (in KBr disc: Frequencies are in cm^{-1})

s = strong; m = medium; br = broad

$UO_2A\cdot 2dmso$: ν_{UO_2}, 888s; $\nu_{C=N}$ 1600; ν_{SO} 1000; $\nu_{Phenolic\ CO}$ 1535 m. Other frequencies: 1580s, 1480s, 1470s, 1395m, 1330s, 1320s, 1300s, 1285m, 1170m, 1150m, 1120m, 955s, 840m, 750s, 600m, 535m, 490m. $UO_2A\cdot dmso\cdot H_2O$: ν_{UO_2} 905s; $\nu_{C=N}$ 1600s; ν_{SO} 1002 s; ν_{O-H} 3400br, m; $\nu_{Phenolic\ CO}$ 1530 m. Other frequencies: 1580s, 1472s, 1460s, 1390m, 1375m, 1330s, 1305br, s, 1270s, 1245s, 1170m, 1145m, 1120m, 953s, 830s, 750s, 600m, 500m, 485m

^{1}*H Chemical Shift data* (δ in ppm from TMS)

$UO_2A\cdot 2dmso$ in pyridine-d_5	$\delta_{CH=N}$, 9.57;	$\delta_{CH_3(dmso)}$, 2.73
$UO_2A\cdot dmso\cdot H_2O$ in dmso-d_6	$\delta_{CH=N}$, 9.60 $\delta_{CH_3(dmso)}$, 2.54 δ_{H_2O}, 3.28	

Thermogravimetry data

Ti = Temperature at which mass loss starts
Tf = Temperature at which mass loss stops

		Temp. (°C) for loss of dmso and H_2O		Weight loss %	
		Ti	Tf	Calcd	Found
$UO_2A\cdot 2dmso$	1st step	212	255	12.2	11.9
	2nd step	265	325	12.8	12.9
$UO_2A\cdot dmso\cdot H_2O$		165	325	16.6	16.3

(Both dmso and H_2O are lost in overlapping step)

brownish-red crystals of $UO_2A\cdot dmso\cdot H_2O$ were formed. The crystals were filtered off and were washed with aqueous ethanol. The complex was then dried in air. Yield, 60%. *Anal.* Calcd. for $UO_2A\cdot dmso\cdot H_2O$: C, 31.25; H, 2.95; H, 2.43; U, 41.32. Found: C, 31.42; H, 3.08; N, 2.45; U, 41.28%.

Physical Properties

$UO_2A\cdot 2dmso$

Reddish-brown crystals, insoluble in CCl_4, $CHCl_3$, benzene and water. Soluble in pyridine, dimethylformamide (dmf) and dmso. Melting point, above 250 °C.

$UO_2A\cdot dmso\cdot H_2O$

Brownish-red crystals, insoluble in CCl_4, $CHCl_3$, benzene and water. Soluble in pyridine, dmf and dmso. On heating, the colour of the complexes slowly changes to brown around 120 °C and does not melt up to 250 °C.

Growing of crystals of $UO_2A\cdot 2dmso$

Crystals suitable for X-ray study were obtained by the slow evaporation of a saturated solution of $UO_2A\cdot 2dmso$ in dry dmso. The crystals were washed with a small amount of CCl_4 and were then dried in a desiccator over anhydrous calcium chloride.

IR Spectra

ν_{SO} is considerably lower than that in free dmso ($\cong 1055\ cm^{-1}$) suggesting binding of the dmso molecules at the oxygen end. ν_3 vibration of the UO_2 moiety in $UO_2A\cdot dmso$ appears at 888 cm^{-1}.

In the IR spectrum of $UO_2A\cdot dmso\cdot H_2O$, a broad, medium band centered at 3400 cm^{-1} due to ν_{O-H} of H_2O is present. ν_3 of UO_2 moiety appears at 905 cm^{-1}.

^{1}H NMR Spectra

Due to solubility reasons, the NMR spectrum of $UO_2A\cdot dmso$ was recorded in pyridine-d_5 (and not in $CDCl_3$). Signals for the tridentate ligand and for dmso are displayed. The PMR spectrum of $UO_2A\cdot dmso\cdot H_2O$, studied in dmso-$d_6$, exhibits a signal for the proton of H_2O. The signal for dmso and H_2O ligands do not exhibit any shifts from the free ligand values. It is likely that donors are completely displaced from the metal ion by the deuterated solvent molecules.

Thermal Analysis

Thermal analysis was carried out in air atmosphere under non-isothermal conditions. The two dmso

TABLE II. Crystal Data.

$C_{17}H_{13}NO_6S_2U$	FW 629
Crystal description	brown prisms
Systematic absences	h0l with h + 1 ≠ 2n
	0k0 with 0k0 ≠ 2n
System	monoclinic
Space group	$P2_1/n$ (C^5_{2h})
General positions	$\pm(x,y,z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$
Cell dimensions	*a* 20.76(2) A
	b 8.10(1) A
	c 12.98(2) A
	β 96.84(4)°
	V 2167 A^3
Density	obs. 1.92 g cm^{-3}, calcd. 1.93 g cm^{-3} for $Z = 4$
μ(MoKα)	113 cm^{-1}
Measured intensities	4296
Observed $I > 3\sigma(I)$	2946
Final *R* factor	0.073

molecules in $UO_2A \cdot 2dmso$ are lost endothermically one by one in two clearly observable steps (Fig. 1). In contrast $UO_2A \cdot dmso \cdot H_2O$ species loses dmso and H_2O in overlapping steps.

Spectroscopic and analytical data are listed in Table I.

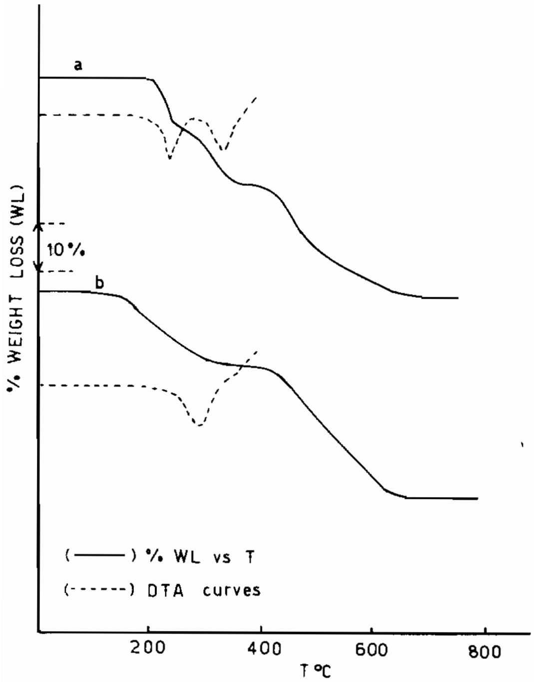


Fig. 1. Thermograms of (a) $UO_2A \cdot 2dmso$, and (b) $UO_2A \cdot dmso \cdot H_2O$.

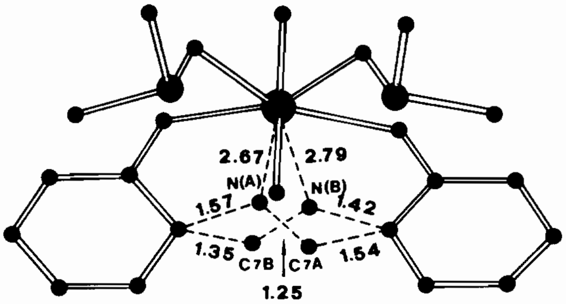


Fig. 2. A representation of the ligand disorder in the molecular structure (projection down *b*).

X-ray Analysis

A prismatic crystal, of approximate dimensions 0.1 X 0.2 X 0.2 mm was used for data collection. The X-ray experimental work was performed on a Philips PW 1100 four-circle diffractometer using MoKα radiation. Unit cell parameters were obtained by a least-squares refinement of 25 carefully determined angular settings. Intensities were collected over the range $\theta = 3-25°$ by the $\omega-2\theta$ scan mode with a scan rate of 2° min^{-1}. Two standard reflections, monitored before every 100 measurements, were constant within counting statistics. All data were corrected for Lp. No absorption correction was applied. Crystal data are summarized in Table II.

The structure was solved by the heavy-atom method. Some difficulties were encountered in the location of N and C(7) because of the presence of diffuse and very near peaks in the space between the two phenylene rings. After some unsuccessful attempts to assign unique positions to these atoms, it was definitely clear that there were two alternative peaks for each of them in the Fourier map, corresponding to two alternative orientations of the entire ligand in the same region. However, such disorder was found only at the bridging N and C(7) atoms, because the phenylene groups, owing to their geometry, were quite superimposed.

Accordingly, N and C(7) were introduced and refined, following this model, with an occupancy factor of 0.5 which was maintained constant on the assumption, confirmed by the values of the temperature factors, that the two orientations (A and B) were present by the same fraction. A final difference synthesis showed no other significant peaks apart from some residuals in the proximity of uranium, which can be ascribed to series termination effect. The final least-squares refinement minimizing the function $\Sigma w(Fo - Fc)$ with w = 1, reduced the conventional *R* factor to 0.073. The scattering factors were those of Cromer and Waber [2] for neutral U and those of Cromer and Mann [3] for neutral S, O, N and C.

TABLE III. Positional Atomic Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^3$) in the Form $\exp[-2\pi^2 \Sigma U_{ij} a_i^* a_j^* h_i h_j]$.

Atom	x	y	z
U	3317(0)	2742(1)	5140(1)
O(1)	3687(9)	1580(18)	4160(13)
O(2)	2947(9)	3955(18)	6104(12)
O(3)	2381(10)	1716(29)	4459(15)
O(4)	4112(9)	1930(27)	6295(13)
O(5)	4130(7)	4901(19)	5187(12)
O(6)	2891(8)	4806(19)	3882(11)
S(1)	2555(4)	6386(8)	4160(5)
S(2)	4212(3)	6409(8)	5899(5)
N(A)*	2792(20)	263(41)	6107(28)
N(B)*	3140(22)	192(57)	6530(30)
C(1)	1900(11)	715(30)	4804(19)
C(2)	1304(12)	621(32)	4250(20)
C(3)	804(13)	−369(35)	4606(22)
C(4)	938(15)	−1193(39)	5546(25)
C(5)	1539(16)	−1145(42)	6118(26)
C(6)	2058(12)	−165(33)	5758(21)
C(7A)*	2951(20)	−542(32)	6918(22)
C(7B)*	2576(21)	−351(31)	6482(24)
C(8)	3656(13)	−128(35)	7328(22)
C(9)	3733(15)	−1247(39)	8210(25)
C(10)	4328(16)	−1317(41)	8835(26)
C(11)	4848(13)	−347(35)	8614(21)
C(12)	4790(12)	699(31)	7746(19)
C(13)	4206(12)	861(31)	7122(19)
C(14)	2691(16)	7843(48)	3178(28)
C(15)	1730(20)	5961(53)	3750(33)
C(16)	4892(16)	5923(42)	6800(27)
C(17)	4575(13)	7993(38)	5191(23)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	51	37	39	−3	20	3
O(1)	105	33	70	−4	58	−13
O(2)	104	38	63	−2	59	−9
O(3)	80	131	68	−41	28	−7
O(4)	99	114	62	−2	39	20
O(5)	66	55	61	−24	20	−19
O(6)	74	60	47	16	21	12
S(1)	113	50	53	17	21	1
S(2)	74	51	78	−14	44	−18
N(A)*	91	28	23	−10	43	2
N(B)*	87	50	30	11	−14	−21
C(1)	52	48	57	2	21	−18
C(2)	45	49	71	−11	−5	−8
C(3)	62	72	73	−8	35	−17
C(4)	114	76	64	−38	42	−1
C(5)	134	68	61	−29	14	−2
C(6)	65	52	60	10	0	−11
C(7A)*	59	66	40	24	45	2
C(7B)*	29	43	81	1	29	−6
C(8)	62	59	83	16	20	−36
C(9)	68	69	106	2	33	0
C(10)	128	57	72	8	50	21
C(11)	69	68	48	33	14	−2
C(12)	67	48	62	13	20	−5
C(13)	70	47	52	24	23	−6
C(14)	208	52	82	30	55	20
C(15)	116	103	167	43	15	−28
C(16)	103	104	60	−30	17	−8
C(17)	94	24	132	−8	46	1

*These atoms were introduced with a population parameter of 0.5.

TABLE IV. Bond Distances (Å).*

Coordination			
U–O(1)	1.82(2)	U–O(3)	2.20(2)
U–O(2)	1.83(2)	U–O(4)	2.19(2)
U–N(A)	2.67(4)	U–O(5)	2.43(2)
U–N(B)	2.79(4)	U–O(6)	2.43(1)
Ligand			
O(3)–C(1)	1.40(2)	O(4)–C(13)	1.37(2)
N(B)–C(8)	1.42(4)	N(A)–C(6)	1.57(3)
N(B)–C(7B)	1.25(4)	N(A)–C(7A)	1.25(4)
C(7B)–C(6)	1.35(3)	C(7A)–C(8)	1.54(2)
C(1)–C(2)	1.36(3)	C(3)–C(9)	1.45(4)
C(2)–C(3)	1.43(4)	C(9)–C(10)	1.39(4)
C(3)–C(4)	1.40(4)	C(10)–C(11)	1.39(4)
C(4)–C(5)	1.37(4)	C(11)–C(12)	1.40(4)
C(5)–C(6)	1.45(4)	C(12)–C(13)	1.39(3)
C(6)–C(1)	1.43(3)	C(13)–C(8)	1.44(4)
DMSO			
S(1)–O(6)	1.52(2)	S(2)–O(5)	1.53(2)
S(1)–C(17)	1.78(1)	S(2)–C(16)	1.77(1)
S(1)–C(15)	1.77(1)	S(2)–C(17)	1.79(1)

*Atoms N(A), N(B), C(7A), and C(7B) are present in statistical positions and were introduced with a population parameter of 0.5.

Correction for anomalous dispersion was applied for the uranium atom (Δf′ = −9.19, Δf″ = 9.09). All calculations were performed using the X-ray '73 program system [4]. The final positional parameters are given in Table III*.

Description of the Structure

As shown in Fig. 3 the compound provides one more example of 7-coordination to uranium, which lies at the center of a very distorted pentagonal

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*A list of the observed and calculated structure factors is available from the journal.

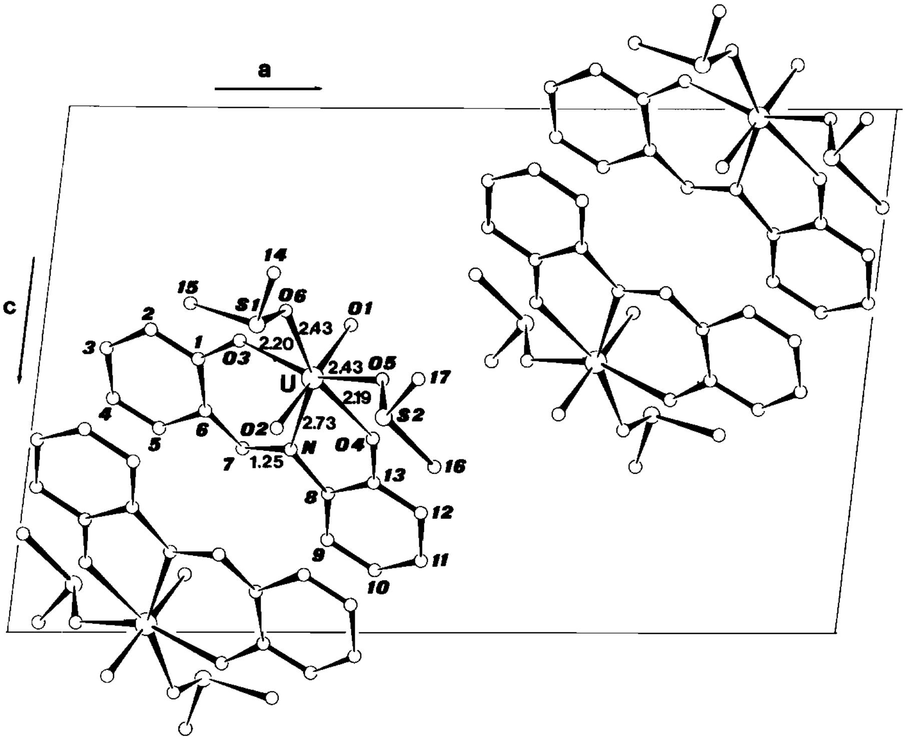

Fig. 3. Projection down *b*. In this figure only one of the ligand orientations is reporter for clarity.

TABLE V. Bond Angles (°).[a]

Coordination			
O(1)–U–O(2)	179		
O(1)–U–O(3)	87	O(2)–U–O(3)	93
O(1)–U–O(4)	89	O(2)–U–O(4)	92
O(1)–U–O(5)	92	O(2)–U–O(5)	87
O(1)–U–O(6)	92	O(2)–U–O(6)	87
O(1)–U–N(A)	99	O(2)–U–N(A)	82
O(1)–U–N(B)	100	O(2)–U–N(B)	82
O(5)–U–O(6)	74		
O(3)–U–O(6)	76	O(4)–U–O(5)	75
O(3)–U–N(A)	62	O(4)–U–N(B)	59
O(7)–U–N(A)	76	O(3)–U–N(B)	79
Ligand			
U–C(3)–C(1)	136	U–C(4)–C(13)	138
O(3)–C(1)–C(6)	118	O(4)–C(13)–C(8)	117
O(3)–C(1)–C(2)	120	O(4)–C(13)–C(12)	123
U–N(A)–C(6)	117	U–N(B)–C(8)	118
U–N(A)–C(A)	138	U–N(B)–C(B)	116
C(6)–N(A)–C(A)	104	C(8)–N(B)–C(B)	124
N(A)–C(6)–C(1)	105	N(B)–C(8)–C(13)	107
N(A)–C(6)–C(5)	138	N(B)–C(8)–C(9)	135
N(A)–C(A)–C(8)	106	N(B)–C(B)–C(6)	130
C(A)–C(8)–C(13)	142	C(B)–C(6)–C(1)	138
C(A)–C(8)–C(9)	98	C(B)–C(6)–C(5)	106

[a] Bond angles in the phenylene rings are in the range 117–122°. Standard deviations are 1° for angles where heavy atoms are involved and 2° for all other angles.

TABLE V. *(continued)*

DMSO			
U–O(6)–S(1)	124	U–O(5)–S(2)	128
O(6)–S(1)–C(14)	105	O(5)–S(2)–C(16)	104
O(6)–S(1)–C(15)	103	O(5)–S(2)–C(17)	106
C(14)–S(1)–C(15)	98	C(16)–S(2)–C(17)	98

bipyramid. In this figure only one of the possible orientations of the ligand has been reported for clarity of the drawing, but a detailed representation of the geometry resulting from the statistical presence of N and C(7) is done in Fig. 2.

From this point of view, although the molecular model is completely asymmetric, the crystallographic unit consisting of A and B can be approximately assigned Cs symmetry.

The uranyl group is linear and the U–O (apical) bond distances are fully comparable. The main interatomic distances and angles are given in Tables IV and V, whereas a detailed picture of the statistical disorder at N and C(7) is given in Fig. 2. The three O–U–O bond angles in the equatorial plane are very similar, but the O–U–N angles differ considerably owing to the asymmetry of the ligand geometry. It is noticeable that, at least for the angles are concerned, the values for the orientations A and B agree

TABLE VI. Least Squares Planes and Distances (Å) of Atoms from the Planes. X, Y and Z are Fractional Coordinates in the Direct Cell.

Plane I: U, O(3) to O(6)
$10.998X - 3.745Y - 9.983Z = -2.485$
[U −0.02, O(3) 0.01, O(4) 0.00, O(5) 0.01, O(6) −0.01, *N(A) −0.64, *N(B) −0.64]

Plane II: C(1) to C(6)
$7.397X - 6.405Y - 6.967Z = -2.391$
[C(1) 0.00, C(2) 0.00, C(3) 0.01, C(4) −0.01, C(5) 0.00, C(6) 0.01, *O(3) −0.05, *N(A) 0.03]

Plane III: C(8) to C(13)
$-7.492X + 5.925Y + 8.012Z = 3.051$
[C(8) 0.00, C(9) −0.01, C(10) 0.00, C(11) 0.01, C(12) −0.02, C(13) 0.02, *O(4) 0.06, *N(B) −0.06]

Angles between the planes

Plane	Angle (°)
I–II	24.7
I–III	19.8
II–III	5.7

*Atom not used in the plane calculation.

well (62 and 76° for A, 59 and 79° for B). On the other hand, bonding of nitrogen to uranium, with the concomitant formation of the five-membered and six-membered metallocycles which share U and N along a common edge, is apparently not easy. Angles at C(6) and C(8) agree well for A and B but deviate considerably from the ideal value of 120°, which is indicative of strain of the bonds. A further indication of this is the fact that, as shown in Table VI where the equations of selected planes are given, both N(A) and N(B) lie significantly out (by 0.64 Å) of the equatorial plane. However, the oxygen and uranium atoms are coplanar within the experimental errors. Bond angles confirm that nitrogen (A and B) is displaced from this plane toward O(2), but this does not apparently have any influence on the linearity of the uranyl group, contrarily to what was sometimes reported [5]. The U–O(A) bond lengths are chemically equivalent (2.20 and 2.19 Å) and significantly shorter than the U–O (dmso) ones (2.43 Å) as expected for negatively charged with respect to neutral coordinated oxygen atoms. It seems that the U–N bond (mean 2.74 Å) is rather long if compared with other U–N determinations. However a discussion of this value is meaningless owing to the differences between U–N(A) (2.67 Å) and U–N(B) (2.79 Å). As indicated by the high e.s.d. these values are scarcely significant, because of the relative uncertainty in the positions of this atom, due to crystal disorder. Surely the U–N bond suffers, almost in part, of the same geometrical constraints which prevent nitrogen to lye in the equatorial plane.

Coordination of nitrogen does not affect the localized N=C double bond which has, for both orientations, the same value of 1.25 Å. As shown in Table VI the planes of the phenylene rings make a dihedral angle of about 5°, that is they are almost parallel, but are markedly tilted (by 25° and 20° respectively) with respect to the equatorial plane; thus the entire ligand takes in this complex a chair-like conformation.

Relevant intramolecular contacts are: O(3)···O(6) 2.85 Å, O(4)···O(5) 2.81 Å, O(5)···O(6) 2.90 Å, N(A)···O(3) 2.52 Å, and N(B)···O(4) 2.51 Å. In addition the molecules pack in such a way that there are several contacts in the range 3.7–4 Å between atoms of the C(1)–C(6) ring and atoms of the C(8)–C(13) ring at $\frac{1}{2} - x$, $\frac{1}{2} + y$, $1.5 - z$.

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