Preparation, Properties, and Crystal Structure of Bis(ethyl carbamate)-dinitratodioxouranium(VI)

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A monomeric complex of formula $[UO_2(NO_3)_2L_2]$ (L = ethyl carbamate) has been synthesized and characterized. The crystal structure has been determined by X-ray analysis from three-dimensional counter data, and refined by least-squares to R 0·076 for 1369 reflections. Crystals are monoclinic, space group $P2_1/a$, with $a = 12·176(3)$, $b = 8·364(3)$, $c = 7·847(3)$ Å, $\beta = 90·42°(5)$, and $Z = 2$. The linear uranyl group is perpendicular to the equatorial plane in which four oxygen atoms of two nitrate groups and two amidic oxygen atoms of the organic ligands occupy the corners of an irregular hexagon. The crystallographic results are related to i.r. and n.m.r. measurements.

IN a preliminary note[1] the preparation of a number of addition complexes of ethyl carbamate (L) with a variety of uranyl compounds has been reported. The complexes obtained $\{[UO_2(NO_3)_2L_2]$, $[UO_2(\text{tropolonate})_2L]$, $[UO_2(\text{acetate})(OH)L]_2$, $[UO_2(\text{oxalate})L]_n$, and $[UO_2(\text{phthalate})L]_n\}$ showed quite different stoicheiometry, molecular complexity, and co-ordination number depending on the anionic ligands used. In all cases i.r. analysis[1] seems to indicate co-ordination through the amidic oxygen, although the spectra are complicated due to the presence of hydrogen bonding in the free ligand and possibly in the complexes. Only the nitrate complex, which is moderately soluble in many solvents, can be obtained as well shaped crystals. In this case it was possible to carry out a complete characterization by i.r. spectroscopy in the solid state and solution, ^1H n.m.r., and X-ray diffraction.

EXPERIMENTAL

Materials.—Reagent grade uranyl nitrate hexahydrate and ethyl carbamate were used without further purification.

Preparation of the Complex.—A mixture of uranyl nitrate hexahydrate and a large excess of ethyl carbamate was slowly heated until completely molten (70—100 °C). The homogeneous thick solution was stirred for 2 h and the solid anhydrous product was obtained after sublimation of the excess of ligand under vacuum. It was washed with dry benzene, dried *in vacuo*, and recrystallized from benzene as brilliant yellow crystals, m.p. 115 °C (Found: C, 12·3; H, 2·35; N, 9·65; U, 41·7. $C_6H_{14}N_4O_{12}U$ requires C, 12·6; H, 2·45; N, 9·8; U, 41·5%). Uranium was determined as U_3O_8 by ignition of the complex at 750—800 °C.

Physical Measurements.—Molar conductivity at 25° was measured on 10^{-3}M-solutions in chloroform and acetonitrile with an LKB 3216B conductivity bridge. I.r. spectra (4000—400 cm⁻¹) were recorded on a Perkin-Elmer 621 i.r. spectrophotometer in Nujol mull, KBr discs, and chloro-

form solution. Room temperature u.v. spectra for chloroform and acetonitrile solutions (600—250 nm) were recorded with an Optica CF4/R spectrophotometer. N.m.r. measurements were carried out with a Perkin-Elmer R 12 instrument for solutions in deuterioacetone. Molecular weight was determined at 37 °C for chloroform solution with a Mechrolab 302 osmometer. Some results are summarized in Table 1.

TABLE 1

Some physical data for $[UO_2(NO_3)_2L_2]$

$\Lambda_M/\text{ohm}^{-1}$ $\text{cm}^2\ \text{mol}^{-1}$	$\nu_{as}(UO_2)/$ cm^{-1}	M	Band maxima/nm
3 [a]	937 [b]		483, 466, 451, 436, 423, 414sh, 405sh, 394sh, 382sh, 369, 357 [a]
<1 [c]	930, 945 [c]	550 [c]	485, 468, 451, 435sh, 422sh, 415, 405, 395sh, 383sh, 369, 358 [c]

[a] MeCN solution.   [b] Nujol mull and KBr pellets.   [c] CHCl₃ solution.

CRYSTAL STRUCTURE

Crystals are well formed and elongated along the [010] direction.

Crystal Data.—$C_6H_{14}N_4O_{12}U$, M 572·21, Monoclinic, $a = 12·176(3)$, $b = 8·364(3)$, $c = 7·847(3)$ Å, $\beta = 90·42°$ (5), $U = 799$ Å³, $D_m = 2·37$ (flotation), $Z = 2$, $D_c = 2·38$. Space group $P2_1/a$. Mo-K_α radiation, $\lambda = 0·7107$ Å; $\mu(\text{Mo-}K_\alpha) = 54$ cm⁻¹.

A crystal of dimensions *ca.* $0·02 \times 0·03 \times 0·02$ cm was used for the measurements. From preliminary X-ray Weissenberg and precession films approximate unit-cell parameters were obtained, and the space group was determined. Precise values of the unit-cell parameters were derived by the method of least-squares from angle data recorded with the diffractometer.

Intensity Data.—The crystal was mounted with the [010]

[1] L. Cattalini, L. Baracco, S. Degetto, G. Marangoni, L. Maresca, and L. Sindellari, *Atti Accad. Peloritana*, in the press.

direction parallel to the ϕ-axis of the goniometer. A total of 1369 independent reflections were collected on a computer controlled Siemens automated diffractometer, by use of the θ—2θ scan and the five-point measuring procedure. About 280 very weak reflections were considered unobserved and were given zero weight in the subsequent refinement. Intensities were measured up to $\theta_{max.}$ 25°. No absorption correction was made. Structure factors

convergence was reached at R 0·076, when no parameter shift was $>0·2\sigma$. A final three-dimensional difference map was then computed which showed no interpretable features about the positions of the hydrogen atoms.

The final atomic parameters along with their estimated standard deviations are given in Table 2. Bond lengths and angles are listed in Tables 3 and 4. Equations of some relevant planes in the molecule are reported in Table 5.

TABLE 2

Final atomic parameters ($\times 10^4$) of $[UO_2(NO_3)_2L_2]$, with estimated standard deviations *

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	5000	5000	0	346	455	489	−65	−142	−136
O(1)	5031(14)	6724(26)	1222(39)	134	438	1226	25	−111	393
O(2)	3025(15)	5599(25)	−773(27)	293	572	691	−50	−351	97
O(3)	3244(14)	4188(25)	1532(25)	261	607	555	−48	−11	164
O(4)	1589(15)	4674(35)	570(28)	236	1213	653	−38	−83	123
O(5)	5235(14)	3495(25)	2575(21)	356	698	241	−196	−228	191
O(6)	5827(14)	1783(23)	4560(23)	383	416	491	−55	−34	152
N(1)	2562(18)	4815(31)	445(28)	379	407	488	−13	−55	−58
N(2)	478(19)	1077(33)	2893(29)	460	618	415	−142	−228	127
C(1)	5178(19)	2118(33)	3198(29)	243	498	237	−21	−136	101
C(2)	6336(22)	3027(38)	5000(35)	374	616	349	−84	−220	51
C(3)	7413(26)	2294(43)	6314(48)	489	577	905	59	−243	47

* Thermal parameters, U_{ij} ($\text{Å}^2 \times 10^4$) are defined by: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

were calculated using scattering factors for neutral atoms taken from ref. 2, and for uranium the real part of the correction for the anomalous scattering was applied.[3] All calculations were carried out on a CDC 6600 computer with the program system of ref. 4.

Some intra- and inter-molecular contacts are given in Table 6. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20560 (2 p., 1 microfiche).*

TABLE 3

Intramolecular bond lengths (Å)

U—O(1)	1·73(2)	N(1)—O(4)	1·19(3)
U—O(2)	2·53(2)	O(5)—C(1)	1·25(3)
U—O(3)	2·53(2)	C(1)—N(2)	1·24(4)
U—O(5)	2·40(2)	C(1)—O(6)	1·36(3)
N(1)—O(2)	1·29(3)	O(6)—C(2)	1·48(3)
N(1)—O(3)	1·30(3)	C(2)—C(3)	1·53(4)

TABLE 4

Bond angles (°)

O(1)—U—O(2)	88(1)	O(2)—N(1)—O(4)	123(2)
O(1)—U—O(3)	91(1)	O(3)—N(1)—O(4)	123(2)
O(1)—U—O(5)	92(1)	U—O(5)—C(1)	144(2)
O(2)—U—O(3)	51(1)	O(5)—C(1)—N(2)	127(2)
O(2)—U—O(5^I)	65(1)	O(5)—C(1)—O(6)	118(2)
O(3)—U—O(5)	64(1)	N(2)—C(1)—O(6)	114(2)
U—O(2)—N(1)	97(1)	C(1)—O(6)—C(2)	115(2)
U—O(3)—N(1)	97(1)	O(6)—C(2)—C(3)	107(2)
O(2)—N(1)—O(3)	114(2)		

O(5^I) is at $1 - x$, $1 - y$, $-z$.

Determination of the Structure.—The unit cell contains two molecules, and the uranium atoms occupy special positions at centres of symmetry. The structure was solved by the heavy-atom method. The co-ordinates of the atoms with isotropic vibration parameters and one overall scale-factor were then subjected to several cycles of full-matrix least-squares refinement. The function minimized was $\Sigma w[|F_o| - |F_c|]^2$ with $w = 1$. Refinement was then continued with anisotropic thermal parameters and

² ' International Tables for *X*-Ray Crystallography, vol. III, Kynoch Press, Birmingham, 1962, p. 201.

TABLE 5

Equations of best least-squares planes and, in brackets, deviations (Å) of the relevant atoms from these planes. The equations are in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates referred to the crystallographic axes

	A	B	C	D
Plane (1):				
O(2), O(3), O(5), O(2^I), O(3^I), O(5^I)	0·441	7·087	4·159	3·764

[O(2) 0·016, O(3) −0·016, O(5) 0·015, O(2^I) −0·016, O(3^I) 0·016, O(5^I) −0·016, N(1) −0·054, O(4) −0·144]

	A	B	C	D
Plane (2):				
O(2), O(3), N(1), O(4)	−0·457	6·976	4·317	3·434

[These atoms are perfectly coplanar]

	A	B	C	D
Plane (3):				
O(5), C(1), N(2), O(6), C(2)	7·973	−3·173	−5·092	1·774

[O(5) −0·019, C(1) 0·054, N(2) −0·019, O(6) −0·016, C(2) 0·004, C(3) 0·193]

Angles (°) between the planes

(1)—(2)	4·5	(2)—(3)	45·5
(1)—(3)	50·0		

DISCUSSION

Description of the Structure.—A view of the model of the molecule showing the numbering scheme used in the analysis is given in Figure 1. Figure 2 shows a projection of the structure. Eight-co-ordination of the uranium atom is realized by an irregular hexagon of six oxygen atoms bonded in the equatorial plane which is

³ Ref. 2, p. 216.

⁴ J. M. Stewart, F. A. Kundell, and J. C. Baldwin, ' *X*-Ray '70 ' System of Crystallographic Programs.'

TABLE 6

(a) Intermolecular contacts <3.5 Å

O(4) $\cdots$ N(2$^{\mathrm{II}}$)	3·24	O(3) $\cdots$ O(2$^{\mathrm{IV}}$)	3·43
N(2) $\cdots$ O(6$^{\mathrm{III}}$)	3·14	O(2) $\cdots$ C(3$^{\mathrm{V}}$)	3·42
O(2) $\cdots$ O(4$^{\mathrm{II}}$)	3·44	C(1) $\cdots$ O(4$^{\mathrm{VI}}$)	3·07
O(1) $\cdots$ O(4$^{\mathrm{II}}$)	3·42		

(b) Some intramolecular contacts <3.5 Å

O(2) $\cdots$ O(3)	2·18	O(5) $\cdots$ O(6)	2·24
O(2) $\cdots$ O(4)	2·18	O(5) $\cdots$ N(2)	2·24
O(3) $\cdots$ O(4)	2·19	O(5) $\cdots$ C(2)	2·60
O(3) $\cdots$ O(5)	2·63	O(6) $\cdots$ N(2)	2·19
O(2) $\cdots$ O(5$^{\mathrm{I}}$)	2·65		

Roman numerals as superscripts refer to atoms in the following equivalent positions relative to the reference molecule at x, y, z:

I	$1 - x, 1 - y, -z$	IV $\frac{1}{2} - x, -\frac{1}{2} + y, -z$
II	$\frac{1}{2} - x, \frac{1}{2} + y, -z$	V $x - \frac{1}{2}, \frac{1}{2} - y, z - 1$
III	$1 - x, -y, 1 - z$	VI $\frac{1}{2} + x, \frac{1}{2} - y, z$

normal to the linear uranyl group. The two nitrate groups, crystallographically equivalent, are co-ordinated as bidentate ligands, and lie approximately in the base plane, together with the two oxygen atoms from the equivalent ethyl carbamate groups so that the symmetry of the immediate co-ordination to the uranium atom is D_{2h}. The six oxygen atoms are coplanar (Table 5).

The Uranyl Group.—The U–O bond lengths of the uranyl group [1·73(2) Å], which is symmetrical and linear, agree with reported values (see Table 7).[5-10]

The $\nu_{\mathrm{as}}(UO_2)$ is observed at 937 cm^{-1}, very close to that of the compounds listed in Table 7. The Raman
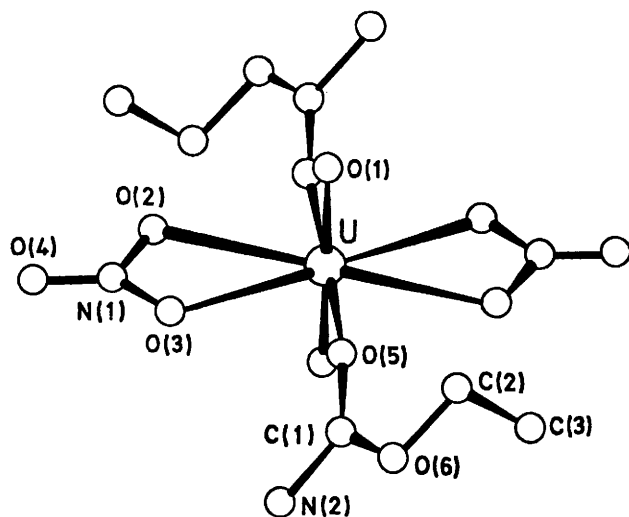

FIGURE 1

spectra show two strong absorptions at 855 and 862 cm^{-1} due to $\nu_{\mathrm{sym}}(UO_2)$. Owing to the high symmetry of the

compound being examined the $\nu_{\mathrm{sym}}(UO_2)$ present in the aforementioned compounds, might be absent in the i.r. region; unfortunately the presence of a weak absorption of the ligand at 855 cm^{-1} masks this region.

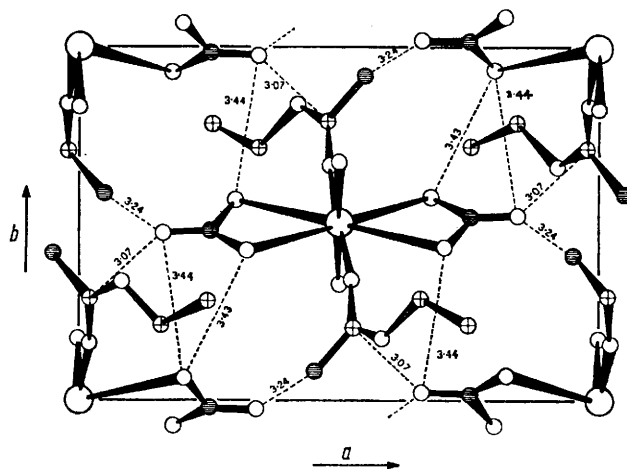

FIGURE 2

The Nitrate Group.—Bond lengths and angles in the nitrate group are not different from the normal values, and compare very favourably with those reported for other similar compounds (Table 7).

As expected, the D_{3h} symmetry of the free nitrate group is lowered to C_{2v} in the complex because of asymmetry introduced by co-ordination. As shown in Table 5, the group is perfectly planar and is tilted 4·5° with respect to the equatorial plane. The i.r. absorptions of the NO$_3^-$ group are in accordance with these results. In fact the single strong absorption, which occurs in the region 1390—1350 cm^{-1} for ionic nitrates, is split so that a pair of bands at 1270 and 1290 cm^{-1} and a strong absorption at 1523 cm^{-1} with a shoulder at 1510 cm^{-1} are observed; they are characteristic of a chelate nitrato-group according to general diagnostic criteria.[9,11-13]

The characteristic absorptions of some uranyl nitrato complexes are summarized in Table 7.

The Ligand.—The ethyl carbamate ligand is co-ordinated to the uranium atom through the amidic oxygen atom. The U–O(ligand) distance of 2·40(2) Å is equal to that found for U–O(water) in [UO$_2$(NO$_3$)$_2$-(H$_2$O)$_2$],4H$_2$O [2·39(2) Å].[7] The U–O(5)–C(1) angle is *ca.* 10° lower than the U–O–As or U–O–P angles found in [UO$_2$(NO$_3$)$_2$(Ph$_3$AsO)$_2$][14] and in a series of similar complexes.[15-17] This feature has no immediate explanation but the value of the angle at the oxygen atom

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could perhaps be correlated with the steric hindrance of the neutral ligand.

Bond distances and angles in the co-ordinated ethyl carbamate are reported for comparison in Figure **3** together with those of the free ligand, whose structure was determined by the *X*-ray analysis.[18]

very short $O(6) \cdots N(2)$ contact of 2·19 Å allows for the formation of intramolecular hydrogen bonds between these two atoms. Some type of interaction could also explain the existence of the asymmetry in the angles at the C(1) atom which in principle should be equivalent.

Co-ordination of ethyl carbamate to the uranium atom

TABLE 7

Some interatomic distances (Å), angles (°), and vibrational frequencies (cm⁻¹) of some nitrato-uranyl complexes

Complex	U–O (uranyl)	U–O (eq. bond with neutral ligand)	N–O (co-ord. O)	N–O (unco-ord. O)	O–N–O (chelat- ing site)	$\nu_{as}(UO_2)$	$\nu_{sym}(UO_2)$	$\nu_{as}(NO_2)$ (str)	$\nu_{sym}(NO_2)$ (str)
$[UO_2(NO_3)_2L_2]$	1·73(2)	2·40(2)	1·29(3) 1·30(3)	1·19(3)	114(2)	937	855 862	1510sh 1523	1270 1290
$[UO_2(NO_3)_2(H_2O)_2],4H_2O$ [a-c]	1·770 1·749	2·397	1·260 1·271	1·207 1·231	114·6 115·6	941	864		
$UO_2(NO_3)_2,3H_2O$ [b]			1·269			948	874	1517 1545	1284 1308
$[UO_2(NO_3)_2(H_2O)_2]$ [d,e]	1·754 1·763	2·446 2·457	1·253 1·275 1·262	1·190 1·213	114·4 115·3	951		1515 1547	1280 1311
α-$[UO_2(NO_3)_2(urea)_2]$ [f]						938		1510 1520	1300 1320

[a] Ref. 5.　[b] Ref. 6.　[c] Ref. 7.　[d] Ref. 8.　[e] Ref. 9.　[f] Ref. 10.

Atom C(1) appears to be essentially sp^2 hybridized thus allowing the unhybridized p orbital to join in partial π bonding with O(5), O(6), and N(2). The angle of 115° at the O(6) atom indicates that this atom is
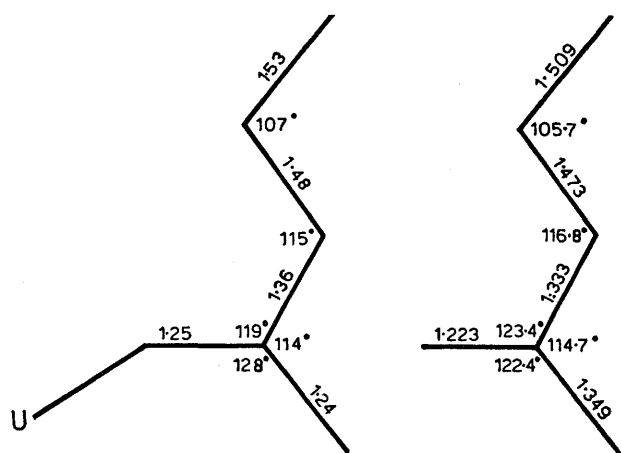

FIGURE 3

partially sp^2 in character and this may account for the approximate planarity of the entire co-ordinated ligand, as well as in the free ligand. The C(2)–C(3) distance is normal. The short C–N bond distance in the complex indicates the possibility of the nitrogen lone-pair participating in some way in the delocalized system of the ligand. This is also supported by the n.m.r. results.

There is no evidence of strong intermolecular hydrogen bonding which is certainly present in the structure of the free ligand, the shortest contacts of this type being of the order of 3·14 and 3·24 Å (Table 6). However the

causes a lowering of the C=O stretching frequency from 1690 to 1670 cm⁻¹ in KBr and from 1740 to 1680 cm⁻¹ in chloroform solution. The different absorption frequencies observed for the free ligand in solid and solution must be attributed to the strong hydrogen bonding which is present in the solid. The same is true for the stretching frequencies of the NH_2 group. In fact the broad absorption observed in the 3360—3570 cm⁻¹ region for the solid is resolved in the spectra of the chloroform solution so that five strong peaks at 3200, 3280, 3350, 3450, and 3525 cm⁻¹ are observed. As far as the stretching frequencies of the NH_2 group in the complex are concerned, the two strong absorption peaks at 3350 and 3490 cm⁻¹ in the solid are shifted to 3420 and 3540 cm⁻¹ respectively for chloroform solution, probably owing to weak intermolecular interaction through hydrogen bonding.

The co-ordination seems to have very little influence on the amidic C=O bond length (with respect to that of the free ligand). However, strong co-ordination of the ligand to uranium atom is clearly indicated by ¹H n.m.r. measurements. In fact a large withdrawing of electrons from the entire molecule induced by co-ordination is observed. Free ligand (p.p.m., 15% in CD_3COCD_3): 4·09 (br, 2H), 5·94 (q, 2H), 8·81 (t, 3H); complex: 3·17 (br, 2H), 5·47 (q, 2H), 8·61 (t, 3H).

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