Additionally, it must discussed whether the structural instabilities caused by a trigonal planar coordination of water molecules can be compensated by a deviation from sp^3 hydridization of the water oxygen, *i.e.* partly sp^2 hybridization. This could explain the enlarged intramolecular H—O—H angle (see Table 3), which is obviously due to metal–oxygen interaction. This interaction might also be responsible for the low frequency of the H_2O bending fundamental (1604 cm^{-1}, 95 K; Henning, 1988); see the discussion given by Falk (1984) and Lutz (1988).

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References

CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.

ECKERS, W. & LUTZ, H. D. (1985). *Spectrochim. Acta Part A*, **41**, 1321–26.

FALK, M. (1984). *Spectrochim. Acta Part A*, **40**, 43–48.

HENNING, J. (1988). Dissertation. Univ. of Siegen, Federal Republic of Germany.

KARTHA, G. (1952*a*). *Acta Cryst.* **5**, 845–846.

KARTHA, G. (1952*b*). *Proc. Ind. Acad. Sci. Sect. A*, **36**, 501–529.

LEHMANN, M. S., KUHS, W. F., MCINTYRE, G. J., WILKINSON, C. & ALLIBON, J. R. (1989). *J. Appl. Cryst.* **22**, 562–568.

LUTZ, H. D. (1988). *Struct. Bonding (Berlin)*, **69**, 97–125.

LUTZ, H. D., ALICI, E. & BUCHMEIER, W. (1985). *Z. Anorg. Allg. Chem.* **535**, 31–38.

LUTZ, H. D. & KLÜPPEL, H. J. (1975). *Ber. Bunsenges. Phys. Chem.* **79**, 98–104.

LUTZ, H. D., KLÜPPEL, H. J. & KESTERKE, H. J. (1976). *Z. Anorg. Allg. Chem.* **423**, 83–90.

LUTZ, H. D. & LANGE, N. (Undated). Unpublished results.

MANOTTI LANFREDI, A. M., PELLINGHELLI, M. A., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1972). *Acta Cryst.* B**28**, 679–682.

SEARS, V. F. (1986). In *Neutron Scattering, Methods in Experimental Physics*, Vol. 23, edited by K. SKÖLD & D. L. PRICE, pp. 521–550. New York: Academic Press.

SHELDRICK, G. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SIKKA, S. K., MOMIN, S. N., RAJAGOPAL, H. & CHIDAMBARAM, R. (1968). *J. Chem. Phys.* **48**, 1883–1890.

WILKINSON, C., KHAMIS, H. W., STANSFIELD, R. D. & MCINTYRE, G. J. (1988). *J. Appl. Cryst.* **21**, 471–478.

Acta Cryst. (1990). C**46**, 981–983

Actinide Structural Studies. 19.* Structure of *af*-Dinitrato-*bd*-dioxo-*ce*-bis(urea)uranium(VI)

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Abstract. $[U(NO_3)_2(O)_2(CH_4N_2O)_2]$, $M_r = 514{\cdot}09$, monoclinic, $P2_1/c$, $a = 14{\cdot}109\ (3)$, $b = 7{\cdot}727\ (3)$, $c = 11{\cdot}210\ (3)$ Å, $\beta = 99{\cdot}02\ (2)°$, $V = 1207{\cdot}0\ (5)$ Å^3, $Z = 4$, $D_m = 2{\cdot}81$, $D_x = 2{\cdot}83$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 128{\cdot}4$ cm^{-1}, $T = 290$ K, $R = 0{\cdot}028$ for 1799 unique observed $[I/\sigma(I) \geq 2{\cdot}0]$ reflections. The title compound contains a UO_2 group [mean U—O 1·754 (6) Å] coordinated by two *trans* urea molecules [mean U—O 2·345 (4) Å] and two *trans* bidentate nitrate groups [mean U—O 2·530 (5) Å]. Two weak intramolecular N—H···O bonds are formed between urea molecules and one of the uranyl O atoms [N···O 3·15 (1) Å].

Introduction. All uranyl complexes with urea previously studied by X-ray and neutron diffraction show pentagonal bipyramidal coordination by O atoms around the uranyl group. In the case of nitrate complexes, the coordination about the UO_2 group was reported to consist either of five oxygens contributed by the urea molecules (Zalkin, Ruben & Templeton, 1979) or of four oxygens belonging to the urea molecules and one water molecule respectively (Dalley, Mueller & Simonsen, 1972), and in each

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* Part 18: Alcock, Kemp, Leciejewicz & Pennington (1989).

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case nitrate groups are not bonded to the uranyl group. We considered it worthwhile to study the structure of the uranyl nitrate complex with the smallest reported number of urea molecules, *i.e.* $UO_2(NO_3)_2[CO(NH_2)_2]_2$, to determine the effect of the reduced UO_2:urea ratio on the coordination.

Experimental. The title compound was obtained by adding solid urea to a solution of uranyl nitrate in ethanol, the ratio of UO_2^{2+} to $CO(NH_2)_2$ being 1:2. After a few days yellow platy single crystals separated out, some of which were twinned. Data were collected with a Nicolet $P2_1$ four-circle diffractometer in $\omega/2\theta$ mode. Crystal dimensions were $0{\cdot}06 \times 0{\cdot}28 \times 0{\cdot}38$ mm. Maximum 2θ was 50°, with scan range $\pm 1{\cdot}1°$ (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 5–29° $\min^{-1}$, depending on the intensity of a 2 s prescan; the background was measured at each end of the scan for 0·25 of the scan time. *hkl* ranges were: 0/16; 0/9; −13/13. Three standard reflections were monitored every 200 reflections and showed no significant changes during data collection. Unit-cell dimensions and standard deviations were obtained by least squares using 15 reflections $(28 < 2\theta < 30°)$. Reflections were processed using profile analysis to give 2121 unique reflections $(R_{\rm int} = 0{\cdot}025)$; 1799 were considered observed $[I/\sigma(I) \geq 2{\cdot}0]$ and used in refinement; they were corrected for Lorentz, polarization and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0·43 and 0·22.

The U atom was located by the Patterson interpretation section of the *SHELXTL* program and the light atoms then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. One urea ligand was very well defined, and its H atoms appeared on difference syntheses; these were included riding on the corresponding N atoms with fixed $U = 0{\cdot}08$ Å^2. In the other urea ligand, the N atoms had much larger thermal parameters, no H-atom positions could be seen and so none were included in refinement. Final refinement was on F by cascaded least-squares methods refining 173 parameters including a secondary-extinction parameter of 0·00036 (4). The largest positive and negative values in a final difference synthesis were 1·1 and $-0{\cdot}8$ e Å^{-3} (ripples around U). A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0{\cdot}002$ was used and shown to be satisfactory by a weight analysis. Final $R = 0{\cdot}028$ (0·036 for all data), $wR = 0{\cdot}033$. Maximum shift/e.s.d. in final cycle 0·4. Computing was performed with *SHEXTL-PLUS* (Sheldrick, 1986) on a DEC MicroVAXII computer. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1 and bond lengths and angles in Table 2.* Fig. 1 shows a view of the molecule, and Fig. 2 a projection of the unit cell along the *c* axis.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å$^2 \times 10^3$)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	$U_{\rm eq}$
U	2531·7 (2)	3672·2 (4)	5944·1 (2)	30 (1)
O(1)	2744 (4)	2810 (8)	7419 (5)	43 (2)
O(2)	2355 (4)	4585 (8)	4504 (5)	41 (2)
O(11)	1561 (4)	6141 (8)	6646 (6)	49 (2)
O(12)	3052 (4)	6661 (7)	6683 (6)	49 (2)
O(13)	2128 (6)	8693 (8)	7137 (7)	68 (3)
O(21)	3478 (4)	1181 (8)	5279 (6)	54 (2)
O(22)	1969 (4)	888 (8)	4867 (6)	54 (2)
O(23)	2857 (6)	−1116 (9)	4318 (7)	71 (3)
N(1)	2256 (5)	7241 (10)	6826 (6)	42 (3)
N(2)	2776 (5)	273 (10)	4803 (6)	43 (3)
O(3)	4182 (3)	4221 (8)	6079 (5)	46 (2)
N(31)	4905 (6)	3977 (14)	8014 (8)	92 (5)
N(32)	5772 (4)	4567 (12)	6523 (8)	65 (3)
C(3)	4925 (6)	4259 (12)	6854 (8)	44 (3)
O(4)	886 (4)	3133 (8)	5804 (6)	52 (2)
N(41)	483 (7)	2140 (21)	7579 (12)	125 (6)
N(42)	−596 (7)	2615 (30)	6004 (13)	171 (8)
C(4)	263 (6)	2588 (14)	6400 (10)	58 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

U—O(1)	1·764 (6)	U—O(2)	1·744 (6)
U—O(11)	2·544 (6)	U—O(12)	2·524 (6)
U—O(21)	2·521 (6)	U—O(22)	2·533 (6)
U—O(3)	2·348 (5)	U—O(4)	2·341 (5)
O(11)—N(1)	1·290 (9)	O(12)—N(1)	1·243 (10)
O(13)—N(1)	1·197 (10)	O(12)—N(2)	1·262 (9)
O(22)—N(2)	1·247 (10)	O(23)—N(2)	1·217 (10)
O(3)—C(3)	1·252 (9)	N(31)—C(3)	1·324 (12)
N(32)—C(3)	1·328 (11)	O(4)—C(4)	1·256 (12)
N(41)—C(4)	1·354 (17)	N(42)—C(4)	1·224 (13)
N(41)—O(1)	3·263 (17)		
N(31)—O(1)	3·149 (12)		
O(1)—H(31a)	2·361 (30)		
N(31)—H(31a)	1·094 (30)		
O(1)—U—O(2)	177·8 (2)	O(1)—U—O(11)	90·8 (2)
O(2)—U—O(11)	88·7 (2)	O(1)—U—O(12)	92·3 (2)
O(2)—U—O(12)	85·7 (2)		
O(1)—U—O(21)	88·2 (2)	O(2)—U—O(21)	92·3 (2)
O(1)—U—O(22)	96·9 (2)	O(2)—U—O(22)	85·0 (2)
O(1)—U—O(3)	89·3 (2)	O(2)—U—O(3)	89·0 (2)
		O(12)—U—O(3)	65·1 (2)
O(21)—U—O(3)	65·9 (2)		
O(1)—U—O(4)	90·9 (2)	O(2)—U—O(4)	90·8 (2)
O(11)—U—O(4)	65·0 (2)		
		O(22)—U—O(4)	65·4 (2)
O(3)—U—O(4)	179·8 (4)		
		U—O(3)—C(3)	139·7 (6)
O(3)—C(3)—N(31)	122·2 (8)	O(3)—C(3)—N(32)	120·2 (8)
N(31)—C(3)—N(32)	117·6 (8)	U—O(4)—C(4)	142·5 (6)
O(4)—C(4)—N(41)	122·1 (8)	O(4)—C(4)—N(42)	122·4 (12)
N(41)—C(4)—N(42)	114·9 (11)		
N(31)—H(31a)—O(1)	127·5		

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* Lists of structure factors, H-atom parameters, anisotropic thermal parameters and full angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52593 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The title compound is monomeric and displays hexagonal bipyramidal coordination about the U atom (Fig. 1) resulting from the two uranyl O atoms, the O atoms from the two urea molecules and four O atoms from two bidentate nitrate groups. Thus it shows a significant difference from the previous urea complexes which lack coordinated nitrate (Dalley *et al.*, 1972; Zalkin *et al.*, 1979), but the overall coordination is that typical of UO_2^{2+} with at least two short-bite bidentate ligands, as in $[UO_2(Ph_3PO)_2(NO_3)_2]$ (Alcock, Roberts & Brown, 1982), or $[UO_2(H_2O)_2(NO_3)_2]$ (Dalley, Mueller & Simonsen, 1971). The observed bond lengths and angles are in good agreement with those reported earlier for the UO_2 group, nitrate and urea molecules respectively. The UO_2 is nearly linear with a U—O bond distance of 1·754 (4) Å (mean), close to the value of 1·73 Å deduced from Raman and infrared spectroscopy data (Bullock, 1969).

The U—O(NO_3) distance [mean 2·530 (5) Å] is significantly longer than the U—O(urea) distance [2·345 (4) Å]. Such distinction between U—O distances is also found in $[UO_2(NO_3)_2(H_2O)_2]$, with averaged U—O(NO_3) of 2·497 (5) and U—O(OH_2) of 2·452 (5) Å (Dalley *et al.*, 1971). The most striking feature of the coordination of the urea molecule containing C(3) is its orientation, with its molecular plane perpendicular to the equatorial plane of the U atom with a dihedral angle of 105·0 (8)°. (The dihedral angle of the other urea molecule is 94·9°.) The direct location of the H-atom positions on the urea molecule containing C(3) from a difference synthesis confirms that they lie as expected, in the N_2CO plane, allowing conjugation between the *p* orbitals on these atoms. This orientation permits a weak N—H···O interaction with one of the uranyl O atoms with an H···O distance of 2·36 (3) Å, *i.e.* just within the 2·4 Å distance criterion for O···H hydrogen bonding suggested by Hamilton & Ibers (1968). $N—\hat{H}···O$ is 127·5°. The other urea is bent out of the equatorial plane on the same side; it probably interacts similarly with this O (although its H atoms cannot be directly located). This probably explains why this U—O bond is slightly longer than that on the other side. Two such N—H···O interactions are also present in the $[UO_2(H_2O)(urea)_4]^{2+}$ ion (Dalley *et al.*, 1972), though they were not considered significant when the structure was originally described. They have an (N)H···O(U) distance of 2·26 (3) Å and $N—\hat{H}···O$ of 143·7 (1·3)° for one bond and 2·39 (3) Å and 135·3 (1·4)° for the other. The crystal packing (Fig. 2) shows that the molecules are aligned in planes perpendicular to **a**, with O···O van der Waals contacts within the planes, and face-to-face contacts between urea molecules between planes. Surprisingly, no intermolecular N—H···O hydrogen bonds can be identified.

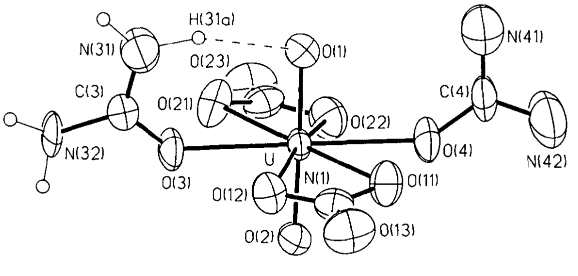

Fig. 1. The $UO_2[CO(NH_2)_2]_2(NO_3)_2$ complex showing the atomic numbering.

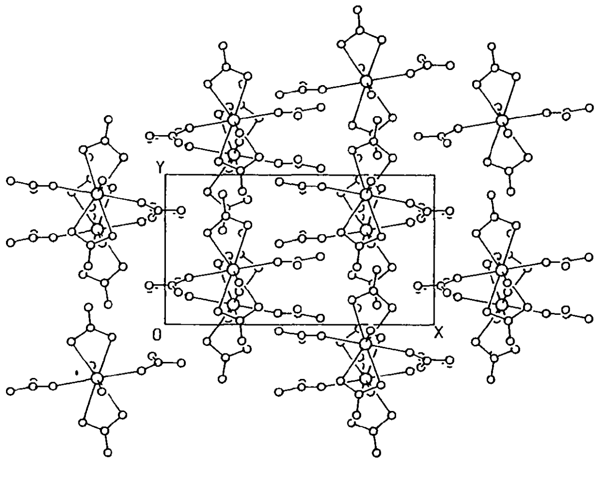

Fig. 2. View of the unit cell down the *c* axis.

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References

Alcock, N. W., Kemp, T. J., Leciejewicz, J. & Pennington, M. (1989). *Acta Cryst.* C**45**, 719–721.

Alcock, N. W., Roberts, M. M. & Brown, D. (1982). *J. Chem. Soc. Dalton Trans.* pp. 25–31.

Bullock, J. I. (1969). *J. Chem. Soc. A*, pp. 781–784.

Dalley, N. K., Mueller, M. H. & Simonsen, S. H. (1971). *Inorg. Chem.* **10**, 323–328.

Dalley, N. K., Mueller, M. H. & Simonsen, S. H. (1972). *Inorg. Chem.* **11**, 1840–1845.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination.* New York: W. A. Benjamin.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Sheldrick, G. M. (1986). *SHELXTL-PLUS. Users Manual.* Nicolet XRD Corporation, Madison, Wisconsin, USA.

Zalkin, A., Ruben, H. & Templeton, D. H. (1979). *Inorg. Chem.* **18**, 519–521.