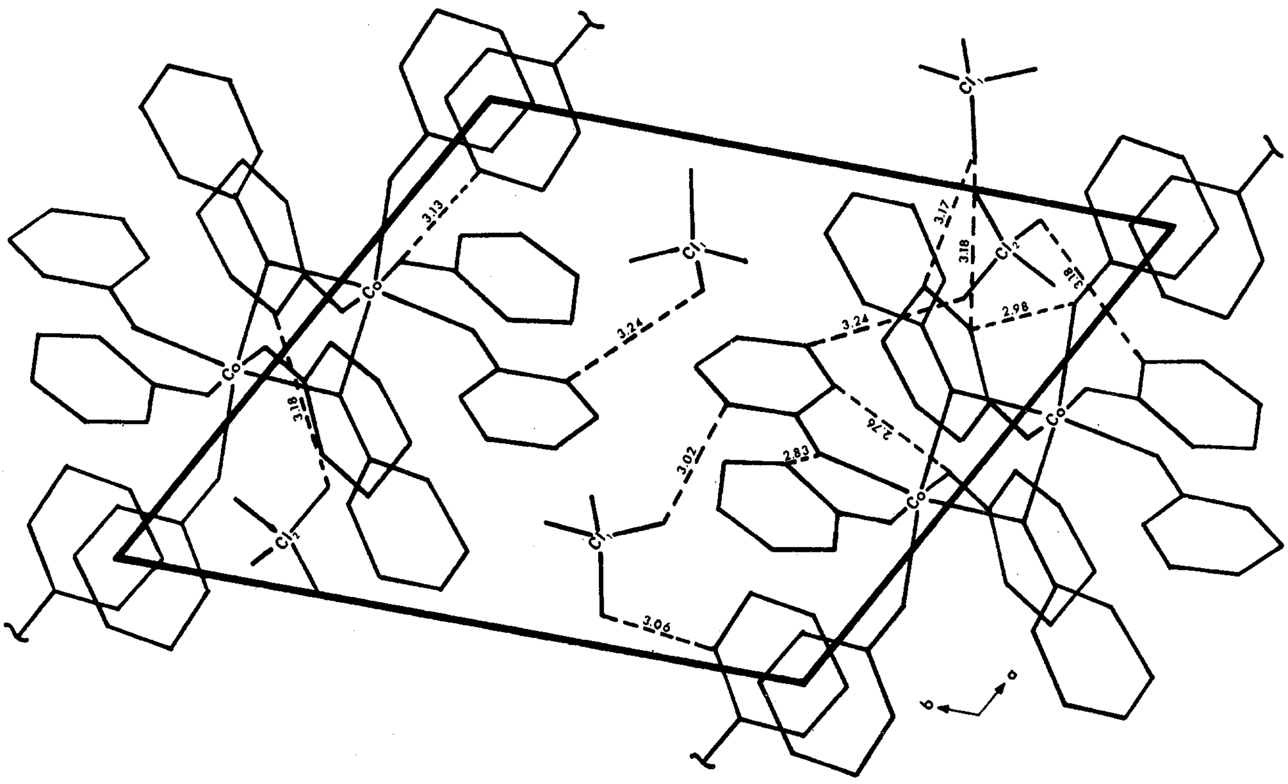

Figure 4.—Projection of the unit cell contents down the (00*l*) axis showing hydrogen-bonding scheme.

liable tool. Actually, the best prediction of bonding sites in substituted ureas is to assume that metal to oxygen bonds are the primary factor in the coordination.

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Contribution from the Materials Science Division,
Argonne National Laboratory, Argonne, Illinois 60439

A Neutron Diffraction Study of Monoaquotetraureadioxouranium(VI) Nitrate[1]

By N. K. DALLEY, M. H. MUELLER,* and S. H. SIMONSEN

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The crystal structure of $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$ has been determined by neutron diffraction. The compound is monoclinic with $a = 9.99$ (2), $b = 14.99$ (3), $c = 13.18$ (3) Å, $\beta = 100.08$ (3)°, and space group $P2_1/c$ with $Z = 4$. Preliminary X-ray data were used to locate the approximate positions of the uranium and nonhydrogen atoms of the urea and water ligands, utilizing the heavy atom method. The atoms of the nitrate ions and hydrogen atoms were located and a least-squares refinement completed using neutron data to an $R_w = 4.7\%$. The uranyl ion is nearly linear with a U—O distance of 1.77 (2) Å and is surrounded by a planar pentagon consisting of five oxygen atoms, four from urea ligands at distances of 2.34 (1)–2.38 (1) Å and one from the water ligand at a distance of 2.46 (2) Å. The plane formed by these oxygen atoms is nearly perpendicular to the axis of the O—U—O ion. The structure is connected by an extensive system of hydrogen bonds which involve nitrate ions both through coordination and through bridging *via* hydrogen bonds.

Introduction

The coordination of the uranyl ion in $UO_2(H_2O)[CO(NH_2)_2]_4(NO_3)_2$ has been a matter of some disagreement. Campisi,[2] on the basis of infrared results, postulated that the compound should be formulated as $\{UO_2(H_2O)[CO(NH_2)_2]_4(NO_3)\}NO_3$ with the uranyl ion surrounded by six oxygen atoms—four from urea ligands, one from a water ligand, and one from a monodentate nitrato group. Gentile[3] proposed a polymeric structure with a sixfold coordination about the uranyl consisting of four oxygen atoms from urea ligands, an

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[1] Research supported by the U. S. Atomic Energy Commission.

[2] L. S. Campisi, Ph.D. Dissertation, Fordham University, New York, N. Y., 1965.

[3] P. S. Gentile, Fordham University, private communication.

oxygen atom from a water ligand, and a uranyl oxygen from a neighboring complex. A third type of coordination is also possible, a uranyl ion coordinated to only five oxygen atoms. The likelihood of such an arrangement was supported by Babaeva, *et al.*,[4] who established from infrared results that a urea ligand replaces a nitrato ligand in uranyl complexes, and by Evans,[5] who pointed out that fivefold coordination is geometrically stable, allowing oxygen atoms to approach at an optimum distance in a plane without overcrowding, and that sixfold coordination of an uranyl ion was unlikely unless a highly polarizing bidentate ligand, such as nitrato group, was involved. A number of examples of fivefold coordination are known: $UO_2(C_5H_7O_2)_2 \cdot H_2O$,[6] U_3O_8,[7] $K_3UO_2F_5$,[8] $Ca(H_3O)_2(UO_2)_2(SiO_4)_2 \cdot 3H_2O$,[9] $Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$,[10] $Cs_2(UO_2)_2(SO_4)_3$,[11] $Cs_2(UO_2)_2V_2O_8$,[12] $Cs_{0.9}UO_2OCl_{0.9}$,[13] $[UO_2(C_9H_6NO)_2C_9H_7NO] \cdot CHCl_3$,[14] $UO_2(C_9H_6NO)_2C_9H_6NOH$,[15] $(NH_4)_2(UO_2)_2(C_2O_4)_3$,[16] $UO_2(NO_3)_2 \cdot 2(C_6H_5)_3AsO$,[17] $[UO_2(CH_3COO)_2(C_6H_5)_3PO]_2$,[18] $[UO_2(OH) \cdot 3CO(NH_2)_2]I_4$,[19] and $UO_2[(C_2H_5)_2NCS_2]_2(C_6H_5)_3AsO$.[20] In light of this, the most probable formation of the title compound would be $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$, with the uranyl ion coordinated to four oxygen atoms from urea ligands and to the oxygen atom of a water ligand.

A neutron diffraction study was undertaken because the presence of the uranium atom would have made it difficult or impossible to obtain accurate parameters of the light atoms using X-ray methods. The bonding of the urea ligands was of interest because very few structural studies have been made of urea complexes. Also, the hydrogen bonding scheme was important. There are a total of 18 hydrogen atoms present in the compound, and with 16 urea hydrogens the possibility of finding N—H···O hydrogen bonds was likely. Relatively little information from neutron diffraction has been reported regarding this type of bonding.

Experimental Section

The crystals used in this study were furnished by Dr. P. S. Gentile and Dr. D. Conklin of Fordham University. Spherical crystals used in the X-ray investigation were ground in a sphere grinder and large spherical crystals for the neutron study were shaped manually using sandpaper and wet filter paper.

The preliminary X-ray study was undertaken to obtain a trial structure. The compound was found to be monoclinic, space group $P2_1/c$. Lattice constants were determined by a least-squares fit of 2θ values obtained at ambient temperature using a GE diffractometer and zirconium filtered molybdenum radiation. The lattice parameters are listed in Table I, together with those obtained from the neutron diffraction study. Since the crystal used for the X-ray study had a somewhat irregular shape, there may be considerable error in the 2θ values; hence, the lattice parameters given in the abstract are based on neutron results. Intensity data were collected to a $\sin \theta/\lambda$ limit of 0.43 by the stationary crystal–stationary counter technique using Mo Kα radiation and balanced filters. Corrections for α_1–α_2 splitting and an approximate correction for absorption were applied based on a spherical crystal even though it had an irregular shape (μ = 104.6 cm^{-1}; μr = 0.68).

TABLE I

CRYSTALLOGRAPHIC DATA FOR $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$

	X-Ray data[a]	Neutron data[a]
a, Å	9.969 (6)	9.99 (2)
b, Å	14.888 (9)	14.99 (3)
c, Å	13.113 (8)	13.18 (3)
β, deg	99.96 (7)	100.08 (3)
	ρ_{obsd} 2.223	ρ_{calcd} 2.258
	$Z = 4$	

[a] Numbers in parentheses are standard errors that occur in last recorded decimal place.

Neutron data were obtained from a large spherical crystal with r = 0.5 cm weighing 1.292 g by means of the Arcade system controlled with an IBM 1130 computer.[21] A 2θ step-scan technique was used with an increment of 0.10° and with counting time controlled by a fission counter monitor. The average counting time per reflection was about 15 min. A wavelength of 1.063 Å was obtained from the (110) plane of a beryllium monochromator. A 1-in. diameter Reuter–Stokes BF_3 counter with an active length of 7.5 in. was employed as a detector. A total of 3702 reflections were collected to a $\sin \theta/\lambda$ limit of 0.61. The intensities were placed on a nearly absolute scale by comparison with the (400) reflection of a standard sodium chloride crystal. Reflections were considered to be unobserved or have zero intensity if the adjusted background was equal to or greater than the integrated intensity from the scan. A spherical absorption correction was applied using μ_{obsd} = 1.38 cm^{-1}; μr = 0.69.

Solution and Refinement of the Structure

A trial structure was obtained using the X-ray data. The uranium parameters were deduced from a Patterson map, and probable locations for the uranyl oxygens and the nonhydrogen atoms of the urea and water ligands were found in a Fourier map phased by the uranium. All subsequent refinement was carried out using neutron data. A difference map indicated that three atoms of the X-ray trial model were in error; a difference map based on the corrected model revealed the positions of the atoms in the nitrate ions; and in the next difference map all 18 hydrogen atoms were found. The neutron scattering cross sections used were 0.94 (N), 0.85 (U), 0.66 (C), 0.577 (O), and −0.378 (H) (all × 10^{-12} cm/atom).[22]

Refinement was carried out using the full-matrix least-squares program of Busing, Martin, and Levy;[23] the Evans[24] weighting scheme was applied. Of the 3702 reflections observed 183 were considered unobserved and were not included in the refinement. Initial refinement was carried out using isotropic temperature factors to a weighted R value of 11%, after which anisotropic temperature factors were used for all atoms. In this paper R and weighted R or R_w are defined as

$$R = \frac{\sum|F_o| - s_q|F_o|}{\sum|F_o|} \text{ and } R_w = \sqrt{\frac{\sum(w|F_o| - s_q|F_c|)^2}{\sum w|F_o|^2}}$$

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TABLE II

POSITIONAL AND THERMAL[a] PARAMETERS OF $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0.0062 (2)[b]	0.1670 (1)	0.3333 (2)	0.0048	0.0025	0.0039	−0.0002	−0.0002	−0.0003
O(6)	0.0750 (3)	0.1548 (2)	0.4659 (2)	0.0086	0.0043	0.0035	−0.0010	0.0005	−0.0006
O(7)	−0.0569 (3)	0.1816 (2)	0.1996 (2)	0.0073	0.0040	0.0046	−0.0006	−0.0014	0.0004
O(1)	0.0475 (3)	0.3233 (2)	0.3370 (3)	0.0071	0.0025	0.0077	−0.0004	−0.0009	−0.0005
C(1)	0.1228 (2)	0.3798 (2)	0.3923 (2)	0.0058	0.0029	0.0063	−0.0005	−0.0002	0.0001
N(11)	0.2521 (2)	0.3604 (2)	0.4299 (3)	0.0073	0.0045	0.0073	0.0001	−0.0018	−0.0006
H(1)N(11)	0.3127 (6)	0.4040 (4)	0.4760 (5)	0.0128	0.0055	0.0088	−0.0010	−0.0029	−0.0008
H(2)N(11)	0.2878 (6)	0.3033 (5)	0.4150 (6)	0.0110	0.0072	0.0099	0.0012	−0.0032	−0.0017
N(12)	0.0755 (2)	0.4595 (3)	0.4096 (2)	0.0093	0.0036	0.0126	0.0003	−0.0015	−0.0026
H(1)N(12)	0.1333 (6)	0.5061 (5)	0.4499 (7)	0.0112	0.0047	0.0195	−0.0006	−0.0030	−0.0033
H(2)N(12)	−0.0172 (8)	0.4738 (5)	0.3748 (9)	0.0152	0.0067	0.0250	0.0037	−0.0093	−0.0061
O(2)	0.2343 (3)	0.1885 (2)	0.3072 (2)	0.0047	0.0047	0.0036	0.0003	0.0013	0.0004
C(2)	0.2898 (3)	0.2117 (2)	0.2337 (2)	0.0076	0.0036	0.0044	−0.0003	0.0013	−0.0001
N(21)	0.4254 (2)	0.2102 (2)	0.2421 (2)	0.0070	0.0083	0.0076	0.0002	0.0020	0.0007
H(1)N(21)	0.4689 (7)	0.2258 (6)	0.1926 (6)	0.0111	0.0118	0.0087	0.0004	0.0007	0.0012
H(2)N(21)	0.4789 (6)	0.1857 (6)	0.3095 (6)	0.0088	0.0127	0.0091	0.0018	0.0005	0.0015
N(22)	0.2211 (2)	0.2417 (2)	0.1438 (2)	0.0113	0.0084	0.0047	0.0009	0.0001	0.0022
H(1)N(22)	0.1194 (7)	0.2397 (6)	0.1348 (5)	0.0136	0.0115	0.0083	0.0008	0.0005	0.0020
H(2)N(22)	0.2623 (8)	0.2619 (7)	0.0900 (6)	0.0183	0.0131	0.0080	−0.0002	−0.0001	0.0018
O(3)	0.0954 (3)	0.0275 (2)	0.3009 (3)	0.0086	0.0028	0.0058	0.0009	−0.0011	−0.0002
C(3)	0.1773 (3)	−0.0264 (2)	0.3549 (2)	0.0075	0.0026	0.0059	0.0006	−0.0009	−0.0006
N(31)	0.1523 (2)	−0.1136 (1)	0.3501 (2)	0.0017	0.0030	0.0104	−0.0001	−0.0022	−0.0004
H(1)N(31)	0.0721 (7)	−0.1319 (4)	0.2962 (7)	0.0123	0.0048	0.0151	−0.0014	−0.0038	−0.0002
H(2)N(31)	0.2214 (7)	−0.1559 (5)	0.3860 (8)	0.0146	0.0051	0.0188	0.0015	−0.0032	−0.0001
N(32)	0.2899 (2)	0.0037 (2)	0.4169 (2)	0.0092	0.0040	0.0083	0.0003	−0.0026	−0.0007
H(1)N(32)	0.3472 (7)	−0.0385 (5)	0.4632 (6)	0.0148	0.0064	0.0127	0.0028	−0.0049	−0.0017
H(2)N(32)	0.3098 (6)	0.0667 (5)	0.4160 (6)	0.0122	0.0056	0.0126	−0.0003	−0.0035	−0.0003
O(4)	−0.1706 (3)	0.0667 (2)	0.3417 (3)	0.0077	0.0036	0.0056	−0.0011	0.0004	0.0004
C(4)	−0.2747 (3)	0.0349 (2)	0.2842 (2)	0.0061	0.0031	0.0060	−0.0010	0.0013	−0.0002
N(41)	−0.3332 (3)	−0.0383 (2)	0.3134 (2)	0.0150	0.0054	0.0091	−0.0045	0.0008	0.0003
H(1)N(41)	−0.2895 (10)	−0.0678 (6)	0.3787 (8)	0.0265	0.0085	0.0143	−0.0055	−0.0012	0.0041
H(2)N(41)	−0.4164 (8)	−0.0635 (5)	0.2702 (7)	0.0176	0.0077	0.0130	−0.0069	−0.0010	0.0027
N(42)	−0.3299 (2)	0.0723 (2)	0.1956 (2)	0.0076	0.0047	0.0084	−0.0010	−0.0016	0.0007
H(1)N(42)	−0.4154 (6)	0.0468 (5)	0.1525 (5)	0.0120	0.0070	0.0099	−0.0031	−0.0021	0.0011
H(2)N(42)	−0.2944 (8)	0.1256 (5)	0.1725 (7)	0.0169	0.0076	0.0125	−0.0034	−0.0031	0.0025
O(5)	−0.1906 (4)	0.2446 (3)	0.3819 (3)	0.0089	0.0037	0.0110	0.0008	0.0037	−0.0013
H(1)O(5)	−0.2016 (6)	0.3102 (4)	0.3922 (6)	0.0085	0.0048	0.0131	0.0009	0.0011	−0.0014
H(2)O(5)	−0.2597 (6)	0.2142 (5)	0.4090 (6)	0.0100	0.0062	0.0120	0.0002	0.0025	−0.0014
N(1)	−0.3531 (2)	0.4434 (2)	0.3916 (2)	0.0075	0.0043	0.0098	0.0011	−0.0023	−0.0018
O(11)	−0.4204 (4)	0.3949 (4)	0.3278 (5)	0.0122	0.0075	0.0175	0.0036	−0.0082	−0.0060
O(12)	−0.4011 (4)	0.5132 (3)	0.4173 (4)	0.0119	0.0062	0.0161	0.0035	−0.0059	−0.0042
O(13)	−0.2356 (4)	0.4198 (3)	0.4321 (4)	0.0078	0.0055	0.0122	0.0015	−0.0026	−0.0022
N(2)	−0.4651 (2)	0.1974 (1)	0.5173 (2)	0.0069	0.0047	0.0047	0.0008	0.0007	−0.0001
O(21)	−0.4007 (5)	0.2476 (4)	0.5776 (5)	0.0162	0.0123	0.0156	−0.0044	0.0052	−0.0072
O(22)	−0.5932 (4)	0.1803 (4)	0.5237 (4)	0.0108	0.0099	0.0096	0.0005	0.0034	−0.0010
O(23)	−0.4084 (4)	0.1572 (3)	0.4553 (3)	0.0107	0.0053	0.0070	0.0023	0.0036	−0.0002

[a] The thermal parameters are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses are standard deviations × 10^4. [c] Standard deviations for β_{11}, β_{22}, and β_{33} range from ±0.0001 to ±0.0005. Standard deviations for β_{12}, β_{13}, and β_{23} range from ±0.0001 to ±0.0002.

where s_q is the scale factor. Because of core limitations of the CDC 3600 computer, when anisotropic temperature factors were used, the atoms were divided into two groups, one containing all the positive scattering atoms and the other the hydrogen atoms; these groups were refined in alternate cycles. When the standard errors on the parameters were larger than the shifts, the refinement was terminated. The final R and R_w were 11.6 and 4.7%, respectively; an error in unit weight of 4.4 was obtained which suggests that the weighting scheme is slightly in error. We found previously[25] that when the weights were modified in an attempt to produce near unit weight of 1.0 the structural parameters and temperature factors did not change by more than one standard deviation. The present data did indicate that the weight was somewhat too great on the reflections with the largest intensities. Calculated and observed structure factors are available from the microfilm edition;[26] positional and thermal parameters are listed in Table II.

Discussion of the Structure

The asymmetric unit with the exception of the hydrogen atoms of the urea ligands is shown in Figure 1, and the atom labeling symbols are given. The omitted hydrogen atoms are named in a manner consistent with the figure; for example, the hydrogen atoms bonded to nitrogen N(11) are named H(1)N(11) and H(2)N(11). Interatomic distances and angles were calculated with the ORFFE program[27] and are listed in Table III.

Uranium Coordination.—The uranyl ion is almost linear, O—U—O angle = 177.7 (4)°, with the oxygens occupying the apical positions of the pentagonal bipyramid polygon of the heptacoordinated uranium atom (see Figure 1). Five oxygen atoms, four from urea molecules and one from a water molecule, lie in the equatorial plane forming a slightly irreg-

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(25) N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, **10**, 323 (1971).

(26) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1840. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(27) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," Report No. ORNL-TM-306, U. S. Atomic Energy Commission, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

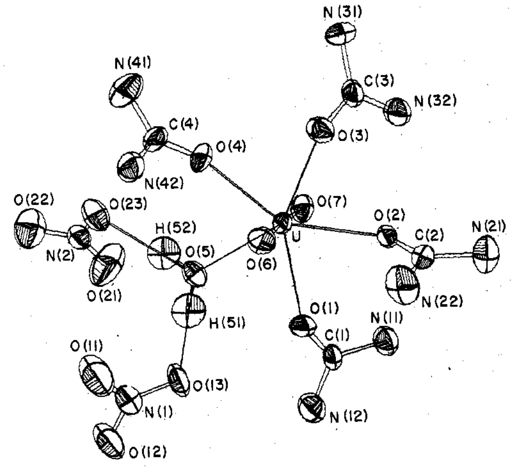

Figure 1.—Structure of $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$, except urea hydrogens, illustrating the thermal motion of these atoms. The plot was prepared using C. K. Johnson's ORTEP Program: C. K. Johnson, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report No. ORNL-3794, U.S. Atomic Energy Commission, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) IN $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$

U–O (uranyl)		O–H (water)	
U–O(6)	1.77 (2)	O(5)–H(1)–O(5)	1.00 (2)
U–O(7)	1.78 (2)	O(5)–H(2)–O(5)	0.95 (2)
U–O (coordination)		C–N (urea)	
U–O(1)	2.38 (1)	C(1)–N(11)	1.33 (2)
U–O(2)	2.38 (1)	C(1)–N(12)	1.32 (1)
U–O(3)	2.34 (1)	C(2)–N(21)	1.34 (1)
U–O(4)	2.34 (1)	C(2)–N(22)	1.34 (2)
U–O(5)	2.46 (2)	C(3)–N(31)	1.33 (1)
O–O (contacts in pentagon)		C(3)–N(32)	1.35 (2)
O(1)–O(2)	2.82 (1)	C(4)–N(41)	1.33 (1)
O(2)–O(3)	2.78 (1)	C(4)–N(42)	1.32 (2)
O(3)–O(4)	2.86 (2)	N–H (urea)	
O(4)–O(5)	2.73 (1)	N(11)–H(1)N(11)	1.02 (2)
O(5)–O(1)	2.81 (2)	N(11)–H(2)N(11)	0.96 (2)
		N(12)–H(1)N(12)	1.00 (2)
C–O (urea)		N(12)–H(2)N(12)	0.98 (2)
C(1)–O(1)	1.28 (2)	N(21)–H(1)N(21)	0.88 (2)
C(2)–O(2)	1.25 (2)	N(21)–H(2)N(21)	1.02 (2)
C(3)–O(3)	1.27 (2)	N(22)–H(1)N(22)	1.00 (2)
C(4)–O(4)	1.27 (2)	N(22)–H(2)N(22)	0.93 (2)
		N(31)–H(2)N(31)	0.99 (2)
N–O (nitrate)		N(31)–H(1)N(31)	1.02 (2)
N(1)–O(11)	1.22 (2)	N(32)–H(1)N(32)	0.99 (2)
N(1)–O(12)	1.22 (1)	N(32)–H(2)N(32)	0.97 (2)
N(1)–O(13)	1.25 (2)	N(41)–H(1)N(41)	1.00 (2)
N(2)–O(21)	1.20 (2)	N(41)–H(2)N(41)	1.00 (2)
N(2)–O(22)	1.22 (1)	N(42)–H(1)N(42)	1.01 (2)
N(2)–O(23)	1.23 (2)	N(42)–H(2)N(42)	0.99 (2)
Angles in nitrate ions		O–U–O angles	
O(11)–N(1)–O(13)	119.2 (1.0)	O(6)–U–O(7) uranyl	177.7 (0.4)
O(11)–N(1)–O(12)	120.3 (0.9)	O(1)–U–O(2)	72.7 (0.3)
O(12)–N(1)–O(13)	119.0 (1.7)	O(2)–U–O(3)	72.0 (0.5)
O(21)–N(2)–O(22)	119.9 (1.3)	O(3)–U–O(4)	75.5 (0.5)
O(21)–N(2)–O(23)	119.5 (0.8)	O(4)–U–O(5)	69.4 (0.5)
O(22)–N(2)–O(23)	120.3 (1.4)	O(5)–U–O(1)	70.9 (0.4)

ular pentagon; the U—O bond lengths average 2.38 (1) Å. A regular pentagon with this circumscribed radius would have sides of 2.80 Å; the observed O–O contacts are nearly equal and average 2.80 (2) Å (see Table III) which is the sum of the covalent nonbonding radii for two oxygen atoms.[28] The oxygens in the pentagon are slightly puckered; the equation of the least-squares plane and the deviations of the atoms from it are listed in Table IV. The uranyl U—O bond lengths of 1.77 (2) and 1.78 (2) Å are similar to those found in uranyl nitrate dihydrate[25] and uranyl nitrate hexahydrate.[29] The four U—O bonds of 2.38 (1), 2.38 (1), 2.34 (1), and 2.34 (1) Å, involving the carbonyl oxygens of urea, are not significantly different from each other, but differ significantly[30] from the 2.46 (2) Å U—O bond to the water molecule. The shorter bond lengths are in agreement with the distances of 2.39 (3), 2.38 (3), 2.33 (3), and 2.35 (3) Å found in $[UO_2(CH_3COO)_2(C_6H_5)_3PO]_2$.[18] Panattoni, *et al.*,[17] stated that the normal covalent U—O bond lies between 2.35 and 2.40 Å.

TABLE IV

LEAST-SQUARES PLANE FOR URANIUM AND OXYGEN PENTAGON

Equation of Plane

$$1.861x - 1.559y + 12.237z = 3.825$$

Deviations from Plane

Atom	Dist from plane, Å	Atom	Dist from plane, Å
U	0.004	O(3)	−0.009
O(1)	−0.117	O(4)	−0.066
O(2)	0.076	O(5)	0.112

Nitrate Ions.—The interatomic distances and angles of the nitrate ions are listed in Table III. Both ions are bound to the water oxygen by hydrogen bonds. Ferraro and Walker[31] have suggested that in such a situation the deviation of the ion from D_{3h} symmetry would not be as large as that which occurs in bidentate nitrato groups. The results of the diffraction experiment support this view. The average N—O bond length was found to be 1.22 (2) Å with none of the individual values differing by more than two σ values from the average. Also none of the N—O—N angles differ significantly from 120°. This is in contrast to the results obtained for the bond lengths and angles of bidentate nitrato groups in which there were significant differences in both bond lengths and angles.[28,29,32–37] The N—O interatomic distance of 1.22 (2) Å is shorter than the values of 1.27 (2) Å found by Hamilton[38] in lead nitrate and 1.241 (2) Å by Cherin, Hamilton, and Post[39] in sodium nitrate. However, when a correction is made for thermal motion using the riding model of the ORFFE program,[27] the average value obtained for a N—O bond is 1.27 (3) Å which may err on the high side as much as the original uncorrected value is low. The atoms of each nitrate ion are coplanar within the experimental error as determined by least-squares plane calculations.

The nitrate ions perform an important cohesive function in the structure as shown in Figure 2. Because both ions are hydrogen bonded to the same aquo

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TABLE V

BOND LENGTHS (Å) AND ANGLES (DEG) IN UREA

Compound	C-O	C-N	O-C-N	N-C-N
$\{UO_2(H_2O)[OC(NH_2)_2]_4\}(NO_3)_2$[a,b]	1.266 (13)	1.333 (10)	121 (1.5)	118 (1.6)
$CO(NH_2)_2$[40]	1.270 (7)	1.326 (6)	121.0 (3)	118.1 (6)
$CO(NH_2)_2$[41 b]	1.243 (6)	1.351 (7)	121.5 (2)	117.0 (3)
$CO(NH_2)_2$[42]	1.260 (4)	1.352 (2)	121.7 (1)	Not given
$CO(NH_2)_2$[43]	1.264 (6)	1.336 (7)	120.9 (3)	118.2 (3)
$(NH_2)_2COH^+NO_3^-$[44 b]	1.298 (2)	1.313 (1)	121.7 (1)	121.7 (1)
$Ti[OC(NH_2)_2]_6I_3$[45]	1.273 (9)	1.286 (10)	119.9 (7)	119.4 (8)
		1.331 (10)	120.6 (7)	
$[Cu(O_2CH)_2OC(NH_2)_2]_2$[46]	1.29 (2)	1.29 (2)	121.9 (17)	118.7 (16)
		1.34 (2)	119.2 (18)	

[a] This investigation. [b] Neutron diffraction data.

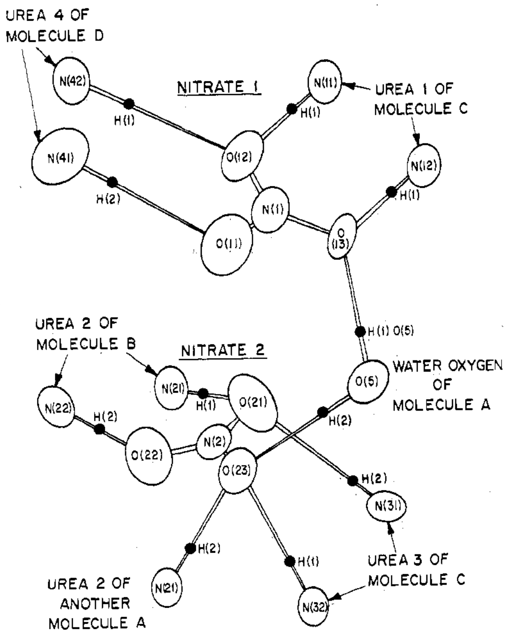

Figure 2.—Network of nitrate ions and hydrogen bonds in $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$.

TABLE VI

HYDROGEN BONDS AND CLOSE VAN DER WAALS CONTACTS

X-H···O	X-O, Å	H-O, Å	∠X-H-O, deg
O(5)—H(1)O(5)···O(13)	2.76 (1)	1.77 (2)	168.4 (1.3)
O(5)—H(2)O(5)···O(23)	2.85 (3)	1.90 (2)	175.6 (1.4)
N(22)—H(2)N(22)···O(22)	2.96 (4)	2.09 (3)	155.6 (1.6)
N(42)—H(1)N(42)···O(12)	2.97 (4)	1.97 (3)	169.4 (1.4)
N(11)—H(1)N(11)···O(12)	2.97 (4)	2.05 (3)	168.3 (1.4)
N(41)—H(2)N(41)···O(11)	2.99 (5)	2.00 (4)	173.9 (1.4)
N(12)—H(1)N(12)···O(13)	3.00 (4)	2.03 (3)	162.7 (1.7)
N(32)—H(1)N(32)···O(23)	3.06 (2)	2.11 (2)	159.6 (1.2)
N(21)—H(1)N(21)···O(21)	3.07 (4)	2.20 (4)	172.3 (1.4)
N(21)—H(2)N(21)···O(23)	3.11 (5)	2.09 (4)[a]	170.7 (1.6)
N(42)—H(2)N(42)···O(21)	3.14 (2)	2.45 (3)[a]	125.3 (1.3)
N(32)—H(2)N(32)···O(22)	3.16 (2)	2.35 (3)[a]	140.7 (1.2)
N(31)—H(2)N(31)···O(21)	3.21 (3)	2.24 (2)	162.8 (1.8)
N(11)—H(2)N(11)···O(2)	3.03 (1)	2.24 (2)	139.4 (1.3)
N(31)—H(1)N(31)···O(1)	3.04 (5)	2.07 (3)	163.6 (1.6)
N(32)—H(2)N(32)···O(2)	3.13 (1)	2.36 (2)[a]	135.9 (1.3)
N(12)—H(2)N(12)···O(3)	3.16 (4)	2.44 (4)[a]	129.3 (2.6)
N(22)—H(1)N(22)···O(7)	3.13 (2)	2.26 (3)	143.7 (1.3)
N(42)—H(2)N(42)···O(7)	3.17 (1)	2.39 (3)[a]	135.3 (1.4)

[a] Omitted from Figure 2.

TABLE VII

THERMAL DISPLACEMENTS AND THE COMPONENTS ALONG THE PRINCIPAL AXES R_1, R_2, AND R_3 OF THE VIBRATIONAL ELLIPSOIDS

Atom	R_1, Å	R_2, Å	R_3, Å
U	0.14	0.17	0.1962
O(6)	0.1654	0.2023	0.2315
O(7)	0.1551	0.2057	0.2442
O(1)	0.1588	0.1844	0.2736
C(1)	0.1600	0.1851	0.2415
N(11)	0.1674	0.2244	0.2800
H(1)N(11)	0.1947	0.2573	0.3263
H(2)N(11)	0.1945	0.2682	0.3494
N(12)	0.1787	0.2073	0.3574
H(1)N(12)	0.1917	0.2433	0.4395
H(2)N(12)	0.2135	0.2325	0.5428
O(2)	0.1445	0.1764	0.2337
C(2)	0.1854	0.1949	0.2067
N(21)	0.1814	0.2522	0.3102
H(1)N(21)	0.2301	0.2755	0.3696
H(2)N(21)	0.2010	0.2800	0.3861
N(22)	0.1747	0.2457	0.3209
H(1)N(22)	0.2394	0.2786	0.3704
H(2)N(22)	0.2459	0.3129	0.3927
O(3)	0.1666	0.1878	0.2565
C(3)	0.1674	0.1751	0.2522
N(31)	0.1824	0.2147	0.3320
H(1)N(31)	0.2013	0.2467	0.3960
H(2)N(31)	0.2224	0.2643	0.4306
N(32)	0.1784	0.2118	0.3083
H(1)N(32)	0.2097	0.2589	0.4011
H(2)N(32)	0.2103	0.2536	0.3688
O(4)	0.1758	0.2056	0.2350
C(4)	0.1570	0.1991	0.2274
N(41)	0.1833	0.2739	0.3278
H(1)N(41)	0.2399	0.3175	0.4484
H(2)N(41)	0.1841	0.2974	0.4136
N(42)	0.1737	0.2252	0.2963
H(1)N(42)	0.2008	0.2672	0.3478
H(2)N(42)	0.2400	0.2658	0.4009
O(5)	0.1716	0.2209	0.3126
H(1)O(5)	0.1957	0.2332	0.3429
H(2)O(5)	0.2178	0.2569	0.3274
N(1)	0.1709	0.2048	0.3288
O(11)	0.1751	0.2294	0.4862
O(12)	0.1879	0.2274	0.4465
O(13)	0.1744	0.2295	0.3630
N(2)	0.1780	0.2017	0.2353
O(21)	0.2459	0.2736	0.4597
O(22)	0.2149	0.2848	0.3401
O(23)	0.1737	0.2493	0.2743

oxygen atom, O(5), they could be considered a unit. This unit, which is a part of the asymmetric unit referred to as molecule A, is attached to the other three symmetry related molecules, B, C, and D, through at least two N—H···O hydrogen bonds. This creates a web of hydrogen bonds and nitrate ions which traverses the entire structure.

Urea Ligands.—The urea groups are planar as would be expected. The averages of the bond lengths and angles for the four crystallographically independent ligands are shown in Table V together with the results of some other investigations of the urea molecule.[40-46]

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The ligands are not greatly distorted with respect to the urea molecule.

Hydrogen Bonds.—Possible hydrogen bonds are listed in Table VI, the table listing X—O and H···O distances and X—H···O angles. The criterion for a possible hydrogen bond is taken from Hamilton and Ibers,[47] who state that hydrogen bonds likely exist when the H···O distance is significantly shorter than the sum of the van der Waal radii of hydrogen and oxygen atoms or less than 2.6 Å. They suggest a 0.2-Å shortening which would make an upper limit of about 2.4 Å. It can be seen in Table VI that both water hydrogen atoms are involved in hydrogen bonds as well as several hydrogen atoms of urea ligand. Most of the hydrogen bonds involving hydrogen atoms of urea ligands terminate at nitrate oxygens though two such bonds terminate at urea oxygens and one at a uranyl oxygen atom. Those atom combinations marked with an asterisk are not considered to be hydrogen bonds because of the H···O distance which is very near the 2.4 Å limit and the X—H···O angle deviates by a large amount from 180°. One hydrogen, H(1)N(41), is not included in this table because the shortest H···O distance involving this atom is 2.59 (2) Å. Two hydrogens, H(2)N(32) and H(2)N(42), are included twice but both entries are in the questionable class as is H(2)N(12).

The N—H···O bonds are weaker than the O—H···O bonds, as indicated by both the X—O and O···H distances. This is as would be expected as nitrogen is lower in the electronegativity scale than oxygen. The average N—H···O distance is longer than those reported for similar bonds in the study of Jönsson and Hamilton.[48] The hydrogen bonding involving the nitrate ions is shown in Figure 2 and is discussed in the nitrate ion section.

Thermal Motion.—The rms component of displacement along the three principle axes of the vibrational ellipsoids are listed in Table VII. Also, an indication of the thermal motion for all the atoms except the urea hydrogens is illustrated in Figure 1. The motion of the uranium is the smallest, and generally the farther the atom from the uranium atom the larger the motion, with the exception that the carbons of three of the urea ligands have slightly less motion than the oxygens. The motion of the nitrogen atoms is largely a function of the strength of the hydrogen bond in which it is involved. The hydrogen atoms which are involved in weak hydrogen bonds or no hydrogen bonds at all, for example, H(2)N(12) and H(1)N(41), have very large thermal motions. This is reflected in the motions of the adjoining nitrogen atoms N(12) and N(41) as is shown in Table VII. The nitrate oxygens which are not hydrogen bonded to the water ligand have very large thermal motions.

Conclusions

The fivefold coordination of the uranyl ion found in this study is reasonable in the light of present knowledge of coordination chemistry. The earlier attempts to justify a sixfold coordination were based on incomplete chemical analyses and interpretation of a very complex infrared spectrum. The results of this investigation illustrate the need for correlation of spectroscopic and diffraction techniques.

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