Synthesis and Characterization of some Actinoid Iminodiacetato-complexes; Crystal Structure and Normal Co-ordinate Analysis of Iminodiacetatodioxouranium(VI)

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The preparation and the characterization, mainly by i.r. data, of uranium(VI) iminodiacetato-complexes with metal : ligand ratios of 1 : 1 and 1 : 2 and of their pyridine *N*-oxide adducts are reported. The photochemical preparation and related studies of a uranium(IV) complex with the same ligand are also described. The crystal and molecular structure of the title complex $[\{UO_2(ida)\}_n]$ has been determined by three-dimensional *X*-ray data collected by counter techniques. The compound crystallizes in an orthorhombic cell of dimensions $a = 10.881(5)$, $b = 10.132(5)$, $c = 6.907(4)$ Å, space group *Pnma* (D_{2h}^{16}), and $Z = 4$. The final *R* factor for the least-squares refinement is 0.069 for 609 observed reflections. The linear uranyl ion is equatorially surrounded by one ligand, *via* the two carboxylic oxygen atoms [U–O 2.38(2) and 2.39(2) Å], the imino-nitrogen atom [U–N 2.59(4) Å], and by two other ligands *via* two symmetry-related oxygen atoms, forming an irregular pentagonal bipyramid. The structure is polymeric with a double system of chains, one linear running along *b* and the other helicoidal along *c*; a symmetric bifurcated hydrogen bond joins two adjacent helicoidal systems spaced by *a*/2. For this complex the fundamental vibrations have been assigned on the basis of a normal co-ordinate analysis and potential-energy distribution obtained by use of a 39-parameter Urey–Bradley force field. The stretching force constant of the U–N(imino) bond is much greater than that of the corresponding U–O(ether) bond in the analogous oxydiacetatodioxouranium(VI) complex (2.48×10^2 *versus* 1.1×10^2 N m^{-1} respectively) and this is attributed to the different covalent character of the two bonds.

THE crystal and molecular structures have been determined[1] of some lanthanoid iminodiacetato-complexes and the ligand shown to co-ordinate to the central metal ion by forming two condensed five-membered chelate rings and a metal–nitrogen bond. Until now, the only known actinoid iminodiacetato-complex was $[UO_2(Hida)_2]$[2,]† which possesses a crystal structure in which the carboxylate groups are both ionized, one uni- the other bi-dentate, and co-ordinated to two adjacent U atoms, the co-ordination of the imino-group being inhibited by protonation.[3]

In this paper we report the preparation and characterization, mainly by i.r. spectral data, of some actinoid iminodiacetato-complexes in which the imino-group is co-ordinated to the metal atom, and the structure of one of these where the assignment of the relative fundamental vibrations has been made by normal-co-ordinate analysis.

EXPERIMENTAL

Materials.—Commercial reagent-grade chemicals were used; other chemicals were prepared by standard methods. Uranium and thorium were determined gravimetrically as U_3O_8 and ThO_2.

Apparatus.—Infrared spectra (KBr pellets) were recorded with Perkin-Elmer 621 (300—4 000 cm^{-1}) and Beckman IR-11 (50—300 cm^{-1}) spectrophotometers. Luminescence spectra were recorded on a Perkin-Elmer MPF-2A spectrofluorimeter at excitation and emission wavelengths of 410 and 510 nm respectively. Measurements of the luminescence lifetime were made with a model K-347 frequency doubled laser ($\lambda = 347$ nm) (J. K. Lasers Ltd., England). The emission of (UO_2^{2+}) * was monitored at 510 nm and recorded with a Polaroid camera. The customary procedure[4] was used to obtain radiations of 404 and 436 nm. The irradiation and the measurements of the incident light intensity were performed in accordance with the previously reported procedure.[5,6] Raman spectra of the powder were recorded on a Jarrell–Ash 25–300 spectrometer with a Spectra Physics model 125 A He–Ne laser as exciting source. The *N*-deuterio-derivative of iminodiacetatodioxouranium(VI) was obtained by crystallization from D_2O (99.75%). The extent of deuteriation was *ca.* 80%. Intensity data were collected on a Philips PW 1100 automatic diffractometer equipped with a graphite monochromator using Mo-K_α radiation ($\lambda = 0.710\ 7$ Å).

Syntheses of Complexes.—$[\{UO_2(ida)\}_n]$ (1) (ida = $^-O_2CCH_2NHCH_2CO_2^-$). The compound was prepared by addition of an equimolar amount of $Na_2[ida]$ to an aqueous solution of uranyl nitrate hexahydrate at pH >3.2. From this solution yellow crystals were separated (Found: C, 12.0; H, 1.30; N, 3.50; U, 59.0. Calc.: C, 11.95; H, 1.25; N, 3.50; U, 59.35%). The compound $[\{UO_2(ida)(OH_2)\}_n]$ (2) and $[UO_2(ida)(OH_2)_2]$ (3) were prepared similarly from methanol–water solutions. Yellow precipitates were formed on concentration of these solutions [Found: C, 11.55; H, 1.60; N, 3.35; U, 56.5. Calc. for (2): C, 11.45; H, 1.65; N, 3.35; U, 56.8. Found: C, 11.05; H, 2.05; N, 3.20; U, 54.3. Calc. for (3): C, 11.0; H, 2.05; N, 3.20; U, 54.45%].

$[UO_2(ida)(pyo)_2]$ (4) (pyo = *pyridine N-oxide*). This compound was obtained by addition of an excess of pyridine *N*-oxide to complex (1). The mixture was slowly heated until completely molten. Addition of benzene separated the yellow solid (Found: C, 28.35; H, 2.65; N, 7.10; U, 40.1. Calc.: C, 28.45; H, 2.55; N, 7.10; U, 40.25%).

$[\{UO_2(ida)(pyo)\}_n]$ (5). The compound was obtained by addition of a large excess of pyo to complex (2) in methanolic solution. By concentration the yellow precipitate was obtained (Found: C, 21.6; H, 2.00; N, 5.55; U, 47.5. Calc.: C, 21.75; H, 2.00; N, 5.65; U, 48.0%).

$[\{UO_2(mida)\}_n]$ (6) (mida = $^-O_2CCH_2NCH_3CH_2CO_2^-$). The compound was prepared by addition of $Na_2[mida]$ to an aqueous solution of uranyl nitrate (1 : 1). From this solution yellow crystals were separated (Found: C, 14.45;

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† Hida = Monoprotonated iminodiacetate(2−).

H, 1.80; N, 3.35; U, 57.15. Calc.: C, 14.45; H, 1.70; N, 3.35; U, 57.3%).

$Na_2[UO_2(ida)_2]\cdot 2H_2O$ (7). The compound was prepared by addition of uranyl nitrate to a methanolic solution of $Na_2[ida]$ (1 : 2). The yellow solid precipitated immediately (Found: C, 15.55; H, 2.15; N, 4.50; U, 38.6. Calc.: C, 15.65; H, 2.30; N, 4.55; U, 38.75%).

$Na_2[(UO_2)_2(ida)_2(OH)_2]\cdot 4H_2O$ (8). The compound was prepared by addition of uranyl nitrate to an aqueous solution of an excess of $Na_2[ida]$. Addition of ethanol separated immediately the yellow solid (Found: C, 9.95; H, 2.00; N, 2.95; U, 49.7. Calc.: C, 10.05; H, 2.10; N, 2.95; U, 49.9%).

$[ThO(ida)]\cdot 2H_2O$ (9). The compound was obtained by addition of thorium(IV) nitrate to an aqueous solution of $Na_2[ida]$ (mol ratio 1 : 1 or 1 : 2). The white solid precipitated immediately (Found: C, 11.5; H, 2.15; N, 3.35; Th, 55.7. Calc.: C, 11.55; H, 2.15; N, 3.35; Th, 55.9%).

$[Th(ida)_2]\cdot 4H_2O$ (10). The compound was obtained by dissolving freshly prepared $Th[OH]_4$ in an excess of H_2ida in aqueous solution. Addition of methanol separated the white solid (Found: C, 16.9; H, 3.15; N, 4.25; Th, 40.2. Calc.: C, 16.95; H, 3.20; N, 4.25; Th, 41.0%).

$[UO(ida)]\cdot H_2O\cdot \frac{1}{2}Na[NO_3]$ (11). In a quartz reaction vessel a solution (20 cm^3) containing 1.5×10^{-2} mol dm^{-3} uranyl nitrate and 1.5×10^{-1} mol dm^{-3} H_2ida was irradiated with either 404 or 436 nm light for 10 h. A green solution was obtained from which a pale green powder was separated (Found: C, 10.8; H, 1.60; N, 4.70; U, 53.2. Calc.: C, 10.75; H, 1.55; N, 4.70; U, 53.4%).

Quenching and Photoreaction Studies.—These studies were carried out following the previously reported procedures.[5,6]

Crystal Data.—$C_4H_5NO_6U$, (1), $M = 401.1$, Orthorhombic, $a = 10.881(5)$,* $b = 10.132(5)$, $c = 6.907(4)$ Å, $U = 761.5$ Å^3, $D_m = 3.51$ g cm^{-3}, $Z = 4$, $D_c = 3.50$ g cm^{-3}, $F(000) = 704$, $\mu(Mo\text{-}K_\alpha) = 267.3$ cm^{-1}, space group *Pnma* (D_{2h}^{16}, no. 62),[7] from systematic absences $0kl$ where $k + l = 2n$, $hk0$ where $h = 2n$.

Unit-cell and orientation parameters were obtained by a least-squares fit to the setting angles of 25 reflections ($2\theta = 45$—$55°$). Systematic absences are consistent also with space group $Pn2_1a$ (non-standard setting of C_{2v}^9, no. 33).[7] The centrosymmetric space group was initially chosen on the basis of the data and later confirmed by the successful structure determination.

Collection and Reduction of X-*Ray Intensity Data.*—Single crystals of complex (1) were obtained by slow (2 weeks) evaporation of an aqueous solution. Although the crystal shape was extremely anisotropic (this gives rise to uncertainty of the thermal factors especially for heavily absorbing materials), it was decided to use such a crystal because of the difficulty in obtaining a more suitable crystal. The crystal was coated with I.S.12 cyanoacrylate adhesive (Loctite Corporation) and mounted on a glass capillary using this cement such that the longest crystal dimension (*b* axis) was approximately parallel to the capillary axis. 2 103 Independent reflections ($2\theta \leqslant 56°$) were measured by use of the θ—2θ scan technique, of which 973 having $I > 3\sigma(I)$ were used in the subsequent calculations. The net count of three reflections, monitored throughout, showed a small linear decrease (*ca.* 2.5%) during data collection. Lorentz and polarization corrections were applied. An absorption correction was made following the method of Flack,[8] 12 reflections and their equivalents being processed. A total of 1 337 measurements at intervals of 10° in ψ for the range 0—170° ($\mu\bar{R} = 0.81$) was used for the absorption correction. The transmission factors ranged from 0.74 to 0.99.

Structure Determination and Refinement.—The observed density indicated that $Z = 4$, which in the centrosymmetric space group *Pnma* would require the molecule to have internal symmetry, the only crystallographically possible symmetry being a mirror plane (no extra conditions limiting possible reflections are present) (Figure 1). The Patterson function was readily solved for a planar UO_4N group which, when used to phase a Fourier synthesis, revealed all non-hydrogen atoms. Full-matrix least-squares refinement was undertaken, in which the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. For the approximately constant counting statistics in the measurement of the data, unit weights were given to each reflection in the refinement. Anisotropic thermal parameters of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$ were used for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions (C–H 0.95 and N–H 0.87 Å,[9] positions being recalculated every few refinement cycles) as fixed contributions, each with an isotropic temperature factor *ca.* 20% larger than that of its parent atom. Atomic scattering factors for all atoms except hydrogen were taken from ref. 10, Stewart's hydrogen-atom scattering factors were used,[11] and anomalous-dispersion terms [12] for the uranium were included in F_c.

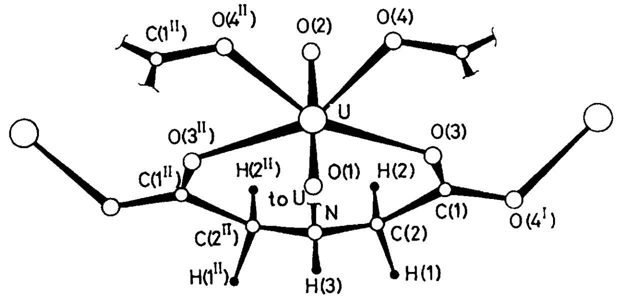

FIGURE 1 Molecular model of the repeating $UO_2(ida)$ unit with the atomic numbering. The superscripts, defined in Table 2, code symmetry-related atoms

Refinement converged to the *R* value of 0.069. No parameter shifted by more than 0.2 times its standard deviation in the final cycle of refinement. The function $\Sigma w(|F_o| - |F_c|)^2/N$ showed no appreciable variation as a function of $|F_o|$ or $(\sin\theta)/\lambda$. The weighting scheme is thus satisfactory. A final ΔF Fourier showed a number of peaks up to maximum of 2.2 e Å^{-3} in the vicinity of the uranium atom. The reasons for the noise level here are probably related to an inappropriate treatment of the uranium scattering and to errors in the published [13] values of μ/ρ used in the absorption correction. Unsuccessful attempts were made to carry out refinement with a space group $Pn2_1a$.

The final positional parameters are in Table 1. The U_{22} component of thermal tensor for all the atoms is remarkably lower than U_{11} and U_{33}; the U_{22} component for the nitrogen atom is dramatically low. This fact is surely due to absorption, the crystal being grown along the *b* axis; in addition, polymerization, running along the *b* axis, may freeze thermal motion in this direction.

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* Estimated standard deviations in parentheses refer to the last significant digit. This also holds for all the Tables.

TABLE 1

Positional parameters with estimated standard deviations (e.s.d.s) in parentheses

Atom	x/a	y/b	z/c
U	0.241 8(2)	0.250 0	0.163 2(2)
O(1)	0.355(3)	0.250	0.339(7)
O(2)	0.139(3)	0.250	−0.029(6)
O(3)	0.315(2)	0.463(2)	0.068(4)
O(4)	0.115(2)	0.398(2)	0.342(4)
N	0.415(4)	0.250	−0.094(6)
C(1)	0.368(3)	0.484(3)	−0.091(5)
C(2)	0.419(3)	0.370(3)	−0.212(4)
H(1)	0.509	0.392	−0.259
H(2)	0.361	0.355	−0.338
H(3)	0.491	0.250	−0.021

TABLE 2

Interatomic distances (Å) and interbond angles (°) with e.s.d.s in parentheses *

U–O(1)	1.73(4)	O(1)–U–O(2)	174.6(1.8)
U–O(2)	1.74(4)	O(3)–U–O(4)	76.6(0.8)
U–O(3)	2.39(2)	O(3)–U–N	64.5(0.6)
U–O(4)	2.38(2)	O(4)–U–O(4^{II})	77.9(0.7)
U–N	2.59(4)	N–C(2)–C(1)	108.2(2.6)
O(3)–C(1)	1.26(4)	C(2)–C(1)–O(3)	121.4(2.6)
C(1)–O(4^{I})	1.30(3)		
N–C(2)	1.47(4)		
C(1)–C(2)	1.52(4)		

The codes for symmetry-related atoms are as follows: I $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$; II $x, \frac{1}{2} - y, z$.

* Taking into account the accuracy of cell dimensions.

In the present study the experimental absorption corrections are probably inadequate. Indeed, during the refinement using various weighting schemes, the U_{22} values varied greatly with high standard deviations and, in an extreme case, a negative value for the nitrogen atom occurred. This extreme case was considered by Coppens,[14] and it derives from incomplete allowances for absorption and extinction.

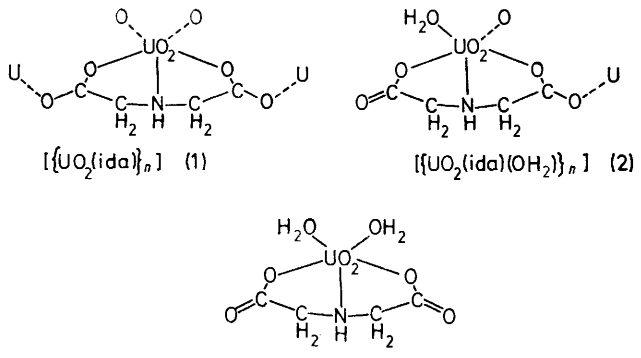
Electronic spectra, thermal parameters, least-squares planes, angles between the mean planes, and the observed and calculated structure amplitudes are available as Supplementary Publication No. SUP 22612 (11 pp.).*

Interatomic distances and angles are in Table 2. Figure 3 shows the geometry of the hydrogen bonding. The principal computer programs used in the calculations were the 'X-Ray '72' system (eds. J. M. Stewart, F. A. Kundall, and J. C. Baldwin), the thermal ellipsoid plotting program (ORTEP), and a program, written by H. D. Flack, for absorption corrections. All calculations were performed on the CDC/CRYBER '76 computer at the Centro Calcolo Elettronico Interuniversitario Italia Nord-Orientale, Casalecchio (Bologna).

RESULTS AND DISCUSSION

The following complexes were obtained, by reaction between uranyl nitrate hexahydrate and sodium iminodiacetate (1 : 1), depending on the pH or the solvent: $[\{UO_2(Hida)\}_n]$, from aqueous solution at pH <3.2, as already reported,[2] where the ligand is N-protonated;[3] $[\{UO_2(ida)\}_n]$ (1) from aqueous solution at pH $\geqslant$3.2, with co-ordination through the imino-group; $[\{UO_2(ida)(OH_2)\}_n]$ (2) from water–methanol; and finally $[UO_2(ida)(OH_2)_2]$ (3) from methanol. Complexes (1) and (2) are insoluble in water and in all common organic solvents, and complex (3) is soluble in water. At pH >6, progressive replacement of ida anion by $[OH]^-$ groups takes place and hydrolytic species such as $[(UO_2)_2(ida)_2(OH)_2]^{2-}$ or with a metal-to-ligand ratio of 3 : 1 were formed. In all these new complexes the ligand co-ordinates to the central metal atom *via* two condensed five-membered chelate rings. A comparison of the spectrum of the ligand with those of its chelate complexes shows that a considerable change in the frequencies has occurred due to the chelation. The i.r. spectra agree with the configurations in Figure 2.

There is a regular shift of the NH stretching mode towards lower wavenumber, on going from (1) to (3), *i.e.* 3 264, 3 240, and 3 220 cm^{-1} respectively with decreasing intensity, while the COO asymmetric stretching mode shows a corresponding shift towards higher frequencies, 1 545, 1 557, and 1 565 cm^{-1} respectively. For the free ligand these absorption bands fall at 3 340 [ν(NH)] and 1 600 [ν_{asym}(COO)] cm^{-1}. The presence of water molecules, in (2) and (3), is confirmed from the peaks at *ca.* 3 400 and 1 630 cm^{-1}, and the presence of free COO groups, in (2), from a shoulder at 1 600 cm^{-1}. Also the symmetric and asymmetric stretching frequencies of the C–N–C group are shifted towards lower wavenumbers (*ca.* 100 cm^{-1}) in comparison with the anionic ligand, confirming the formation of the co-ordinative uranium–nitrogen bond. Thus, we suggest that, on going from (1) to (3), the N–H bond becomes weaker, the strength of the N–U bond increases, and the carboxylic groups show an increase in double-bond character, corresponding to a decrease in the number of the COO groups co-ordinated to the uranium (*i.e.* four, three, and two respectively). Therefore, complexes (1) and (2) have polymeric structures *via* two and one carboxylic oxygen bridges respectively, while complex (3) is a monomeric species. This behaviour is supported by the reaction with pyridine *N*-oxide (pyo). Under drastic conditions (large excess of molten pyo) complete destruction of the carboxylic bridges and replacement of the co-ordinated water molecules take place, with formation of the water-soluble complex $[UO_2(ida)(pyo)_2]$.



$[\{UO_2(ida)\}_n]$ (1)

$[\{UO_2(ida)(OH_2)\}_n]$ (2)

$[UO_2(ida)(OH_2)_2]$ (3)

FIGURE 2 Proposed structures of complexes (1)—(3)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

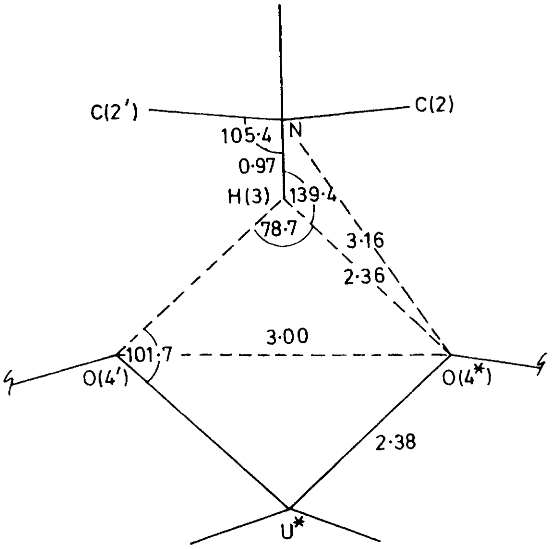

FIGURE 3 Geometry of the symmetric bifurcated hydrogen bond. Asterisks indicated an atom at $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$, primes denote an atom related by the mirror plane

The shift of ν_{asym}(COO) at 1 641 cm^{-1} confirms this formulation. Under mild conditions (methanolic solution of pyo) the polymeric nature of complexes (1) and (2) is maintained and only (2) is converted into $[\{UO_2(ida)(pyo)\}_n]$ due to the presence of one replaceable water molecule.

The reaction between uranyl nitrate and sodium iminodiacetate in methanol (1 : 2) leads to the formation of complex (7) with a metal-to-ligand ratio of 1 : 2. In this case a co-ordination number of six, in the equatorial plane around each uranyl ion, can be suggested. The i.r. spectrum of this complex is very similar to those described above, thus supporting the low extent of coupling between the two halves of the molecule. Also the higher value of ν_{asym}(COO) (1 620 cm^{-1}) is in agreement with the monomeric nature of this complex.

The spectra of the thorium(IV) iminodiacetato-complexes (9) and (10) show features very similar to those of the uranium(IV), (11), and uranium(VI), (7), complexes respectively, and this fact suggests analogous configurations for these complexes.

The photolysis of uranyl carboxylate in aqueous solution leads to the oxidative decarboxylation of the ligand and, in the presence of a large excess of chelating carboxylic ion, the uranium(IV) compound is formed in good yield. The solid complex (11) obtained is very stable to oxidation. Electronic spectral data are very similar to those reported for other eight-co-ordinate carboxylato-complexes of U^{IV},[6,15] and are available as SUP 22612. The quantum yield (ϕ) for U^{VI} consumption and U^{IV} formation are identical: $\phi = 0.75$ at 404 nm and 0.60 at 436 nm; the corresponding values for CO_2 formation are exactly twice these values. The intensity of the uranyl luminescence shows a behaviour identical to those of the other carboxylato-complexes previously reported.[6] The absolute quenching constant K_Q of $[UO_2]^{2+}$ emission by H_2ida in aqueous solution is 2×10^9 dm^3 mol^{-1} s^{-1} and the lifetime, τ^0, for $(UO_2{}^{2+})^*$ in water, determined directly by laser flash photolysis, is 1.3 μs. Thus, under our experimental conditions we can assume that the photoreaction is due to a charge-transfer transition from the carboxylic ligand to $[UO_2]^{2+}$ within a preformed complex; by analogy with the mechanism proposed previously for glycolic and oxydiacetic acids,[6] the reaction may proceed by a photo-induced one-electron reduction, giving the unstable $[UO_2]^+$ species which is then reduced to U^{IV} by the excess of the ligand in a secondary thermal reaction. This mechanism explains the relationship between the quantum yields reported above.

The i.r. spectrum of $[UO(ida)]{\cdot}2H_2O{\cdot}\frac{1}{2}Na[NO_3]$ resembles that of $[ThO(ida)]{\cdot}2H_2O$, except for the characteristic bands of the ionic nitrato-group at 1 381 and 833 cm^{-1}; the ν_{asym}(COO) values for both species occur at 1 614 cm^{-1} and we tentatively suggest a dimeric nature for these complexes, *via* OH or O bridges.

The iminodiacetatodioxouranium(VI) complex (1) shows the linear uranyl ion equatorially surrounded by

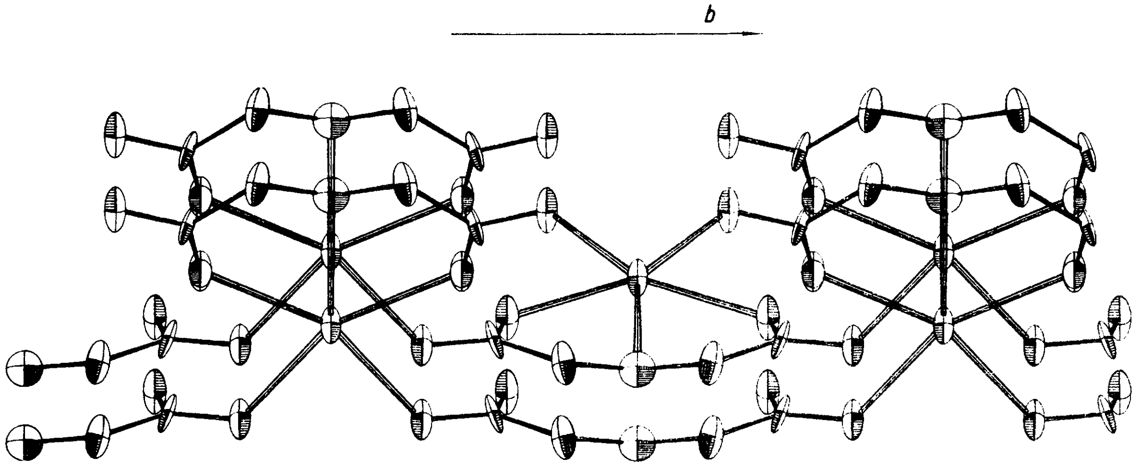

FIGURE 4 ORTEP diagram of the double system of chains in the polymer: one linear running along *b* and the other helicoidal along *c*. The O(1), (O2), and hydrogen atoms would obscure the view, and have therefore been omitted. The nitrogen atom is represented with its isotropic temperature factor

one ligand, *via* the two carboxylate oxygen atoms O(3) and O(3^{II}), the imino-nitrogen atom, and by two other ligands *via* two symmetry-related oxygen atoms O(4) and O(4^{II}), forming an irregular pentagonal bipyramid. Each ligand is shared between three uranium atoms as in oxydiacetatodioxouranium[16] [UO_2(oda)] which possesses a three-dimensional linkage network. In the present complex the polymerization runs along the screw axis parallel to *c* through both the oxygen atoms. The resulting polymer is built up from a two-dimensional network, although a weak bifurcated hydrogen bond (Figure 3) occurs along the *a* axis.

Briefly, the polymer exhibits a double system of chains: one linear running along *b* and the other helicoidal along *c* (Figure 4); a symmetric bifurcated hydrogen bond joins the two adjacent helicoidal systems which are separated by a distance of *a*/2. The conformation of the CH_2COO residue is uncommon (Figure 5), in fact the torsion angles are close to 0 or 180°. Thus it is impossible to code the form of the present residue within the known conformations (*syn,anti, etc.*).[17] The bond distances and angles reveal no surprises when compared with other uranyl structures;[18] in particular, the U–N distance (2.59 Å) parallels those in refs. 18*a*—*f* and it is considerably shorter than that of 2.70 Å in ref. 18*f*, owing to ring constraints, the nitrogen atoms being sp^3 hybridized. The bond distances within the organic ligand seem to be independent of the chemical environment; the C–C distance (1.52 Å) is the same as the average value found in oxydiacetates (1.515 Å)[19] and the N–C distance (1.47 Å) is not different from the average value of 1.488 Å calculated from six structure determinations of iminodiacetic acid residues[20] and also from 13 neutron-diffraction determinations of α-amino-acids.[21] The iminodiacetate ion acts as a tridentate ligand and forms two identical five-membered rings with the uranyl ion, but co-ordination does not produce any significant angular deformation in the ligand (see Table 1 of ref. 19*b*). However, the OOCCNCCOO sequence is not planar, mainly because of the nitrogen atom (0.33 Å out of the plane), while the deviations of the donor atoms from the least-squares equatorial mean plane are of the same order as the estimated standard deviation (e.s.d.s) (see SUP 22612). Apart from the bifurcated hydrogen bond, there is no abnormal feature in the contacts between adjacent helices, none being substantially shorter than normal van der Waals distances.

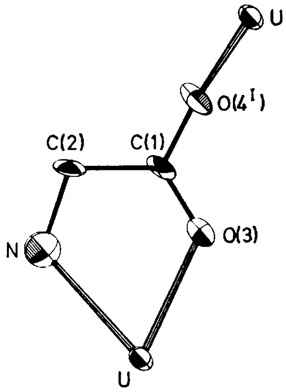

FIGURE 5 The uncommon conformation of the CHCOO residue (drawn with ORTEP), projected onto the acetate plane

The *X*-ray analysis of [{UO_2(ida)}$_n$] has shown that the site symmetry of the UO_2(ida) entity is $C_s(m)$. The vibrational analysis was performed on this entity and on its N-deuterio-derivative by neglecting intermolecular effects, using our computer program UBATOR.[22] In the C_s point group the U(ida) fragment has 39 non-redundant fundamentals which are classified into 21(A') and 18(A'') modes which are all i.r. and Raman active. A Urey–Bradley force field (UBFF) was employed as previously reported.[22] The best set of force constants obtained is shown in Table 3; the measured and calculated frequencies (mean deviation less than 1%) and the assignments for the UO_2(ida) complex and its deuteriated analogue are given in Table 4. Since the observed rather than harmonic frequencies were used the observed isotopic shifts in the deuteriate show a somewhat large deviation from the calculated values.

For brevity, only the assignment of the bands associated with the co-ordinated imino-group will be discussed, since the other absorption bands are generally

TABLE 3

Urey–Bradley force constants (mdyn Å^{-1}) *

Stretching			Bending			Repulsive		
K_1	U–O(3)	1.58	H_1	U–O(3)–C(1)	0.05	F_1	U · · · C(1)	0.07
K_2	C(1)–O(3)	8.95	H_2	O(3)–U–N	0.07	F_2	O(3) · · · U	0.07
K_3	C(1)–O(4^I)	9.20	H_3	O(3)–U–O(3^{II})	0.08	F_3	O(3) · · · O(3^{II})	0.06
K_4	C(1)–C(2)	2.54	H_4	O(3)–C(1)–O(4^I)	0.33	F_4	O(3) · · · O(4^I)	2.49
K_5	C(2)–N	3.96	H_5	O(3)–C(1)–C(2)	0.31	F_5	O(3) · · · C(2)	0.44
K_6	C(2)–H(1)	4.28	H_6	O(4^I)–C(1)–C(2)	0.42	F_6	O(4^I) · · · C(2)	0.82
K_7	N–H(3)	5.69	H_7	C(1)–C(2)–N	0.56	F_7	C(1) · · · N	0.21
K_8	U–N	2.48	H_8	C(1)–C(2)–H(1)	0.26	F_8	C(1) · · · H(1)	0.32
			H_9	H(1)–C(2)–N	0.18	F_9	H(1) · · · N	0.67
			H_{10}	C(2)–N–H(3)	0.18	F_{10}	C(2) · · · H(3)	0.18
			H_{11}	C(2)–N–U	0.03	F_{11}	C(2) · · · U	0.03
			H_{12}	C(2)–N–C(2^{II})	0.23	F_{12}	C(2) · · · C(2^{II})	0.62
			H_{13}	H(1)–C(2)–H(2)	0.39	F_{13}	H(1) · · · H(2)	0.10
			H_{14}	U–N–H(3)	0.29	F_{14}	U · · · H(3)	0.17
VQFF force constants (mdyn Å^{-1}) for the [UO_2]$^{2+}$ entity								
K	U–O(1)	7.08	H	O(1)–U–O(2)	0.83	F	O(1) · · · O(2)	−1.47

* 1 dyn = 10^{-5} N.

unchanged when compared with those of the analogous oxydiacetatodioxouranium complex, the vibrational analysis of which was reported previously.[22] Moreover, we have prepared the *N*-methyliminodiacetato-adduct (6), to obtain more information about the vibration mode of the imino-group, for which few data are available.

TABLE 4

Calculated and observed frequencies (cm^{-1}) and potential-energy distribution (%) *

Species	No.	$[UO_2(ida)]$		*N*-deuteriated		Description
		calc.	obs.	calc.	obs.	
A′	ν_4	3 264	3 264	2 378	2 422	ν(NH) (99)
	ν_5	2 970	2 971	2 971	2 969	$\nu_{sym}(CH_2)$ (99)
	ν_6	2 946	2 945	2 947	2 944	$\nu_{asym}(CH_2)$ (100)
	ν_7	1 547	1 545	1 546	1 545	ν_{asym}(COO) (87)
	ν_8	1 473	1 473	1 028	1 056	δ(NH) (58)
	ν_9	1 445	1 445	1 445	1 449	ν_{sym}(COO) (53), $\delta(CH_2)$ (29)
	ν_{10}	1 406	1 417	1 421	1 419	$\delta(CH_2)$ (41), ν_{sym}(COO) (25)
	ν_{11}	1 287	1 293	1 325	1 300	$\omega(CH_2)$ (63)
	ν_{12}	1 224	1 205	1 224	1 203	$\tau(CH_2)$ (95)
	ν_{13}	1 115	1 117	1 128	1 143	ν_{sym}(CNC) (50), $\omega(CH_2)$ (28)
	ν_{14}	967	971	956	969	ν(CC) (56), δ(COO) (16)
	ν_{15}	881		875		$\rho(CH_2)$ (82)
	ν_{16}	746	723	754	744	δ(COO) (58), ν_{sym}(COO) (12)
	ν_{17}	563	562	554	556	ν(UN) (50), δ(COO) (16)
	ν_{18}	435	485	432	484	δ(ring) (45), δ(COO) (24)
	ν_{19}	347	345	346	345	ν(UO) (50), ν(UN) (13)
	ν_{20}	263	285	260	285	δ(CNC) (40), δ(NH) (23)
	ν_{21}	187	184	187		ν(UO) (24), δ(OUN) (21)
	ν_{22}	58		58		δ(UOC) (40), δ(OUO) (20)
	ν_{23}	44		44		δ(CNC) (25), δ(CCN) (12)
	ν_{24}					
A″	ν_{25}	2 971	2 971	2 971	2 969	$\nu_{sym}(CH_2)$ (99)
	ν_{26}	2 945	2 945	2 945	2 944	$\nu_{asym}(CH_2)$ (100)
	ν_{27}	1 546	1 545	1 545	1 544	ν_{asym}(COO) (89)
	ν_{28}	1 445	1 445	1 445	1 449	ν_{sym}(COO) (52), $\delta(CH_2)$ (31)
	ν_{29}	1 414	1 417	1 414	1 419	$\delta(CH_2)$ (39), ν_{sym}(COO) (38)
	ν_{30}	1 270	1 293	1 267	1 293	$\omega(CH_2)$ (69)
	ν_{31}	1 203	1 205	1 203	1 203	$\tau(CH_2)$ (97)
	ν_{32}	1 049		759	775	δ(NH) (80)
	ν_{33}	1 029	1 026	1 030	1 023	ν_{asym}(CNC) (66), $\omega(CH_2)$ (27)
	ν_{34}	914	912	915	912	ν(CC) (59), δ(COO) (22)
	ν_{35}	829		859		$\rho(CH_2)$ (84)
	ν_{36}	713	723	707	716	δ(COO) (58), ν_{asym}(COO) (13)
	ν_{37}	599	595	580	593	δ(ring) (47), δ(COO) (27)
	ν_{38}	359	366	359	358	ν(UO) (40), δ(COO) (18)
	ν_{39}	242	233	241	233	ν(UO) (45), δ(OUN) (14)
	ν_{40}	92		92		δ(OUN) (48)
	ν_{41}	52		52		δ(CNU) (50)
	ν_{42}	31		31		δ(UOC) (55)
$[UO_2]^{2+}$	ν_1		854			ν_{sym}(OUO)
			(858 Raman)			
	ν_2		257			δ(OUO)
	ν_3		933			ν_{sym}(OUO)
	$\nu_1 + \nu_2$		1 770			combination band

* The rounded percentage potential-energy distribution values for $[\{UO_2(ida)\}_n]$ are shown in parentheses; small values have been neglected. Abbreviations: ν = stretching, δ = scissoring, ω = wagging, τ = twisting, ρ = rocking; and as subscripts, sym = symmetric, asym = asymmetric. The potential-energy distribution for the *N*-deuteriated derivative is very closed to that reported, and can be obtained from the authors on request.

The spectra of complex (1) and its deuteriate are reported in Figure 6. The very sharp band at 3 264 cm^{-1} is due to a pure N–H stretching mode and it shifts to 2 422 cm^{-1} in the deuteriate. The medium band at 1 473 cm^{-1} (1 460 cm^{-1} in the free ligand) is predominantly due (58%) to δ(NH) and it shifts to 1 056 cm^{-1} in the deuteriate; the other band due to the δ(NH) (80%), calculated at 1 049 cm^{-1} and without experimental intensity, shifts to 775 cm^{-1} with weak intensity in the deuteriate spectrum. It is known that the NH deformations are usually very weak in secondary aliphatic amines and they move to higher frequencies on bonding.[23] In the spectrum of complex (6) these absorption bands are not present, confirming the assignment. The ν_{sym}(C–N–C) frequency comprises 50% of the band at 1 117 cm^{-1} which shifts to higher frequency (1 143 cm^{-1}) in the deuteriate; it has been already found that the increase of mass associated with deuteriation can result in the high frequency shift for this vibration. ν_{asym}(C–N–C) falls at 1 026 cm^{-1} without appreciable shift on deuteriation. The medium band at 562 cm^{-1} has a considerable contribution from U–N stretching (50%) and is at a higher wavenumber than the U–O (ether) stretching band in the $[UO_2(oda)]$ complex which is more extensively coupled to complicated mixed vibrations.[23] The values obtained for the force constants are consistent with those expected from simple structural and chemical consider-

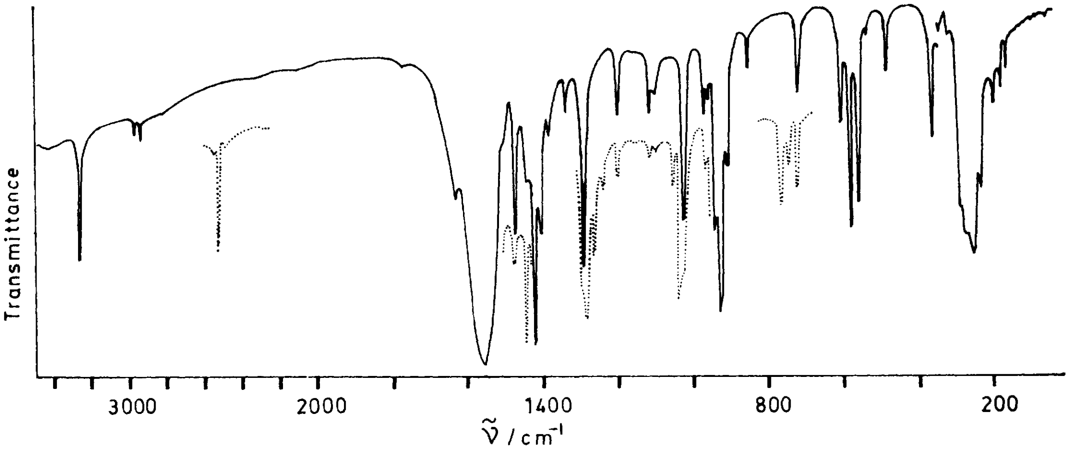

FIGURE 6 Superimposed i.r. spectra of [$\{UO_2(ida)\}_n$] (——) and its N-deuteriate (· · · ·) in KBr discs

ations and are comparable to those of [UO_2(oda)] and other related molecules, demonstrating the transferable nature of these UBFF force constants.

The analysis of the UO_2 entity was carried out separately, using a simple triatomic model. The ideal $D_{\infty h}$ point group in this case becomes C_{2v}, owing to the bending of the O–U–O group. The asymmetric stretching mode is observed in the i.r. spectrum at 933 cm^{-1}, the symmetric stretching mode is observed in the i.r. spectrum at 854 and in the Raman at 858 cm^{-1} as a strong band, and the combination band for these absorption modes is also observed at 1 770 cm^{-1}. The bending mode is assigned to the frequency at 257 cm^{-1} which appears in the far-i.r. region as a medium-intensity band. The Valence Quadratic Force Field (VQFF) force and interaction constants are reported in Table 3.

Let us attempt to correlate the i.r. data and stability constants, measured in solution,[24] for [UO_2(oda)] and [UO_2(ida)]. It seems more reasonable to compare mainly the U–O and U–N stretching force constants with the free energy of formation of the two complexes, because force constants are not a function of mass and bond distances as are the frequencies, which are also highly coupled, and because the $\Delta S^{\ominus}$ values (and hence the solvation energies) are almost equal. For [UO_2(oda)] the $-\Delta G^{\ominus}$ value (29.1 kJ mol^{-1}) is smaller than that for [UO_2(ida)] (50.3 kJ mol^{-1}); similarly the stretching force constant for the U–O(ether) bond (1.1×10^2 N m^{-1}) is smaller than that for the U–N(imino) bond (2.48×10^2 N m^{-1}), while the other force constants U–O(carboxylic) are very similar in both complexes. We suggest that this behaviour can be explained in terms of a greater covalent character of the U–N compared to the U–O bond in this type of complex.

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REFERENCES

[1] A. Oskarsson, *Acta Chem. Scand.*, 1971, **25**, 1206 and refs. therein.

[2] M. Krishnamurty and K. B. Morris, *Inorg. Chem.*, 1969, **8**, 2620.

[3] G. Bombieri, E. Forsellini, G. Tomat, L. Magon, and R. Graziani, *Acta Cryst.*, 1974, **B30**, 2659.

[4] O. Traverso and F. Scandola, *Inorg. Chim. Acta*, 1970, **4**, 493.

[5] G. Sbrignadello, G. A. Battiston, G. Tomat, and O. Traverso, *Inorg. Chim. Acta Letters*, 1977, **24**, L43.

[6] G. Sbrignadello, G. Tomat, G. A. Battiston, P. A. Vigato, and O. Traverso, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1647.

[7] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1965, vol. 1, pp. 119, 151.

[8] H. D. Flack, *Acta Cryst.*, 1974, **A30**, 569.

[9] C. G. Pierpont, L. C. Francesconi, and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2367.

[10] D. T. Cromer and J. A. Waber, *Acta Cryst.*, 1965, **18**, 104.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[13] R. B. Roof, *Phys. Rev.*, 1959, **113**, 820.

[14] P. Coppens, ' Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1969, p. 268.

[15] U. Casellato, M. Vidali, and P. A. Vigato, *Inorg. Chim. Acta Rev.*, 1976, **18**, 77.

[16] G. Bombieri, U. Croatto, R. Graziani, E. Forsellini, and L. Magon, *Acta Cryst.*, 1974, **B30**, 407.

[17] C. Oldham, *Progr. Inorg. Chem.*, 1968, **10**, 223.

[18] (*a*) G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali, and P. A. Vigato, *Chem. Comm.*, 1971, 1330; (*b*) *J.C.S. Dalton*, 1973, 2331; (*c*) D. A. Clemente, G. Bandoli, F. Benetollo, M. Vidali, P. A. Vigato, and U. Casellato, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1999; (*d*) G. Bandoli and D. A. Clemente, *J.C.S. Dalton*, 1975, 612; (*e*) G. Bandoli, D. A. Clemente, G. Marangoni, and G. Paolucci, *J.C.S. Chem. Comm.*, 1978, 235; (*f*) G. Bandoli, D. A. Clemente, and M. Biagani Cingi, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1709; (*g*) C. Panattoni, R. Graziani, G. Bandoli, B. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320; (*h*) D. A. Clemente, G. Bandoli, M. Vidali, P. A. Vigato, R. Portanova, and L. Magon, *J. Cryst. Mol. Struct.*, 1973, **3**, 221.

[19] (*a*) J. Albertsson, ' On the Stereochemistry of Nine-coordinate Lanthanoid Compounds,' Thesis, Lund, 1972; (*b*) A. Oskarsson, *Acta Chem. Scand.*, 1976, **B30**, 125.

[20] A. Oskarsson, *Acta Cryst.*, 1974, **B30**, 780, 1184; *ibid.*, 1973, **B29**, 1747; *Acta Chem. Scand.*, 1974, **A28**, 250; C. E. Boman, H. Herbertsson, and A. Oskarsson, *Acta Cryst.*, 1974, **B30**, 378.

[21] T. F. Koetzle, M. N. Frey, W. C. Hamilton, P. G. Jŏnsson, M. S. Lehmann, and J. J. Verbist, *Acta Cryst.*, 1972, **A28**, S193.

[22] G. A. Battiston and G. Sbrignadello, *Inorg. Chim. Acta*, 1978, **26**, 145.

[23] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Chapman and Hall, London, 1975.

[24] A. Bismondo, P. DiBernardo, G. Tomat, L. Magon, and O. Traverso, XI Congresso Chimica Inorganica, Arcavacata di Rende(Cz), 1978, 1D.