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# Synthesis and Characterization of Uranyl Compounds with Iminodiacetate and Oxydiacetate Displaying Variable Denticity

**J. Jiang,*[†] M. J. Sarsfield,*[‡] J. C. Renshaw,[‡] F. R. Livens,[‡] D. Collison,[†] J. M. Charnock,[§]
M. Helliwell,[†] and H. Eccles[||]**

*Department of Chemistry and Centre for Radiochemistry Research, The University of Manchester, Oxford Road, Manchester M13 9PL, UK, CCLRC Daresbury Laboratory, Warrington WA4 4AD, UK, and Research and Technology, BNFL, Springfields, Salwick, Preston PR4 0XJ, UK*

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Eight uranyl compounds containing the dicarboxylate ligands iminodiacetate (IDA) or oxydiacetate (ODA) have been characterized in the solid state. The published polymeric structures for $[UO_2(C_4H_6NO_4)_2]$ and $[UO_2(C_4H_4O_5)]_n$ have been confirmed, while $Ba[UO_2(C_4H_5NO_4)_2]\cdot 3H_2O$, $[(CH_3)_2NH(CH_2)_2NH(CH_3)_2][UO_2(C_4H_4O_5)_2]$ [orthorhombic space group *Pnma*, $a = 10.996(5)$ Å, $b = 21.42(1)$ Å, $c = 8.700(3)$ Å, $Z = 4$], and $[C_2H_5NH_2(CH_2)_2NH_2C_2H_5][UO_2(C_4H_4O_5)_2]$ [monoclinic space group $P2_1/n$, $a = 6.857(3)$ Å, $b = 9.209(5)$ Å, $c = 16.410(7)$ Å, $\beta = 91.69(3)$, $Z = 2$] contain monomeric anions. The distance from the uranium atom to the central heteroatom (O or N) in the ligand varies. Crystallographic study shows that U–heteroatom (O/N) distances fall into two groups, one 2.6–2.7 Å in length and one 3.1–3.2 Å, the latter implying no bonding interaction. By contrast, EXAFS analysis of bulk samples suggests that either a long U–heteroatom (O/N) distance (2.9 Å) or a range of distances may be present. Three possible structural types, two symmetric and one asymmetric, are identified on the basis of these results and on solid-state $^{13}C$ NMR spectroscopy. The two ligands in the complex can be 1,4,7-tridentate, giving five-membered rings, or 1,7-bidentate, to form an eight-membered ring. $(C_4H_{12}N_2)[(UO_2)_2(C_4H_5NO_4)_2(OH)_2]\cdot 8H_2O$ [monoclinic space group $P2_1/a$, $a = 7.955(9)$ Å, $b = 24.050(8)$ Å, $c = 8.223(6)$ Å, $\beta = 112.24(6)$, $Z = 2$], $(C_2H_{10}N_2)[(UO_2)_2(C_4H_5NO_4)_2(OH)_2]\cdot 4H_2O$, and $(C_6H_{13}N_4)_2[(UO_2)_2(C_4H_4O_5)_2(OH)_2]\cdot 2H_2O$ [monoclinic space group $C2/m$, $a = 19.024(9)$ Å, $b = 7.462(4)$ Å, $c = 2.467(6)$ Å, $\beta = 107.75(4)$, $Z = 4$] have a dimeric structure with two capping tridentate ligands and two $\mu_2$-hydroxo bridges, giving edge-sharing pentagonal bipyramids.

## Introduction

A number of reviews and many papers concerning carboxylate compounds of uranyl in the solid state have been published since the 1970s.[1,2] Over 100 uranyl carboxylates have been synthesized and characterized crystallographically, revealing a number of possible coordination modes for the carboxylate groups dependent on the ligand functionality and steric requirements.[1] Indeed, the polyfunctional ligands iminodiacetate (IDA) and oxydiacetate (ODA) (Figure 1) may almost be regarded as prototypical chelating agents for $UO_2^{2+}$, from pentadentate ODA with two five-membered chelate rings around one uranyl center in the polymeric complex $[UO_2(ODA)]_n$ to the tridentate/monodentate bridging HIDA ligand in $[UO_2(HIDA)_2]$.[1–8]We have carried out

$H_2ODA$ $H_2IDA$

**Figure 1.** Structure of $H_2IDA$ and $H_2ODA$.

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* Corresponding authors. E-mail (M.J.S.): mbdssmjs@mail1.mcc.ac.uk.

[†] Department of Chemistry, The University of Manchester.

[‡] Centre for Radiochemistry Research, The University of Manchester.

[§] CCLRC Daresbury Laboratory.

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**Table 1.** Summary of Analytical Data for Uranyl IDA and ODA Compounds

| compound | microanalysis (%) (calcd in paren) | $\upsilon_{asym}$(COO), $\upsilon_{sym}$(COO) ($cm^{-1}$) | CP MAS $^{13}C$ NMR (ppm)[a] |
|---|---|---|---|
| **2**, barium bis(iminodiacetato) dioxouranate(VI) trihydrate<br>$Ba[UO_2(C_4H_5NO_4)_2]\cdot 3H_2O$ | C 13.21 (13.27), H 2.27 (2.21),<br>N 3.66 (3.87), Ba 18.80 (18.95),<br>U 32.84 (32.92) | 1618, 1403 | 182.9, 180.9 (COO)<br>53.3 ($CH_2$) |
| **3**, piperazinium di-$\mu_2$-hydroxo-bis[iminodiacetato dioxouranate(VI)] octahydrate<br>$(C_4H_{12}N_2)[UO_2(C_4H_5NO_4)_2(OH)_2]\cdot 8H_2O$ | C 13.50 (13.48), H 3.69 (3.74),<br>U 45.01 (44.57) | 1620, 1398 | 182.6, 181.5 (COO)<br>55.7 ($CH_2$) |
| **4**, Ethylenediammonium di-$\mu_2$-hydroxo-bis[iminodiacetato dioxouranate(VI)] tetrahydrate<br>$(C_2H_{10}N_2)[UO_2(C_4H_5NO_4)_2(OH)_2]\cdot 4H_2O$ | C 12.05 (12.37), H 3.06 (3.09),<br>N 5.66 (5.77), U 48.95 (48.95) | 1625, 1398 | 182.2, 180.3 (COO)<br>54.7 ($CH_2$) |
| **6**, *N*,*N*′-diethylethylenediammonium bis(oxydiacetato) **d**ioxouranate(VI)<br>$[C_2H_5NH_2(CH_2)_2NH_2C_2H_5][UO_2(C_4H_4O_5)_2]$ | C 25.79 (25.77), H 4.10 (3.99),<br>N 4.29 (4.29), U 36.33 (36.50) | 1656, 1411 | 175.4 (br) (COO)<br>68.6 ($CH_2$) |
| **7**, *N*,*N*,*N*′,*N*′-tetramethylethylenediammonium bis(oxydiacetato) dioxouranate(VI)<br>$[(CH_3)_2NH(CH_2)_2NH(CH_3)_2][UO_2(C_4H_4O_5)_2]$ | C 25.79 (26.77), H 3.95 (3.99),<br>N 4.29 (4.29), U 36.03 (36.50) | 1638, 1411 | 179.2, 176.0 (COO)<br>69.1 ($CH_2$) |
| **8**, bis(hexamethylenetetrammonium) di-$\mu_2$-hydroxo-bis[iminodiacetato dioxouranate(VI)] dihydrate<br>$(C_6H_{13}N_4)[UO_2(C_4H_4O_5)_2(OH)_2]\cdot 2H_2O$ | C 21.08 (20.76), H 3.57 (3.49),<br>N 9.21 (9.68), U 40.43 (41.17) | 1638, 1384 | 174.6 (COO)<br>70.9 ($CH_2$) |

[a] Solid-state $^{13}C$ NMR data for the anionic fragment only.

**Table 2.** Summary of Crystallographic Information

| | **3** | **6** | **7** | **8** |
|---|---|---|---|---|
| empirical formula | $C_{12}H_{36}N_4O_{22}U_2$ | $C_{14}H_{26}N_2O_{12}U$ | $C_{14}H_{26}N_2O_{12}U$ | $C_{10}H_{20}N_4O_9U$ |
| formula weight | 1064.49 | 652.39 | 652.39 | 580.33 |
| space group | $P2_1/a$ (No. 14) | $P2_1/n$ (No. 14) | *Pnma* (No. 62) | $C2/m$ (No. 12) |
| crystal group | monoclinic | monoclinic | orthorhombic | monoclinic |
| *a* (Å) | 7.955(9) | 6.857(3) | 10.996(5) | 19.024(9) |
| *b* (Å) | 24.050(8) | 9.209(5) | 21.42(1) | 7.462(4) |
| *c* (Å) | 8.223(6) | 16.410(7) | 8.700(3) | 2.467(6) |
| $\beta$ (deg) | 112.24(6) | 91.69(3) | 90 | 107.75(4) |
| $V$ ($Å^3$) | 1456(1) | 1038.4(7) | 2049(1) | 1685(1) |
| Z | 2 | 2 | 4 | 4 |
| $T$ (°C) | 23 | 23 | 23 | 23 |
| $\lambda$ (Å) | 0.71069 | 0.71069 | 0.71069 | 1.54178 |
| $\rho_{calcd}$ (g $cm^{-3}$) | 2.428 | 2.086 | 2.115 | 2.287 |
| $\mu$ ($cm^{-1}$) | 112.05 | 78.81 | 79.88 | 280.47 |
| $R^a$ | 0.042 | 0.051 | 0.043 | 0.044 |
| $R_w{}^a$ | 0.034 | 0.044 | 0.043 | 0.047 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$.

a comprehensive study of the structural motifs found using the $H_2IDA$ and $H_2ODA$ proligands (Figure 1), initially in order to complement a study of solution speciation.[9] Here, we report the synthesis and characterization of a series of IDA and ODA complexes, including X-ray crystallographic analyses of $\mu_2$-hydroxo bridged dimeric complexes and an unusual eight-membered ring bidentate chelate. The ligands show variable denticity in these complexes, with U−heteroatom (O/N) distances from 2.6 to 3.2 Å. Analogous bridged uranyl dimers and polymers have previously been reported for other ligands such as nitrate, formate, hydroxide, and chloride.[10−14]

## Experimental Section

**Synthesis.** All chemicals were reagent grade, purchased from BDH, Aldrich, or Lancaster, and used without further purification unless otherwise specified. $[UO_2(HIDA)_2]_n$ (**1**)[2] and $[UO_2(ODA)]_n$ (**5**)[4] were prepared by literature methods. Uranyl iminodiacetato and oxydiacetato products were prepared in hydroxylic media ($H_2O$, EtOH or MeOH), with an initial uranyl-to-ligand ratio of 1:1 or 1:2, using inorganic or organic countercations. The general approach to synthesis is to react a solution of proligand, neutralized where necessary with base, with a solution of $UO_2(NO_3)_2\cdot 6H_2O$ in water. Where alkylammonium countercations were used, the alkylamine was sufficient to neutralize the mixture. Full details of synthesis are available in Supporting Information. Analytical and spectroscopic results are summarized in Table 1.

**Crystallography.** X-ray crystallography was used to confirm the structure **5** and to determine the structures of **3** and **6**−**8**. A summary of the crystallographic data is given in Table 2 with selected bond lengths in Table 3. Further details are given in the Supporting Information.

**Solid-State $^{13}C$ Nuclear Magnetic Resonance (NMR) Spectroscopy.** The high resolution, solid-state $^{13}C$ NMR spectra were recorded at 75.4 kHz (22 °C) using the cross polarization-magic angle spinning (CPMAS) technique on a Varian Unity 300 spectrometer with a spinning speed of about 4.5 kHz. The acquisition time was 0.050 s, spectral width was 30 007.5 Hz,

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**Table 3.** Selected Bond Distances for Uranyl IDA/ODA Complexes(Å)

| | **1**[a] | **3** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|
| U=O | 1.80(1) | 1.781(8) | 1.77(1) | 1.75(1) | 1.76(1) | 1.777(9) |
| $\mathrm{U{-}O_{carboxyl}}$ | 2.58(1)[b] | 2.348(8) | 2.33(1) | 2.400(10) | 2.352(7) | 2.33(1) |
| | 2.53(1)[b] | 2.341(9) | | 2.420(10) | 2.376(8)[d] | 2.32(1) |
| | 2.42(1)[c] | | | | | |
| $\mathrm{U{-}O/N_{heteroatom}}$ | | 2.585(10) | 2.56(2) | 2.621(9) | 2.564(10) | 2.51(1) |
| | | | | | 3.12(1)[d] | |
| $\mathrm{U{-}O_{hydroxyl}}$ | | 2.358(8) | | | | 2.316(10) |
| | | 2.399(8) | | | | 2.32(1) |
| U−U | | 3.848(1) | | | | 3.758(2) |

[a] Literature data.[3] [b] Bidentate carboxyl. [c] Monodentate carboxyl. [d] 1,7-Bidentate ODA.

contact time was 1 ms, and recycle time was 5.000 s. The chemical shift scale was referenced by setting the CH$_3$ peak in a sample of solid hexamethylbenzene, run using the same conditions, to 16.5 ppm.

**Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy.** Data were collected at ambient temperature using finely ground samples, diluted with ca. 60% BN, on station 16.5 of the Daresbury S.R.S. facility, operating at ca. 2.0 GeV with ca. 180 mA current. The monochromator was a channel-cut Si(311) crystal, detuned to 50% of the maximum intensity to minimize harmonic contamination. The data were collected in transmission mode. One scan was measured for each sample and gave an adequate signal-to-noise ratio in each case. The EXAFS data for all samples were calibrated and background subtracted using EXCALIB[15] and EXBACK[16] programs and analyzed with EXCURV98[17] using Rehr-Albers theory.[18] Phase shifts were calculated using Hedin−Lundqvist potentials and von Barth ground states. The results presented in this paper were obtained from the analysis using single scattering. Fits to the small peaks in the Fourier transform at 3−5 Å were deemed to be significant if the *R* value (goodness of fit) improved by 5% or more with their inclusion. Full cluster multiple scattering calculations were also used, but although there was a superficially better fit for the peak at ca. 3.6 Å, the overall goodness of fit was not improved significantly, and the best fit parameters were essentially unchanged. The crystallographically characterized compounds **1**,[3] **3**, **5**,[5,7] **6**, **7**, and **8** were used as models in the analysis.

## Results and Discussion

**Crystallography.** The asymmetric unit of **3** contains half the anion and cation, with the other half being generated in each case by inversion. Hydrogen atoms bonded to carbon were placed in calculated positions. Some hydrogen atoms bonded to the water molecules were located by difference Fourier techniques and fixed in these positions. The anion is a centrosymmetric dimer, whose structure is shown in Figure 2, with selected bond lengths given in Table 3. The two uranyl groups are bonded by two $\mu_2$-bridging hydroxo groups, in which the hydrogen atoms are required for charge balancing. The uranium atoms are at the centers of neighboring pentagonal bipyramids with one common edge. Each IDA ligand is 1,4,7-tridentate to one uranyl ion through two carboxylate oxygens and the central nitrogen. The interatomic distances around the uranium center are quite normal for a pentagonal bipyramidal geometry.[1,3] Uranyl−carboxyl oxygen distances U−O(6) [2.358(8) Å] and U−O(6*) [2.399(8) Å] are notably different, showing that the bridging is asymmetric and the distance from uranium to the nitrogen atom in IDA [U−N(1)] is 2.585(10) Å, which is comparable with the U−N distance of 2.59(4) Å in [UO$_2$(IDA)]$_n$ reported elsewhere.[4] The adjacent equatorial interbond angles range from 63.8(3)° for O(1)−U(1)−N(1) to 81.5(3)° for O(5)−U(1)−O(6). The angle U(1)−O(6)−U(1*) is 108.0(3)°. There are a number of short intermolecular contacts between pairs of O atoms, or O and N atoms, indicating possible H-bonding interactions, which link this dimeric structure into a network.

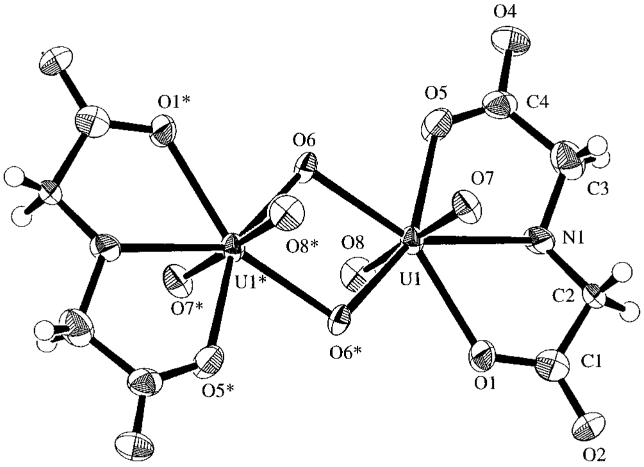

**Figure 2.** Dimeric anion in **3**.

Compound **5** was used as a model in the EXAFS study. The sample used in the EXAFS experiment was first confirmed by crystallography to have the same structure as that for [UO$_2$(ODA)]$_n$ published previously.[5,7]

The asymmetric unit of **6** contains half the molecule, which is related to the other half by a center of symmetry. The anion structure of the molecule is shown in Figure 3, and selected bond lengths are given in Table 3. The uranium atom is at the center of a slightly distorted hexagonal bipyramid. The two ODA groups are both 1,4,7-tridentate to the same uranyl ion, giving this complex a monomeric structure. The interatomic distances around the uranium center are unexceptional[1] and those in the equatorial plane are separated into two groups. The U(1)−O(1) distance is 2.40(1) Å and the U(1)−O(5) distance is 2.42(1) Å, which are both typical for uranium−carboxylate oxygen distances.[1] The U(1)−O(3) distance is 2.621(9) Å, close to the 2.63(1) Å previously

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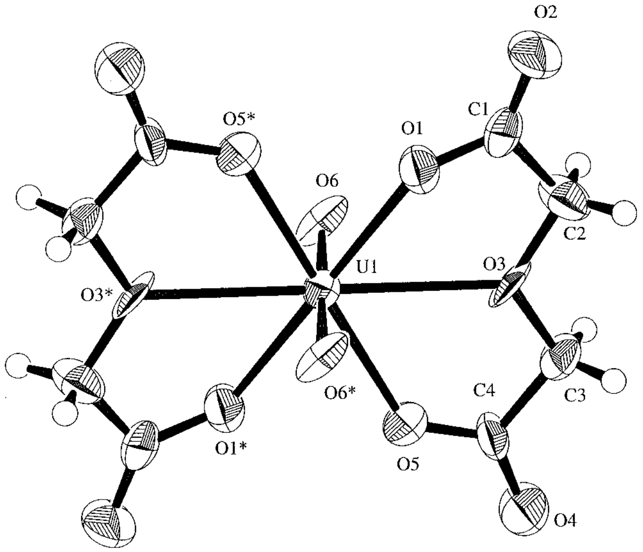

**Figure 3.** Hexadentate equatorial coordination in **6**.

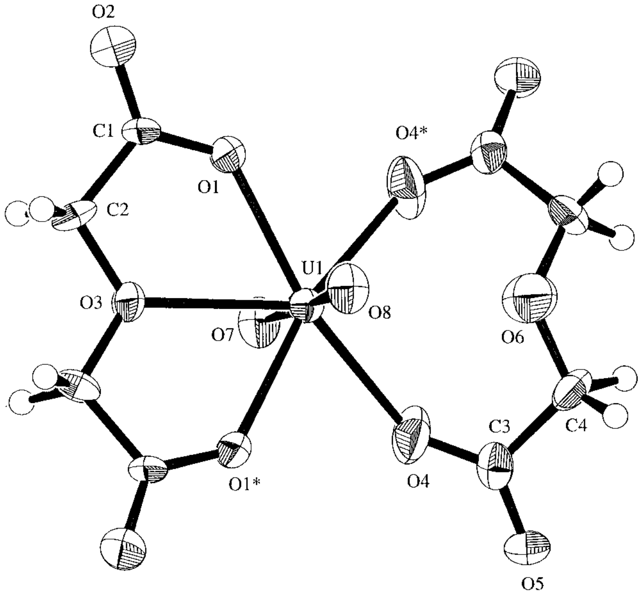

**Figure 4.** Asymmetric equatorial coordination in **7**.

reported for the uranium−ether oxygen distance in Na$_2$[UO$_2$(ODA)$_2$]·2H$_2$O.[6] The adjacent equatorial O−U−O angles range from 58.9(4)° to 62.8(3)°. From these bond lengths and angles, it appears that C(1) and C(4) have similar chemical environments. Solid-state $^{13}$C NMR spectroscopy, discussed later, shows only one signal in the carboxylate carbon region, which supports this suggestion. The distance from the nearest N atom in the cations to O(2)/O(1) is 2.97(2) Å and to O(5) is 2.88(2) Å, which suggests that cation−anion interactions are via H-bonding.

The asymmetric unit of **7** contains half the molecule. The other half of the uranium-containing ion was generated by reflection in a mirror plane containing U(1), O(3), O(6), O(7), and O(8), and the other half of the cation was generated by inversion. Hydrogen atoms were included in calculated positions but were not refined. The anion structure of this compound is shown in Figure 4. Selected bond lengths are given in Table 3. The anion has a monomeric structure with two ODA ligands. One ODA is 1,4,7-tridentate, but the other one is only 1,7-bidentate to the uranyl ion. The distances from the neighboring atoms to the uranium center are normal,[1,5] except for U(1)−O(6), which is 3.12(2) Å, suggesting that there is no U−O bond and that this is an unusual structure in which one ether oxygen in ODA is remote, leaving an eight-membered ring. It is noteworthy that the thermal ellipsoid for O(6) does not show any significant elongation in the direction of U(1), which indicates that this conformation of the 1,7-bidentate ligand is maintained regularly throughout the crystal lattice. In **6** the equatorial distances are 2.400(10), 2.621(9), and 2.420(10) Å, which indicate that the shorter U−O distances found for the tridentate ligand in **7** are compensated by the nonbonding of the ether oxygen in the bidentate ligand. Thus, the bond valence requirements of the uranyl ion with ODA are accommodated either by equatorial 6-coordination and slightly longer bonds or equatorial 5-coordination and slightly shorter bonds. In the IR spectra, the value of $\nu_{\mathrm{asym}}$(COO)−$\nu_{\mathrm{sym}}$(COO) is 226 cm$^{-1}$ for **7**, compared with 205 cm$^{-1}$ for **6**, perhaps reflecting the difference in equatorial coordination between these compounds. C(1) and C(3) have significantly different chemical environments, consistent with the two relatively well-separated carboxylate carbon signals in the $^{13}$C NMR spectrum, discussed later. The short contact between the cation N atom and O(2), 2.72(1) Å, indicates that the cation−anion interactions are via H-bonding.

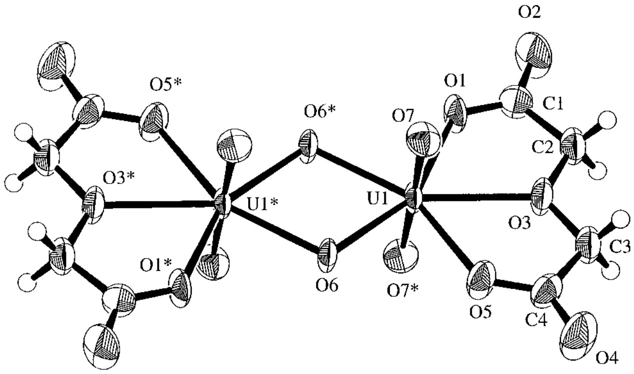

**Figure 5.** Anion structure in **8**.

Figure 5 presents the molecular structure for **8**. In the complex, the central uranium and equatorial oxygen atoms lie on a mirror plane at an occupancy of 0.5, and the space group is *C*2/*m*. The nitrogen atoms of the countercation are disordered over two sites each and have occupancies fixed for N1a at 0.65, for N1b at 0.35, for N2a and N3a at 0.325, and for N2b and N3b at 0.175. Hydrogen atoms bonded to carbon were placed in calculated positions. Selected bond lengths are given in Table 3. This complex has a dimeric structure similar to the 2:2 uranyl-IDA complex (**3**) described earlier, with each uranium atom in pentagonal bipyramidal coordination about each uranium atom. The distances from the $\mu_2$-hydroxo O(6) and O(6)* to the uranium atoms are the same, 2.32(1) Å, which suggests that the bridging is symmetric and contrasts with the asymmetric bridging in **3**. The prism containing the two $\mu_2$-hydroxo bridges and five-membered chelate rings is close to planar. A number of short

**Table 4.** Selected Bond Distances (Å) and Angles (deg) of Hydroxo-Bridged Uranyl Complexes

| | $U-O_{hydroxyl}$[a] | U−U | U−O−U | HO−U−OH | ref |
|---|---|---|---|---|---|
| $[(UO_2)_2(\mu\text{-}OH)_2(ODA)_2]_2$, **8** | 2.32(1) | 3.758(2) | 108.4(4) | 71.(6) | this work |
| $[(UO_2)_2(\mu\text{-}OH)_2(OH_2)_6]^{2+}$ | 2.29(1) | 3.83(1) | 113.5(7) | 66.6(7) | 22 |
| $[(UO_2)_2(\mu\text{-}OH)_2(IDA)_2]_2$, **3** | 2.376(8) | 3.848(1) | 108.0(3) | 72.0(3) | this work |
| $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]_2$ | 2.36(1) | 3.90(1) | 112.9(5) | 67.1(5) | 29 |
| $[(UO_2)(\mu\text{-}OH)(HCOO)(OH_2)]$ | 2.36(2) | 3.927(2) | 111.2(7) | 68.7(6) | 14 |
| $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_2(OH_2)_3]$ | 2.383(22) | 3.939(1) | 111.4(1) | 68.3(8) | 10 |
| $[(UO_2)_2(\mu\text{-}OH)_2(NO_3)_4]_2$ | 2.341(7) | 3.94(1) | 112.6(3) | 67.4(3) | 30 |
| $[(UO_2)_2(\mu\text{-}OH)_2Cl_2(OH_2)_4]$ | 2.359(21) | 3.944(1) | 113.0 (8) | 67.0(7) | 11 |
| $[(UO_2)_2(\mu\text{-}OH)(C_5H_3O_3)(OH_2)_2]$ | 2.293(9) | 4.22(1) | 133.8(6) | N/A | 28 |

[a] Averaged value.

contacts indicate H-bonding interactions among cation, anion, and water molecules, which link the dimeric complex into a three-dimensional framework.

**Structural Comparisons.** Hydroxo-bridged uranyl complexes are of particular importance in understanding solution speciation of the uranyl ion under conditions of hydrolysis.[19−21] The cations $[(UO_2)_2(\mu_2\text{-}OH)_2(OH_2)_6]^{2+}$ and $[(UO_2)_3O(\mu_3\text{-}OH)_2(OH_2)_6]^{+}$ both adopt a pentagonal bipyramidal local geometry about the uranium center with adjacent U−U* distances of 3.83(1) Å and 3.809(2)$_{avg}$ Å, respectively.[22,23] The $\mu_2$-hydroxo bridges in $[(UO_2)_2(\mu_2\text{-}OH)_2(OH_2)_6]^{2+}$ are geometrically similar to those in the 2:2 uranyl−IDA (**3**) and 2:2 uranyl−ODA (**8**) dimeric compounds discussed in this paper. Compared to other structurally similar cationic, neutral, and anionic $\mu_2$-hydroxo bridged uranyl complexes (Table 4), the two anions, **3** and **8**, exhibit unusually short U−U* distances of 3.848(1) and 3.758(2) Å and relatively small U−OH−U bond angles of 108.4(4)° and 108.0(3)°, respectively (see Table 4). The reason for this is not clear, but the interaction of hydroxide oxygen atoms competing for the bonding orbitals of the uranyl oxo bonds, perhaps as a result of the poor electron-donating ability of the 1,4,7-tridentate ligand, cannot be ruled out. In the IR spectrum of compound **8**, $\nu_{asym}(UO_2)$ is 903 cm$^{-1}$, which is significantly lower than those in the spectra of the two 1:2 monomers discussed above (921 and 920 cm$^{-1}$, for **6** and **7**, respectively). A similar feature is described for the monomeric uranyl hydroxide anion $[UO_2(OH)_4]^{2-}$.[21]

Structural confirmation of eight-membered rings, as observed in **7** (Figure 4), that contain the uranyl unit is rare, although they are postulated in the solution speciation of uranyl in citrate[24] and other naturally occurring multifunctional acid systems.[25] To our knowledge the only other structure containing an eight-membered ring to be solved by X-ray crystallography is the amidate-bridged bimetallic complex $[Pt\{cyclo\text{-}NC(O)CH_2CH_2\}_2(Ph_3P)_2]\cdot UO_2(NO_3)_2$, where the lactam carbonyl groups are coordinated to the linear uranyl group.[26]

**Solid-State $^{13}$C Nuclear Magnetic Resonance (NMR) Spectroscopy.** Copies of all the CP-MAS $^{13}$C NMR spectra reported are available in the Supporting Information. The solid-state $^{13}$C NMR data of the iminodiacetato compounds **2**−**4** are summarized in Table 1. All the signals in the carboxylate carbon region split into two components, with an intensity ratio of ca. 1:1, which suggests that, in each complex, there are two types of carboxylate carbon atoms present in equal abundance but in slightly different chemical environments. In the crystal structure of **3** (Figure 1), the U(1)−O(1) and U(1)−O(5) distances [2.348(8) and 2.341(9) Å, respectively] are not significantly different. The two carboxylate signals in the NMR spectra ($\delta_{CO_2}$ 182.6, 181.5 ppm) may, therefore, arise from the difference between the bond angles of O(1)−U(1)−N(1) and O(5)−U(1)−N(1) [63.8(3)° and 65.8(3)°, respectively], the asymmetric $\mu_2$-hydroxo bridging, or the packing in the lattice. The similarity in the stoichiometry, IR, and the carboxylate carbon resonances for **3** and **4** implies that the ethylenediammonium salt (**4**) also contains a $\mu_2$-hydroxo bridged dimeric anion with the metal centers being symmetry related.

Solid-state $^{13}$C NMR chemical shifts of oxydiacetato compounds **6**−**8** are given in Table 1. In the spectrum of **6**, one broad carboxylate carbon signal, centered at 175.4 ppm, suggests the near equivalence of all four carboxylate carbons, confirming the symmetric structure of the anion shown in Figure 3. By contrast, in the spectrum of **7**, there are two carboxylate carbon signals observed, one at 179.2 ppm and the other one at 176.0 ppm, with an intensity ratio of 1:1. The relatively large separation of these two signals suggests that the four carboxylate carbons have two distinct chemical environments, with two atoms in each, consistent with the crystallographic mirror symmetry. The crystal structure (Figure 4) shows that the two ODA ligands coordinate to the uranyl center differently, one tridentate and the other bidentate, and the 3 ppm difference between these two carboxylate carbon signals may be explained by this difference in ligation. By comparison with the spectrum of **6**, it appears that the resonance for the carboxylate carbons in tridentate ODA is ca. 175 ppm. Therefore, in the spectrum of **7**, the signal at 176.0 ppm can be assigned to the carboxylate carbon in the tridentate ligand and the signal at 179.2 ppm to that in the bidentate ligand.

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**Table 5.** Summary of EXAFS Fitting, with Atom, Occupancy,[a] and Debye−Waller Factor ($2\sigma^2$ (Å$^2$)) Values in Parentheses

| shell assignment | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| U=O | 1.79 ± 0.02<br>(O, 2, 0.004) | 1.79 ± 0.02<br>(O, 2, 0.005) | 1.81 ± 0.02<br>(O, 2, 0.005) | 1.80 ± 0.02<br>(O, 2, 0.007) | 1.78 ± 0.02<br>(O, 2, 0.005) | 1.78 ± 0.02<br>(O, 2, 0.004) | 1.79± 0.02<br>(O, 2, 0.006) | 1.80 ± 0.02<br>(O, 2, 0.005) |
| U−O$_{carboxyl}$ | 2.38 ± 0.02<br>(O, 2, 0.017)<br>2.50 ± 0.02<br>(O, 4, 0.013) | 2.46 ± 0.02<br>(O, 4, 0.016) | 2.37 ± 0.02<br>(O, 4, 0.010)[b] | 2.36 ± 0.02<br>(O, 4, 0.012)[b] | 2.37 ± 0.02<br>(O, 4, 0.018)[b] | 2.42 ± 0.02<br>(O, 4, 0.018)[b] | 2.38 ± 0.02<br>(O, 4, 0.012)[b] | 2.34 ± 0.02<br>(O, 4, 0.010)[b] |
| U−O/N$_{heteroatom}$ |  | 2.99 ± 0.02<br>(N, 2, 0.017) | 2.59 ± 0.02<br>(N, 1, 0.001) | 2.59 ± 0.02<br>(N, 1, 0.009) | 2.54 ± 0.02<br>(O, 1, 0.013) | 2.95 ± 0.02<br>(O, 2, 0.021) | 2.58 ± 0.02<br>(O, 1, 0.010)<br>2.90 ± 0.02<br>(O, 1, 0.009) | 2.52 ± 0.02<br>(O, 1, 0.011) |
| U−U |  |  | 3.90 ± 0.05<br>(U, 1, 0.010) | 3.85 ± 0.05<br>(U, 1, 0.008) |  |  |  | 3.79 ± 0.05<br>(U, 1, 0.008) |
| R[c] | 35.2 | 31.1 | 35.8 | 36.2 | 37.7 | 30.7 | 31.6 | 39.4 |

[a] Occupancy is the number of atoms in the shell ± 1. [b] Carboxyl and hydroxyl oxygens are indistinguishable; value is for 4 ± 1 U−O$_{carboxyl/hydroxyl}$ bonds. [c] $R$ is a measure of overall goodness of fit.[21]

It has also been observed that $\delta_{CO_2}$ for ODA is generally less than that for IDA; only one carboxylate signal is observed at 174.6 ppm in the spectrum of **8** (cf. **3** $\delta_{CO_2}$ 182.6, 181.5 ppm), demonstrating the near equivalence of the carboxylate carbons in the tridentate ligands. The anion structure of this compound is shown in Figure 5. The bond lengths (Table 3) show that this compound is a symmetric dimer and the four carboxylate carbons have quite similar geometric environments. Therefore, the $^{13}$C NMR result is consistent with the crystallographic study.

**Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy.** The calibrated, background subtracted, $k^3$-weighted U L3-edge EXAFS for iminodiacetato and oxydiacetato compounds, their Fourier transforms, and the best simulations together with best fit parameters are given in the Supporting Information. A summary of the shell assignments, atom occupancy, and the corresponding Debye−Waller factors is given in Table 5.

The crystal structure for **1** has been solved by Bombieri et al.,[3] and their structural analysis of this compound was used as a model. In this compound, which consists of polymeric chains, six carboxylate oxygen atoms forming an irregular hexagonal bypyramid surround the uranyl ion. Each ligand chelates to one uranyl unit through two oxygen atoms in one carboxylate group and coordinates to another uranyl unit through one of the two oxygen atoms in the other carboxylate group. It has been determined crystallographically that, in the equatorial plane, the U−O distance for the two oxygen atoms from monodentate carboxylate groups is 2.43(1) Å, and the U−O distances for the four oxygen atoms from bidentate carboxylate groups are 2.53(1) and 2.58(1) Å.[3] EXAFS analysis is consistent with the crystallographic data, giving 2.38 Å for two oxygen atoms and 2.50 Å for four oxygen atoms.

In the best simulation for **2**, the first shell contains two oxygen atoms, 1.79 Å from the uranium center, which is a typical U−O distance in the linear uranyl group. There are four oxygen atoms in the second shell at 2.46 Å. This distance is normal for equatorial oxygen atoms in a uranyl carboxylate complex.[27] The two nitrogen atoms in IDA are 2.99 Å from the uranyl center. This value is large compared with the normal U−N bond distances in IDA complexes, which are 2.59(4) Å for $[UO_2(IDA)]_n$[4] and 2.585(10) Å for the dimeric compound **3**. Similarly, the distance between the ether oxygen atom and uranium atom is 2.65(2) Å in the monomeric compound $Na_2[UO_2(ODA)_2]\cdot 2H_2O$.[6]

The unusual U−N distance in **2** suggests two possibilities, for either of which EXAFS analysis could give 2.99 Å as the average value. One possibility is that there are two long bonds or even no formal bonds between the two nitrogen atoms and the uranium center, so both U−N distances are 2.99 Å. The other possibility is that two central nitrogen atoms have different chemical environments, in which one nitrogen, in a 1,4,7-tridentate IDA ligand, coordinates to uranium with a U−N distance of ca. 2.6−2.7 Å, and the other one, in a 1,7-bidentate IDA ligand, is ca. 3.1−3.2 Å from uranium and does not have a formal bond. Crystallographic study of **7**, discussed earlier, has shown that such an asymmetric structure can certainly occur in the uranyl−ODA system. This would also explain the splitting of the carboxylate carbon signal in the NMR spectrum, because the two IDA ligands would coordinate differently with the uranyl center. Eight carbon atoms occupy the fourth shell at 3.41 Å. The inclusion of a fifth shell, as a barium atom at 4.39 Å in the simulation, improved the fit of the model. This distance suggests some bonding between the barium counterion and the carboxylate oxygen atoms in the uranyl−IDA chelate, because a similar U−Ba distance [4.50(2) Å] has been found in the structure of $Ba[UO_2(malonate)_2]\cdot 3H_2O$,[31] in which the barium atom is surrounded by eight nearest neighbor oxygen atoms at distances between 2.67(1) and 2.92(1) Å and two next-nearest neighbors both at 3.02(2) Å. Six of these 10 oxygen atoms are from carboxylate ligands and four of them are from water molecules.

The formulas for the anions in **3** and **4** are the same, and these two compounds have very similar IR and solid-state $^{13}$C NMR spectra. Indeed, similar EXAFS spectra were also

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obtained for them. In **3**, the U−O distances in the equatorial plane are known to be 2.341(9), 2.348(8), 2.358(8), and 2.399(8) Å from crystallography, but EXAFS analysis cannot resolve these distances and only gives an average value, 2.37 Å. In general, there is good agreement between the results of X-ray crystallography and EXAFS. The dimeric structure suggested by the best fit parameters is entirely consistent with the anion structure determined by crystallography. During data simulation of **4**, the results obtained for **3** were used as a model, and from IR, $^{13}$C NMR, and EXAFS analyses, it is concluded that **4** adopts a dimeric anion structure that is schematically the same as that in **3**.

Compound **5**, which has been published previously[5,7] and confirmed in this study, was also studied by EXAFS and used as a model for the study of other uranyl−ODA compounds. Comparison of the best fit parameters obtained from EXAFS with the crystallographic data shows general agreement between these two techniques, although EXAFS cannot distinguish the four equatorial oxygens at 2.33(1) and 2.43(1) Å, only giving 2.37 Å as an average value.

Compounds **6** and **7** have the same anion formula, but X-ray crystallography shows that they have different structures. In the EXAFS analysis of these compounds, the bond distances from the crystallographic study were used as the starting point for the simulation. For **6**, the best fit U−O distance in the uranyl group is 1.78 Å, and the distance from the uranium center to the four carboxylate oxygen atoms in the equatorial plane is 2.42 Å. Both values are consistent with the crystal structure data. The results for the two ether oxygens in the ODA ligands are less satisfactory. The EXAFS analysis gives an average U−O distance of 2.95 Å, but the crystallographic study shows that this U−O distance should be ca. 2.6 Å.

This discrepancy may arise from differences in the molecular structure of the crystal chosen for XRD analysis and the bulk sample used for EXAFS analysis. In such a case, symmetric 1,7-bidentate coordination, with a distance of ca. 2.95 Å between the uranium atom and the ether oxygen atoms, may occur. An alternate possibility would be an asymmetric complex, with one ODA ligand 1,4,7-tridentate to the uranyl group with a U−O(4) distance of 2.6−2.7 Å and the other ODA ligand 1,7-bidentate to uranyl with a U−O(4) distance of 3.1−3.2 Å. In the solid-state $^{13}$C NMR spectrum of this compound, there is only one carboxylate signal, although it is quite broad and its spinning sidebands are split, suggesting that this signal could be a feature made up of overlapping contributions. Therefore, neither of the two possibilities can be excluded. The Debye−Waller factor for the ether oxygen atoms is quite high, which is consistent with the asymmetric structure or the presence of a mixture.

EXAFS analysis of **7** gives similar inconsistent results. Solid-state $^{13}$C NMR and crystallographic studies have shown an asymmetric monomeric structure for this compound. EXAFS suggests that the uranyl oxygens are 1.79 Å from the uranium center, and the U−O distances in the equatorial plane are 2.38 Å for four carboxylate oxygens and 2.58 Å for one ether oxygen. These compare well with the crystallographic results, but another oxygen atom at 2.90 Å, presumably an ether oxygen, was identified in the EXAFS. The distance of 2.90 Å is close to the average of the crystallographically determined distances, 2.564(10) Å (bonded) and 3.12(1) Å (nonbonded). Therefore, besides the crystallographically characterized structure of **7**, which was discussed earlier and shown in Figure 4, the possibility displayed for **6** in Figure 3, in which two ODA ligands are 1,4,7-tridentate to the uranyl center with a U−O distance of 2.5−2.6 Å, cannot be excluded. Once again, the EXAFS sample used may reflect a heterogeneous mixture of symmetric and asymmetric coordination.

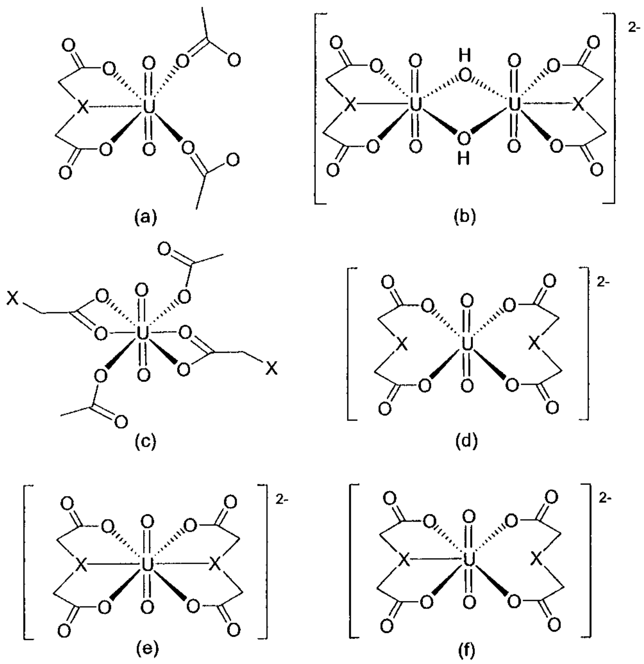

**Figure 6.** Structural motifs of ODA/IDA coordinated to uranyl in the solid state.

Crystallographic study shows that the anion in **8** has a dimeric structure similar to that of **3** and **4**, the 2:2 dimeric uranyl−IDA complexes. EXAFS analysis of **8** shows that the uranium center is surrounded by seven oxygen atoms, two at 1.80 Å and with the U−O distance for the ether oxygen 2.52 Å, longer than the 2.34 Å for the carboxylate and hydroxo oxygens. The U−U distance in the complex is 3.79 Å. The average U−C distance is 3.49 Å. All of these best-fit parameters agree very well with the crystallographic data.

## Conclusions

Multifunctional ODA/IDA ligands can coordinate to uranyl ions in a variety of ways. All of the structural motifs encountered in this study are displayed in Figure 6. Two different coordination modes are found for complexes containing a uranyl:ligand ratio of 1:1 (Figure 6a,b). It is possible for the ligand to utilize all five heteroatoms (O/N) to bind to uranium, as shown in the three-dimensional polymeric network of $[UO_2(IDA)]_n$[4] or $[UO_2(ODA)]_n$[5,7] (Figure 6a). Alternatively, a partial hydrolyses of these systems results in a uranyl dimer bridged by two hydroxide ligands, as in **3** and **8** (Figure 6b), where two IDA/ODA ligands are bound to two uranium centers, in a 1,4,7-tridentate fashion, with a relatively short U−U distance. For complexes with a uranyl:ligand ratio of 1:2, four possible structures are now known. The ligand can bridge two uranyl centers through terminal carboxyl groups to form infinite chains, as in $[UO_2(HIDA)_2]_n$[3] (Figure 6c). Other bonding modes involve monomeric uranyl centers bound to two IDA/ODA ligands in a 1,4,7-tridentate or 1,7-bidentate manner (Figure 6d−f). This solid-state information is essential in order to help provide a comprehensive solution speciation model of these systems.[9]

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**Supporting Information Available:** Information on the collection and refinement of crystallographic data, final values of all refined atomic coordinates, listings of anisotropic thermal parameters, full lists of bond lengths and angles, least-squares planes and atomic deviations there from, intermolecular contacts, unit cell, packing diagrams, EXAFS simulation and best fit parameters and CP MAS $^{13}$C NMR spectra. This material is available free of charge via the Internet at http/::pubs.acs.org.

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