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# Structural studies on monomeric and dimeric uranyl bis(dimethylmalonato)complexes

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## Abstract

The use of tetramethylpropanediammonium (2+) or hexaamminecobalt (III) as counter cations allowed the preparation of monomeric or dimeric uranyl bis(dimethylmalonato) complexes, respectively, which were characterised by solid-state $^{13}$C NMR and X-ray crystallography. These two structures are different from the monomeric and dimeric structures we reported earlier with unsubstituted malonate as ligand [4]. © 1998 Elsevier Science S.A.

*Keywords:* Uranyl; Malonate; Dimethylmalonato; CPMAS; $^{13}$C NMR; X-ray crystallography

## 1. Introduction

The structures and thermodynamics of a series of malonate complexes of uranium are under investigation. The aim of this study is in part to generate a database of structural and thermodynamic information on the reactions of the actinide ions with dicarboxylates. It is anticipated that by varying substituent groups in the parent malonic acid, and using different counter cations, an empirical understanding of uranyl–ligand interactions will be obtained which will lead to a better understanding of actinide behaviour in a variety of environmental and process conditions.

Malonates were selected as the ligand series because some crystallographic information was already available. However, a systematic study has not been previously attempted for malonates or, indeed, for any other relatively simple organic ligand molecules with uranium ions.

Infinite chain structures for uranyl dimalonate have been reported for $(NH_4)_2[UO_2(C_3H_2O_4)_2]\cdot H_2O$ and $Ba[UO_2(C_3H_2O_4)_2]\cdot 3H_2O$ [1–3] and previously we have reported the synthesis and characterisation of monomeric and dimeric uranyl dimalonate complexes with dimethylpiperazinium and tetramethylethylenediammonium as counter cations [4]. In order to investigate the effect of dimethyl groups on the coordination behaviour of malonic acid, a group of uranyl bis(dimethylmalonato) compounds were prepared with a range of inorganic and organic cations. Herein, we report the synthesis and characterisation of monomeric and dimeric uranyl bis-(dimethylmalonato) complexes.

## 2. Experimental

### 2.1. Materials

All chemicals were reagent grade, purchased from Strem chemicals, Aldrich or Lancaster and used without purification.

### 2.2. Physical methods

Elemental analyses were performed by Microanalysis Lab, Department of Chemistry, The University of Manchester. IR spectra were recorded on an ATI Mattson Genesis Series FTIR Spectrometer. TG/DT analyses were made on a Seiko (TG/DTA 220) Thermal Analyzer at a heating rate of 10°C min$^{-1}$ in a static air atmosphere. The solid-state $^{13}$C NMR experiments were performed on a Varian Unity-300 spectrometer with a spinning speed of 4.0 kHz. High resolution solid state $^{13}$C NMR spectra were recorded at 75.4 MHz using the cross polarisation–magic angle spinning (CPMAS) technique. The acquisition time

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was 0.050 s, spectral width 30007.5 Hz, contact time 1.5 ms and recycle time 3.000 s.

### *2.3. Syntheses*

$(C_7H_{20}N_2)[UO_2(C_5H_6O_4)_2]\cdot 3H_2O$ (**1**). A solution of uranyl nitrate hexahydrate (0.50 g, 1 mmol in 5 $cm^3$ $H_2O$) was added to an aqueous solution of dimethylmalonic acid (0.39 g, 3 mmol in 25 $cm^3$ $H_2O$) and tetramethylpropanediamine (0.48 ml, 3 mmol) in a ratio of 1:1. Yellow, diffraction quality crystals formed after two days. Found: C 28.84, H 5.10, N 3.82, U 33.83%. Calc. for $C_{17}H_{38}N_2O_{13}U_1$: C 28.50, H 5.34, N 3.91, U 33.22%. IR (KBr disc) $\nu$ $cm^{-1}$: 3478 s (br), 1654 m, 1603 m, 1550 m, 1465 m, 1410 s, 1352 m, 1313 m, 1198 s, 903 vs., 714 m, 594 m.

$\{[Co(NH_3)_6][UO_2(C_5H_6O_4)_2]Cl\}_2\cdot 7H_2O$ (**2**). A solution of uranyl nitrate hexahydrate (0.50 g, 1 mmol in 5 $cm^3$ $H_2O$) was added to an aqueous solution of dimethylmalonic acid (0.26 g, 2 mmol in 25 $cm^3$ $H_2O$), sodium hydroxide (0.32 g, 8 mmol) and hexaamminecobalt(III) chloride (0.27 g, 1 mmol) in the ratio of 1:4:1. An orange, crystalline product formed after few days. Found: C 15.27, H 4.65, N 10.71, Co 7.21, Cl 4.31, U 30.64%. Calc. for $C_{20}H_{74}N_{12}O_{27}Co_2Cl_2U_2$: C 15.21, H 4.72, N 10.64, Co 7.46, Cl 4.49, U 30.14%. IR (KBr disc) $\nu$ $cm^{-1}$: 3418 vs (br), 1623 m, 1579 w, 1546 m, 1462 w, 1409 s, 1340 m, 1192 m, 907 s, 718 m, 594 m.

### *2.4. Crystallography*

Intensities were measured on a Rigaku AFC5R diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda$=0.71069 Å) in $\omega-2\theta$ mode. Crystal data: $C_{17}H_{38}N_2O_{13}U$ (**1**): $M$=716.52, crystal size 0.07×0.20×0.25 mm, orthorhombic, space group *Pbcn* (#60), yellow tabular, $a$=8.523(4), $b$=16.918(4), $c$=17.753(4) Å, $U$=2559(2) $Å^3$, $Z$=4, $D_c$=1.859 g $cm^{-1}$, $F(000)$=1400, $T$=296°C, $R$=0.031, $R_w$=0.024. Crystal data: $C_{20}H_{70}N_{12}O_{27}Cl_2Co_2U_2$ (**2**): $M$=1575.67, crystal size 0.40×0.20×0.20 mm, triclinic, space group $P\bar{1}$(#2), orange plate, $a$=10.362(4), $b$=15.207(3), $c$=9.274(2) Å, $\alpha$=92.42(2), $\beta$=110.95(2), $\gamma$=108.16(2)°, $U$=1277.2(2) $Å^3$, $Z$=1, $D_c$=2.048 g $cm^{-1}$, $F(000)$=762, $T$=296°C, $R$=0.036, $R_w$=0.033. The cell parameters were refined by least squares from the angular positions of 25 carefully centred reflections with $15.2<\theta<19.8$ (**1**) and $33.3<\theta<40.1°$ (**2**). An empirical absorption correction was applied, based on azimuthal scans of three reflections with transmission factors 0.53 to 1.00 (**1**) and 0.64 to 1.00 (**2**). The data were corrected for Lorentz and polarization effects. A linear decay correction factor was applied for **2**. The structure for **1** was solved by direct methods with SIR 92 [5], whilst the structure for **2** was solved by Patterson methods [6], and expanded using Fourier techniques with DIRDIF94 [7]. Nonhydrogen atoms were refined anisotropically in the case of **2**. For **1**, the disordered solvent molecules were refined isotropically, whilst all other, nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added in calculated positions. Neutral-atom scattering factors were taken from Cromer and Waber [8]. Anomalous dispersion effects were included in $F_{calc}$ [9]; the values for $\Delta f'$ and $\Delta f'$ were those of Creagh and McAuley [10]. The values for the mass attenuation coefficients were those of Creagh and Hubbell [11]. All calculations were performed using the teXsan [12] crystallographic software package (Molecular Structure Corporation).

## 3. Results and discussion

### *3.1. Thermal analysis*

The DTA curve for compound **1** shows two endothermic processes at 106 and 154°C and a strongly exothermic process at 450°C. The first endotherm is caused by loss of two lattice water molecules (calc. 5.0, exp. 5.08%) and the second endotherm is possibly caused by loss of the coordinated water molecule but it overlaps with the ligand decomposition exotherm, which gives a continuous mass loss until the final product $UO_3$ is formed at about 480°C (calc. 40.0, exp. 40.13%). The thermogravimetric curve for compound **2** shows a four-step decomposition, the first one being loss of the seven water molecules (calc. 8.0, exp. 7.92%). The next two steps have similar mass losses which may be caused by decomposition of two ligands (calc. 16.4, exp. about 17.0%), giving an endotherm at 222°C and an exotherm at 304°C. The last step is a continuous mass loss with two exotherms at 366 and 432°C giving the final products $Co_2O_3$ and $2UO_3$ (calc. 46.7, exp. 47.0%) at 480°C.

### *3.2. Crystal structures*

The asymmetric unit for **1** contains half of each ion, and the other half is generated by rotation about a 2-fold axis. There is also a molecule of water contained in the asymmetric unit. The anion structure with atom-numbering scheme together with selected bond lengths and angles are shown in Fig. 1. The uranium atom is at the centre of a slightly distorted pentagonal bipyramid. The two malonate groups are both terminal bidentate on the same uranyl ion with the fifth equatorial position of the uranium atom occupied by a water molecule, forming a monomeric unit, symmetrical about the U-O(6) bond. The uranyl group is nearly linear with an O(5)-U-O(5′) angle of 179.2(4)° and unexceptional U-O distance (1.782(6) Å). The U-O distances in the equatorial plane for **1** are separated into two groups. The U-O distance is 2.503(7) Å for O(6) of the

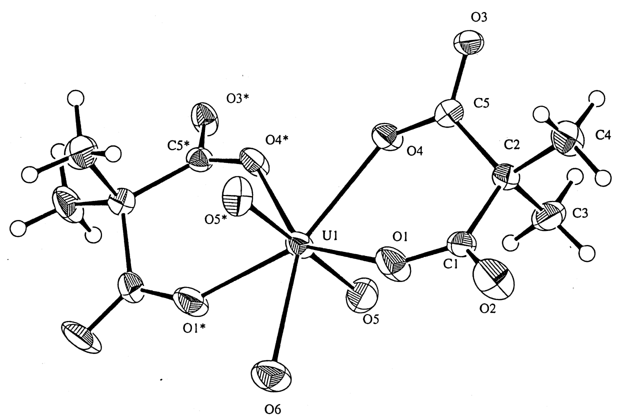

Fig. 1. Anion structure of compound **1**. Selected bond lengths (Å) and angles (°) for compound **1**. U(1)-O(1) 2.310(6); U(1)-O(4) 2.331(5); U(1)-O(5) 1.782(6); U(1)-O(6) 2.503(7); O(1)-C(1) 1.256(9); O(2)-C(1) 1.193(9); C(1)-C(2) 1.55(1); C(2)-C(5) 1.53(1); O(4)-C(5) 1.276(9); O(3)-C(5) 1.226(9); O(1)-U(1)-O(1) 143.5(3); O(1)-U(1)-O(4) 70.0(2); O(1)-U(1)-O(4) 146.4(2); O(1)-U(1)-O(5) 90.2(3); O(1)-U(1)-O(5) 89.6(3); O(1)-U(1)-O(6) 71.8(1); O(4)-U(1)-O(4) 76.4(3); O(1)-U(1)-O(6) 71.8(1); O(4)-U(1)-O(5) 89.9(2); O(5)-U(1)-O(6) 89.6(2); U(1)-O(1)-C(1) 144.2(6); O(1)-C(1)-O(2) 117.8(8); C(1)-C(2)-C(5) 113.7(7); U(1)-O(4)-C(5) 139.5(5); O(4)-C(5)-C(2) 118.7(7).

water molecule and average 2.320(12) Å for the other four oxygen atoms. The equatorial O-U-O angles range from 70.0(2)° to 76.4(3)°. The deviations of the donor atoms from the equatorial plane (U, O(1), O(4), O(1*), O(4*) and O(6)) are between ±0.006 Å. The two six-membered chelate rings have the same boat conformation flattened at one end, the U and C(2) atoms lying −0.153 and −0.316 Å from the O(4), C(5), C(1), O(1) mean plane (see Table 1). The short intermolecular contacts indicate H-bonding interactions between water molecules in the lattice and the carboxylate oxygen atoms. The closest cation–anion contact is 2.793(9) Å from O(3) to a N atom, again suggesting possible cation–anion interactions via H-bonding.

In the case of **2**, the asymmetric unit consists of half the U complex, together with two half $[Co(NH_3)_6]^{3+}$ ions, with each of the Co atoms on a centre of symmetry. In each case, the other halves are generated by inversion. In addition, the asymmetric unit contains a Cl ion, three water molecules, and a disordered half-molecule of water. The anion structure, together with selected bond lengths and angles, is shown in Fig. 2. The two ligands are both terminal bidentate on the same uranium centre, but one of them links to the adjacent uranium atom through a third oxygen atom to give a dimeric, centrosymmetric structure for the anion. The U-O distances for uranyl are quite normal, averaging 1.763(8) Å. The equatorial U-O distances are separated into three groups averaging 2.310(8) Å for O(1), O(4) and 2.402(8) Å for O(7) and O(8). The distance of 2.351(6) Å for U-O(5) lies between the two groups. The equatorial O-U-O angles range from 67.9(2)° to 74.6(2)°. The deviations of donor atoms from the equatorial plane are significant, from −0.648 Å for O(7) to +0.782 Å for O(8) compared to the dimeric structure, $\{(C_6H_{18}N_2)[UO_2(C_3H_2O_4)_2]\}_2\cdot(CH_3OH)_2$ with malonic acid as ligand [4] in which the deviations of donor atoms from the equatorial plane are within ±0.04 Å. The bidentate ligand has a boat conformation flattened at the U end, the U and C(2) atoms lying −0.175 and −0.357 Å, respectively, from the O(1), C(1), C(5), O(4) mean plane, whilst the tridentate ligand is puckered and no ideal conformation can be assigned to it (see Table 1). Short intermolecular contacts indicate H-bonding interactions among the water molecules, the carboxylate oxygen atoms and ammonia ligands in the counter cation. The extensive short O-N contacts suggest that the cation–anion interactions are probably via H-bonding.

### 3.3. NMR spectroscopy

The solid-state $^{13}$C NMR spectra for the two compounds are shown in Figs. 3 and 4. Compound **1** has two chemical

Table 1
Least-squares planes with deviations (Å). The equations of the planes are in the form: $PX+QY+RZ=S$

| Compounds **1** | **2** |
|---|---|
| *P Q R S* | *P Q R S* |
| Plane 1 0.8565 0.0000 −0.5161 5.0094 | Plane 1 9.7486 −8.3622 −4.4605 −2.3155 |
| O(1), O(4), O(6), O(1*), O(4*) | O(1), O(4), O(5), O(7), O(8) |
| [O(1) −0.004; O(4) 0.006; O(6) 0.000;<br>O(1*) 0.004; O(4*) −0.006; U(1) 0.000] | [O(1) −0.074; O(4) −0.324; O(5) 0.019;<br>O(7) −0.648; O(8) 0.782; U(1) 0.246] |
| Plane 2 0.7738 −0.0120 −0.6333 3.8965 | Plane 2 9.0454 −4.2366 −7.0447 −2.2757 |
| O(1), C(1), C(5), O(4) | O(1), C(1), C(5), O(4) |
| [O(1) 0.166; C(1) 0.067; C(5) 0.199;<br>O(4) 0.038; U(1) −0.153; C(2) −0.316] | [O(1) 0.212; C(1) 0.047; C(5) 0.246;<br>O(4) 0.027; U(1) −0.175; C(2) −0.357] |
| Plane 3 0.7738 0.0120 −0.6333 3.6716 | Plane 3 10.2316 −6.9617 −2.9540 −1.0139 |
| O(1*), C(1*), C(5*), O(4*) | O(5), C(6), C(10), O(8) |
| [O(1*) −0.166; C(1*) −0.067; C(5*) −0.199;<br>O(4*) −0.038; U(1) 0.153; C(2*) 0.316] | [O(5) 0.062; C(6) 0.244; C(10) −0.2.2;<br>O(8) 0.520; U(1) −0.287; C(7) −0.338] |

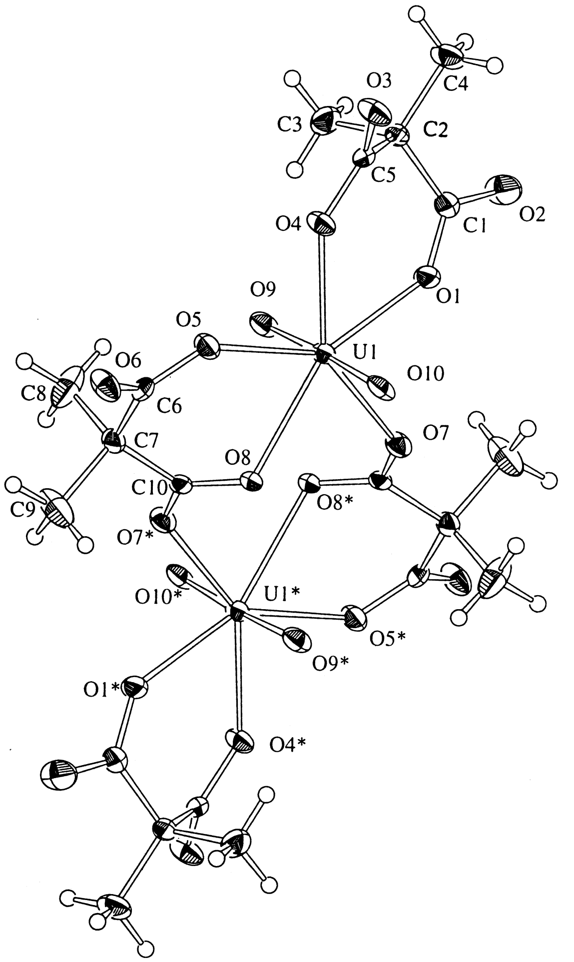

Fig. 2. Anion structure of compound **2**. Selected bond lengths (Å) and angles (°) for compound **2**. U(1)-O(1) 2.296(6); U(1)-O(4) 2.325(5); U(1)-O(5) 2.351(6); U(1)-O(7) 2.393(6); U(1)-O(8) 2.411; U(1)-O(9) 1.761(6); U(1)-O(10) 1.765(6); O(1)-C(1) 1.252(10); O(3)-C(5) 1.245(9); O(4)-C(5) 1.295(9); C(1)-C(2) 1.53(1); C(2)-C(5) 1.51(1); O(5)-C(6) 1.291(9); C(6)-C(7) 1.50(1); C(7)-C(10) 1.55(1); O(8)-C(10) 1.268(9); O(1)-U(1)-O(4) 70.2(2); O(1)-U(1)-O(5) 143.2(2); O(1)-U(1)-O(7) 74.6(2); O(1)-U(1)-O(9) 88.5(2); O(1)-U(1)-O(10) 93.8(2); O(4)-U(1)-O(5) 73.3(2); O(5)-U(1)-O(8) 67.9(2); O(7)-U(1)-O(8) 74.2(2); U(1)-O(1)-C(1) 141.8(6); U(1)-O(4)-C(5) 136.5(5); U(1)-O(5)-C(6) 137.2(5); U(1)-O(7)-C(10) 131.6(6); U(1)-O(8)-C(10) 118.7(5).

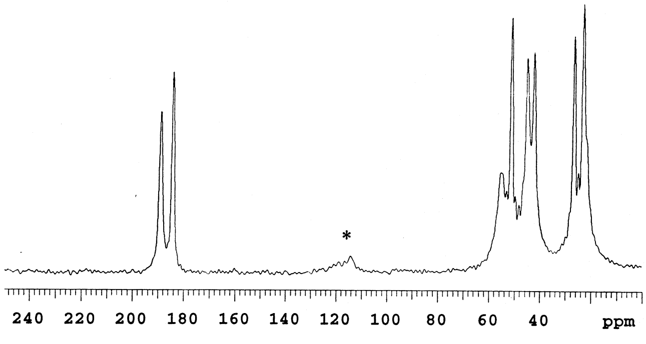

Fig. 3. Solid state $^{13}$C NMR spectrum for compound **1** (* represent spinning sidebands).

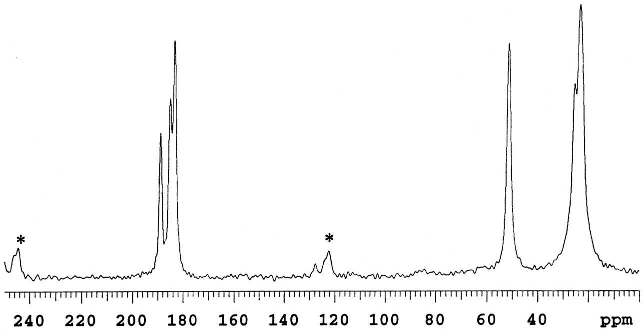

Fig. 4. Solid state $^{13}$C NMR spectrum for compound **2** (* represent spinning sidebands).

shifts at 189.0 and 184.4 ppm in the carbonyl region in the ratio of 1:1 which indicates that a difference between O(1) and O(4) caused by the coordinated water molecule separates the four carboxylate carbon atoms into two distinct groups. The chemical shifts at 23.4 and 26.9 ppm can be assigned to methyl groups whilst those at 42.6 and 45.4 ppm can be assigned to $CH_2$ groups in the cations. The chemical shifts at 51.5 and 55.6 ppm can be assigned to the 4° carbon atoms in the ligands. Compound **2** has three chemical shifts at 188.9, 185.1 and 183.4 ppm in the carbonyl region which suggests that the two carboxylate carbon atoms from the bidentate ligands have the same chemical environment but the two carboxylate carbon atoms in the tridentate ligands are different. The chemical shifts at 51.5, 25.6 and 23.3 ppm in the aliphatic region can be assigned to 4° carbon in the ligands and two kinds of methyl groups.

### *3.4. Structural comparison*

A comparison of the structural and spectroscopic properties of **1** and **2** with two novel monomeric and dimeric malonato complexes reported earlier [4] indicates how solid-state $^{13}$C NMR spectrometry might be used to classify structural types. $(C_6H_{16}N_2)[UO_2(C_3H_2O_4)_2]\cdot 3H_2O$, **3**, also contains a monomeric anion, but with no crystallographic symmetry. The U-O (carboxylate) distances are grouped as one short and three long. **1** and **3** both display two kinds of carboxylate environments in the CP/MAS $^{13}$C NMR spectrum, but the intensity ratios are 1:1 and 1:3 in the respective spectra. Compound **2** and $\{(C_6H_{18}N_2)[UO_2(C_3H_2O_4)_2]\}_2\cdot(CH_3OH)_2$, **4**, are both centrosymmetric dimers, and in each case the bidentate ligand adopts a boat conformation flattened at the U end. In contrast, the tridentate ligand of **2** is puckered, whereas in **4** this ligand has a boat conformation flattened at the C end. The CP/MAS $^{13}$C NMR spectrum can distinguish the two different structures with three kinds of carboxylate environments for **2** and four kinds with approximately 1:1:1:1 ratio for **4.**

## 4. Conclusions

The new monomeric and dimeric structures for uranyl bis(dimethylmalonate) have been prepared and characterised by elemental analysis, thermal analysis, CP/MAS $^{13}C$ NMR and X-ray crystallography. Both complexes are subtly different from those with unsubstituted malonate as ligand.

Our studies to date have demonstrated that the different crystal structures give rise to different and well-defined CP/MAS $^{13}C$ NMR spectra which can be used to distinguish and to characterise solid uranyl dicarboxylato complexes and possibly to fingerprint or to predict structure types.

Different counter cations also have some effects on the aggregation of the uranyl complexes and may influence the structures of compounds in solid state.

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