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Synthesis and Crystal Structure of (*μ*-Malonanilide-*O,O′*)bis[bis(dibenzoylmethanato)dioxouranium(VI)]: A New Coordination Mode of the Malonamide Ligand

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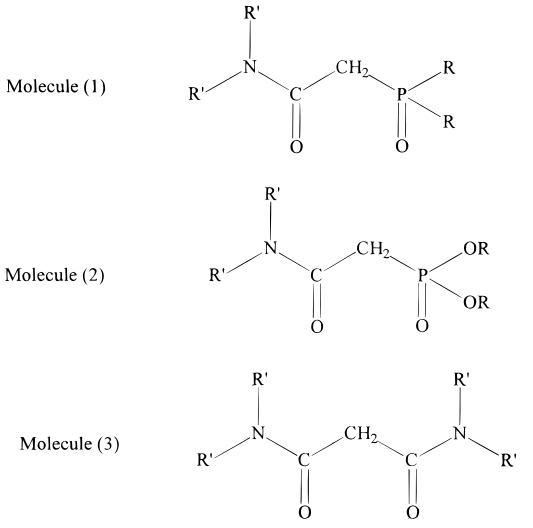
Introduction

Bifunctional (carbamoylmethyl)phosphine oxides (CMPO) (**1**), (carbamoylmethyl)phosphonates[1] (CMP) (**2**), and malonamides[2] (**3**) are known to be effective liquid−liquid extractants for the separation of actinide ions from acid media. Malonamides have been proposed as an alternative to CMPO systems in the nuclear waste management process.[2a,c] Structural studies on the complexes of CMPO (**1**) or CMP (**2**) type ligands with lanthanide and actinide ions show that they act as bidentate chelates.[3] IR and NMR spectral studies on the complexes of malonamide ligands with uranium(VI) and plutonium(IV) ions[4] indicate that they act in a bidentate chelate mode similar to that found for the CMPO or CMP ligands. Recently we have reported IR, NMR, and molar mass data for the complexes of uranyl bis(*β*-diketonates) with the CMP type of ligand and showed that they act as a bridging bidentate species.[5] There have been no previous structural studies to support our spectroscopic and molar mass data, and we report here the first structurally characterized complex of an actinide ion in which the malonamide (malonanilide) moiety acts as a bridging bidentate ligand.



(R, R' = alkyl or aryl group)

Experimental Section

The FTIR spectrum was recorded on a Nicolet Model DXC-20 spectrometer, and the ^{1}H NMR spectrum was recorded on a Varian VXR-300 S spectrometer. The molecular weight was determined in chloroform according to the reported method.[6]

Preparation of [$\{UO_2((C_6H_5CO)_2CH)_2\}_2(C_6H_5NHCO)_2CH_2$] (4). To a chloroform solution of [$UO_2(C_6H_5CO)_2CH$]·$2H_2O$[7] (0.4 g, 0.54 mmol) was added solid malonanilide[8] (0.068 g, 0.27 mmol), and the solution was refluxed for about 2 h. The solvent was removed under vacuum; the residue was extracted with chloroform (20 mL) and filtered. To the filtrate 5 mL of dodecane was added, and the solution was kept for slow evaporation overnight. The red-colored crystalline product obtained was filtered, washed with hexane, and dried in vacuum. Yield: 0.415 g, 92.6%. Anal. Calcd for $C_{75}H_{58}N_2O_{14}U_2$: C, 53.4; H, 3.5; N, 1.7. Found: C, 53.1; H, 3.3; N, 1.6. IR (KBr, Nujol, cm^{-1}): 3276 (br, NH, st), 3205 (br, O−H, st), 1652 (br, sh, O−H, bend), 1640 (NH, bend), 1590 (C═O···M, DBM, st), 1532 (CO, diamide, st), 1315 (C−O···M, DBM, st), 897 (O═U═O, st). ^{1}H NMR ($CDCl_3$, δ ppm): 4.17 (s, CH_2), 6.95 (t, C_6H_5, diamide), 7.04 (t, C_6H_5, DBM), 7.25 (s, CH, DBM), 7.4−7.6 (m, C_6H_5, diamide + DBM), 8.3 (m, C_6H_5, DBM), 8.7 (br, NH). MW: calcd 1687.6, found 1825. (DBM = dibenzolmethanato anion.)

X-ray Crystallography. The single crystals of the complex **4** as its chloroform solvate were obtained by slow evaporation from a chloroform isooctane mixture. The crystallographic data are summarized in Table 1.

Results and Discussion

Structure of [$\{UO_2((C_6H_5CO)_2CH)_2\}_2$·$(C_6H_5NHCO)_2CH_2$]·$CHCl_3$. The molecular structure of complex **4** is shown in Figure 1, and selected interatomic distances and angles are in the Figure 1 legend. The structure clearly shows that the two uranyl bis(*β*-diketonates) moieties are bridged by the diamide ligand. The coordination number of each uranium atom is seven, which gives rise to a pentagonal bipyramidal geometry. The dinuclear structure adopted by the molecule **4** is stabilized by a pair of N−H···O(uranyl oxygen) hydrogen bonds, which gives rise to an eight-membered metallocyclic ring.

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Table 1. Crystallographic Data for **4**·$CHCl_3$

chemical formula	$C_{75}H_{58}N_2O_{14}U_2 \cdot CHCl_3$
fw	1806.66
space group	$P\bar{1}$ (No. 2)
T	21 °C
λ	0.7107 Å
a	10.5801 (8) Å
b	17.732 (2) Å
c	19.309 (4) Å
α	102.467 (12)°
β	90.700 (11)°
γ	91.701 (8)°
V	3534.8 (8) Å^3
Z	2
ρ_{calc}	1.697 g cm^{-3}
μ(Mo Kα)	47.55 cm^{-1}
absorption corrctn	Gaussian
$R(F_o)^a$	0.055 (for 5830 reflections with $I > 2\sigma(I)$)
$R_w(F_o^2)^b$	0.109 (for all 12391 measured reflections)

$^a R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w(F_o^2) = ([\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2])^{0.5}$.

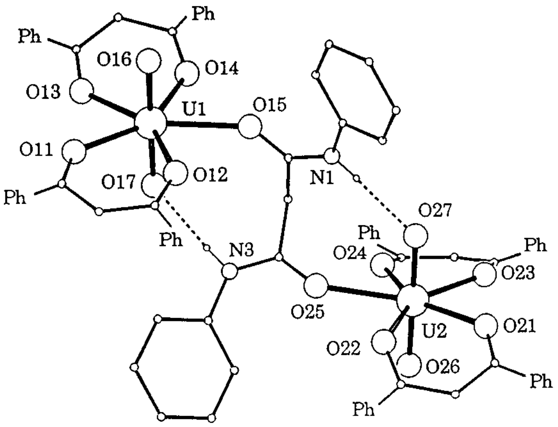

Figure 1. A schematic drawing of $[\{UO_2(C_6H_5COCHCOC_6H_5)_2\}_2(C_6H_5NHCO)_2CH_2]$ (**4**) showing the conformation and the intramolecular N−H···O(uranyl) hydrogen bonds. Principal dimensions include the following: U1−O11 2.335 (7), U1−O12 2.315 (7), U1−O13 2.310 (7), U1−O14 2.309 (7), U1−O15 2.495 (7), U1−O16 1.751 (7), U1−O17 1.773 (7), U2−O21 2.312 (7), U2−O22 2.324 (7), U2−O23 2.306 (7), U2−O24 2.347 (8), U2−O25 2.458 (6), U2−O26 1.743 (8), U2−O27 1.776 (7) N1···O27 2.914 (9), N3···O17 2.908 (10) Å, O11−U1−O12 70.4 (3), O11−U1−O13 76.9 (3), O12−U1−O15 69.2 (2), O13−U1−O14 71.0 (3), O14−U1−O15 72.5 (2), O16−U1−O17 179.1 (3), O21−U2−O22 71.0 (3), O21−U2−O23 75.4 (2), O22−U2−O25 73.5 (2), O23−U2−O24 70.4 (3), O24−U2−O25 70.8 (2), O26−U2−O27 179.4 (3), C1−C2−C3 113.5 (8)°.

A feature of the structure is that, at each uranium, one of the uranyl oxygen atoms is hydrogen bonded to an NH group of an adjacent malonamide ligand; this gives rise to a difference in the uranyl U−O bond lengths (average U═O distances 1.774 (7) and 1.747 (7) Å for the hydrogen-bonded and nonbonded uranyl oxygen atoms, respectively). Such small differences for hydrogen-bonded and non-hydrogen-bonded U═O bonds have been reported previously, e.g., in dioxo(μ^2-selenono)bis(urea)-uranium(VI).[9]

The other bond lengths, U−O(β-diketonate) = 2.306 (7)−2.347 (8) Å and U−O(amido) = 2.458 (6)−2.495 (7)Å, are normal. The U−O(amido) distances in **4** are slightly longer than the U−O(sulfoxide) distances in uranyl sulfoxides[10d,12] (2.37−2.40 (2) Å), phosphine oxide[3e,10a,b,13] (2.26−2.41 (5) Å), or amide[3c,e,12b,14] (2.35−2.41 (5) Å) complexes and shorter than simple aliphatic ketone complexes[11] (2.51−2.56 (2) Å).

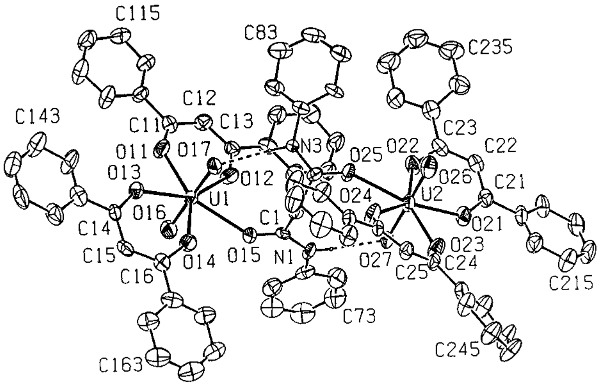

Figure 2. An ORTEP plot (anisotropic displacement ellipsoids drawn at the 30% probability level) for **4** with an indication of the numbering scheme. All hydrogen atoms except those involved in the N−H···O hydrogen bonds have been omitted.

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Supporting Information Available: Prints of the FTIR spectra of compound **4** (4 pages). An X-ray crystallographic file, in CIF format, for compound **4**·$CHCl_3$ is available on the Internet only. Ordering and access information is given on any current masthead page. The crystallographic data have also been placed with the Cambridge Crystallographic Data Centre and are available in CIF or in normal tabular format by e-mail from ferguson@chembio.uoguelph.ca.

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