

Synthesis and characterization of [bis (β -diketonato) uranium (VI)] malonamide adducts[†]

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Malonamide (L) acts as monodentate ligand in $[\text{UO}_2(\text{OO})_2 \cdot \text{L}]$ complexes (where OO = a diketonate, HTTA = thenoyl-trifluoroacetone $[\text{C}_4\text{H}_5\text{S} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COCF}_3]$; HDBM = dibenzoylmethane $[\text{C}_6\text{H}_5\text{CO} \cdot \text{CH}_2 \cdot \text{COC}_6\text{H}_5]$; HBTA = benzoyltrifluoroacetone $[\text{C}_6\text{H}_5\text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CF}_3]$) and coordinating through one of its amido oxygen atoms to the uranyl ion.

Malonamides (Fig. 1a) are known to be an effective liquid–liquid extractants for the separation of actinide ions from acidic media. Malonamide was recommended to be an alternative for carbonyl methyl phosphine oxides (CMPO) in nuclear waste management process¹. However, the fundamental coordination chemistry of these ligands with actinide ions has not been well established.

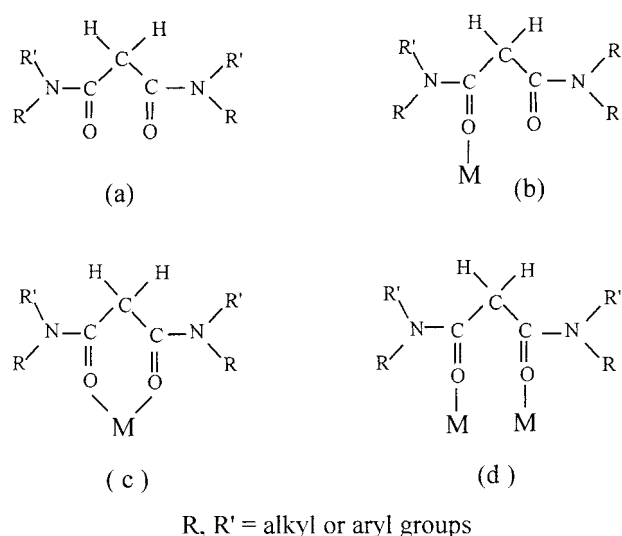


Fig. 1 Possible modes of Coordination for malonamide ligand.

They can act as monodentate (Fig. 1b), bidentate chelate (Fig. 1c) or bridging bidentate (Fig. 1d) ligands. The chelating mode of coordination is well established.^{1,2} We recently established³ the bridging bidentate mode of coordination for these ligands. However, the monodentate mode of coordination has not yet been reported. In continuation of our studies⁴ on the coordination complexes of uranyl bis (β -diketonates) with neutral ligands, I report here the complexes of malonamide with uranyl bis (β -diketonates) in which it acts as monodentate ligand.

Results and discussion

The 1:1 reaction of malonamide (L) with one equivalent of $[\text{UO}_2(\text{OO})_2 \cdot 2\text{H}_2\text{O}]$ in chloroform yielded red or orange colored products of the type $[\text{UO}_2(\text{OO})_2 \cdot \text{L}]$ (OO = TTA, DBM or BTA; L = $(\text{C}_6\text{H}_5\text{NHCO})_2\text{CH}_2$ (L_1), $(p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCO})_2\text{CH}_2$ (L_2) or $(\text{C}_6\text{H}_5\text{CH}_2\text{NHCO})_2\text{CH}_2$ (L_3)). The IR spectra (Table 2) of all the complexes show that the broad peak observed for H_2O (ν_{OH}) of the starting complex $[\text{UO}_2(\text{OO})_2 \cdot 2\text{H}_2\text{O}]$ has

Table 1 Analytical data for complexes $[\text{UO}_2(\text{OO})_2 \cdot \text{L}]$

Complex	Solvents of Crystallization	Mp (°C)	Analysis C	Found / Calcd H	Calcd N
I	Benzene / Dodecane	180	38.6 (38.5)	2.2 (2.3)	2.8 (2.9)
II	Dodecane	130	39.8 (39.8)	2.5 (2.6)	2.8 (2.8)
III	Dodecane	185	39.7 (39.8)	2.6 (2.6)	2.7 (2.8)
IV	Chloroform / dodecane	160	55.8 (55.7)	3.6 (3.6)	2.8 (2.8)
V	Chloroform	165	56.4 (56.5)	3.9 (3.9)	2.7 (2.8)
VI	Chloroform	140	56.5 (56.5)	3.9 (4.0)	2.7 (2.8)
VII	Benzene / hexane	187	46.4 (46.5)	2.6 (2.7)	2.8 (2.9)
VIII	Benzene	152	45.1 (45.2)	3.1 (3.1)	2.8 (2.9)
IX	Hexane	182	45.1 (45.2)	3.1 (3.1)	2.8 (2.9)

completely disappeared and a sharp peak around 3280 cm^{-1} for NH has appeared, indicating that the water molecule from $[\text{UO}_2(\text{OO})_2 \cdot 2\text{H}_2\text{O}]$ has been replaced by malonamide ligand. IR spectra further show the presence of uncoordinated (1670 cm^{-1}) and coordinated (1540 cm^{-1}) amido groups in all the complexes. This observation suggests that the malonamide acts as monodentate ligand and coordinates through one of its amido oxygen to uranyl ion. The observed frequency difference for coordinated and uncoordinated amido groups agrees well with structurally characterized complexes in which the malonamide coordinates through its amido oxygen atom to uranyl ion.^{3,5} The observed C=O...M and C-O...M frequencies show that the diketonates act as chelating ligands.^{3,4,6}

¹H NMR spectra (Table 2) of the complexes show the expected peaks and multiplicities. The CO–CH₂–CO protons of malonamide are deshielded with respect to free ligand in all the complexes. The deshielding is much smaller for the 1:1 complex $[\text{UO}_2(\text{DBM})_2 \cdot \text{L}_1]$ (*ca* 0.25 ppm) than the 2:1 complex $[\text{UO}_2(\text{DBM})_2]_2 \cdot \text{L}_1$ (*ca* 0.60 ppm).³ This can be explained by taking in view that the malonamide coordinates to one metal center in 1:1 complex and results in lesser electron density transfer from ligand to metal on coordination than the 2:1 complex $[\text{UO}_2(\text{DBM})_2]_2 \cdot \text{L}_1$, where malonamide coordinates to two different metal centres and acts as bridging bidentate



Fig. 2 Two Possible exchange isomers of $[\text{UO}_2(\text{OO})_2 \cdot \text{L}]$

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 2 IR, ^1H and ^{19}F NMR data for complexes $[\text{UO}_2(\text{OO})_2 \cdot \text{L}]$

Complex	IR data (ν , cm^{-1})	^{19}F NMR (δ , in ppm)	^1H NMR (δ , in ppm)
I	3320 [NH, st]; 3280 [NH, st]; 1670 [CO, L ₁]; 1650 [NH, bt]; 1600 [C=O..M, TTA]; 1550 [CO, L ₁]; 1310 [C-O..M, TTA]; 915 [O=U=O].	-74.80 [#] -74.87	4.03 [br, CH ₂]; 6.81 [br, CH, TTA]; 7.13 [t, Ph]; 7.24 [m, Ph + th]; 7.60 [d, Ph]; 7.83 [br, th]; 8.2 [br, th]; 9.20 [br, NH].
II	3325 [NH, st]; 3280 [NH, st]; 1670 [CO, L ₂]; 1650 [NH, bt]; 1600 [C=O..M, TTA]; 1550 [CO, L ₂]; 1310 [C-O..M, TTA]; 915 [O=U=O].	-74.75 [#] -74.69	2.28 [s, CH ₃]; 4.09 [br, CH ₂]; 6.79, 6.83 [s, CH, TTA]; 7.09 [d, C ₆ H ₄]; 7.34 [br, th]; 8.25 [br, th]; 9.20 [br, NH].
III	3320 [NH, st]; 3290 [NH, st]; 1655 [CO, L ₃]; 1625 [NH, bt]; 1600 [C=O..M, TTA]; 1560 [CO, L ₃]; 1315 [C-O..M, TTA]; 915 [O=U=O].	-74.48 [#] -74.78	4.10 [br, CH ₂]; 4.78 [br, NCH ₂]; 6.79, 6.82 [s, CH, TTA]; 7.1-7.35 [br, Ph + th + NH]; 7.83 [br, th]; 8.28 [br, th].
IV	3280 [NH, st]; 1670 [CO, L ₁]; 1640 [NH, bt]; 1590 [C=O..M, DBM]; 1565 [CO, L ₁]; 1320 [C-O..M, DBM]; 900 [O=U=O].	-	3.82 [s, CH ₂]; 7.07 [t, Ph, DBM]; 7.18 [t, Ph, L ₁]; 7.25 [s, CH, DBM]; 7.3-7.8 [m, Ph, DBM + L ₁]; 8.39 [br, Ph, DBM]; 9.20 [br, NH].
V	3280 [NH, st]; 1670 [CO, L ₂]; 1640 [NH, bt]; 1590 [C=O..M, DBM]; 1565 [CO, L ₁]; 1320 [C-O..M, DBM]; 900 [O=U=O].	-	2.23 [s, CH ₃]; 3.83 [s, CH ₂]; 6.97 [d, C ₆ H ₄ , L ₂]; 7.25 [s, CH, DBM]; 7.3-7.6 [m, Ph + C ₆ H ₄]; 8.39 [br, Ph, DBM]; 9.2 [br, NH].
VI	3290 [NH, st]; 1655 [CO, L ₃]; 1625 [NH, bt]; 1590 [C=O..M, DBM]; 1560 [CO, L ₃]; 1320 [C-O..M, DBM]; 900 [O=U=O].	-	3.72 [s, CH ₂]; 4.52 [br, NCH ₂]; 7.15 - 7.36 [m, Ph, DBM + Ph, L ₃ + CH, DBM]; 7.46-7.56 [m, Ph, DBM + NH]; 8.41 [br, Ph, DBM].
VII	3330 [NH, st]; 3280 [NH, st]; 1670 [CO, L ₁]; 1650 [NH, bt]; 1600 [C=O..M, BTA]; 1555 [CO, L ₁]; 1320 [C-O..M, BTA]; 920 [O=U=O].	-74.63 [#] -74.85	4.08 [br, CH ₂]; 4.02 [br, CH, BTA]; 7.15 [t, Ph, L ₁]; 7.21-7.7 [m, Ph, BTA + L ₁]; 8.35 [d, Ph, BTA]; 9.20 [br, NH].
VIII	3330 [NH, st]; 3280 [NH, st]; 1670 [CO, L ₂]; 1650 [NH, bt]; 1600 [C=O..M, BTA]; 1550 [CO, L ₂]; 1325 [C-O..M, BTA]; 920 [O=U=O].	-74.64 [#] -74.89	2.28 [s, CH ₃]; 4.14 [br, CH ₂]; 7.01 [br, CH, BTA]; 7.08 [d, C ₆ H ₄ , L ₂]; 7.35-7.71 [m, Ph, BTA]; 8.54 [d, C ₆ H ₄ , L ₂]; 9.18 [br, NH].
IX	3320 [NH, st]; 3280 [NH, st]; 1655 [CO, L ₃]; 1610 [C=O..M, BTA]; 1550 [CO, L ₃]; 1325 [C-O..M, BTA]; 920 [O=U=O].	-74.52 [#] -74.61	4.05 [br, CH ₂]; 4.75 [br, NCH ₂]; 6.98 [br, CH, BTA]; 7.3-7.4 [m, Ph, L ₃ + NH]; 7.51-7.74 [m, Ph, BTA]; 8.54 [d, Ph, BTA].

= major isomer; st = stretching; bt = bending; Ph = C₆H₅; th = thiophene; s = singlet; d = doublet; m = multiplet; br = broad.

ligand.³ The ^1H NMR spectra show the CO-CH₂-CO protons of malonamide in all the complexes as a broad resonance, possibly to exchange of the coordination site of malonamide with one metal (Fig. 2). The -CH- proton of the β -diketonate part gave two resonances for TTA and BTA, indicating that the complexes existing as a mixture of two isomeric products, *cis* and *trans*.^{4d} The ^{19}F NMR further supports this observation by showing two resonances for the CF₃ group.^{4d}

The IR and ^1H NMR spectral studies show that the 1:1 reaction of malonamide with uranyl bis (β -diketonates) yielded a mononuclear complex in which the malonamide acts as monodentate ligand and coordinates through one of its amido oxygen atom.

Experimental

The complexes $[\text{UO}_2(\text{OO})_2 \cdot 2\text{H}_2\text{O}]^7$ and ligands were prepared by the reported methods². The IR spectra were recorded on a Philips PU9510 instrument using KBr discs and the samples were mounted as nujol mulls. The ^1H and ^{19}F NMR spectra were recorded on Varian VXR-300S machine operating at 300 MHz and 282 MHz respectively.

Preparation of $[\text{UO}_2(\text{TTA})_2 \cdot \text{L}^1]$ (a): Malonanilide (L¹) (119 mg, 0.468 mmol) was added to a chloroform solution (30 ml) of $[\text{UO}_2(\text{TTA})_2 \cdot 2\text{H}_2\text{O}]$ (350, mg, 0.468 mmol) and refluxed for 30 min. The solvent was removed under vacuo, the residue was extracted with chloroform and filtered. To the filtrate 3 ml of dodecane was added and kept for crystallisation. The orange colored product obtained was filtered off, washed with hexane and dried. All the other complexes were prepared similarly and the pertinent data are given in Table 1.

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