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New modes of coordination for the β-disulfoxide ligand. The crystal and molecular structure of [{$UO_2(DBM)_2$}$_2$PhSOCH_2SOPh]

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The X-ray structure of the compound [{$UO_2(DBM)_2$}$_2C_6H_5SOCH_2SOC_6H_5$] confirms the bridging bidentate mode of coordination for the β-disulfoxide ligand $C_6H_5SOCH_2SOC_6H_5$.

Keywords: bis sulfoxide, uranyl bis (β-diketonates), X-ray structure, monodentate ligand, bridging bidentate ligand, HDBM (dibenzoyl methane), HBTA (benzoyl trifluoroacetone), HTTA (thenoyl trifluoroacetone)

Neutral bi-functional ligands such as carbamoyl methyl phosphonates (CMP), carbamoyl methyl phosphine oxides (CMPO) and malonamides (MA) are known to be effective liquid – liquid extractants for the separation of actinide ions from acid media, and the fundamental coordination chemistry of these ligands with the actinide ions has been well studied.[9, 13] They can act as monodentate, bidentate chelate or bridging bidentate ligands, depending on the anions and the concentration of metal ions used. However, the coordination chemistry of analogous β-disulfoxides with any of the actinide ions has not yet been studied, though they have similar structural properties to the CMPO, CMP, or malonamide ligands. Some compounds of β-disulfoxides with transition and lanthanide metal ions[14-16] have been reported to show a bidentate chelating mode of coordination for these ligands. However, there is no report of compounds of any of these β-disulfoxides with any metal ions in which they are either acting as monodentate or as bridging bidentate ligands. Herein, we report compounds of a β-disulfoxide-bis (phenylsulfinyl) methane with uranyl bis(β-diketonates), where this ligand acts in a monodentate and a bridging bidentate mode.

The reaction of bis(phenylsulfinyl) methane with one equivalent of [$UO_2(OO)_2.2H_2O$] (where OO = TTA, BTA or DBM) yielded orange coloured products of the type [$UO_2(OO)_2$ $C_6H_5SOCH_2SOC_6H_5$]. IR spectra of all the compounds show that the broad peak observed for the H_2O molecules (ν_{OH} = 3200 – 3500 cm^{-1}) of the starting compound [$UO_2(OO).2H_2O$] has been completely disappeared. This indicates that the water molecules from the starting compound have been replaced completely by the bis(phenylsulfinyl) methane ligand. The spectra further show the presence of both uncoordinated (1043 cm^{-1}) and coordinated (1009 cm^{-1}) sulfoxo-groups in all the compounds (Table 1). These data indicate clearly that the ligand is coordinating through one of the sulfoxide oxygen atom to the uranyl group as a monodentate ligand. The observed frequency difference between the coordinated and free sulfoxide groups [$\Delta\nu_{(S-O)} = (\Delta\nu = \nu_{free} - \nu_{complex}) = 20 - 30\ cm^{-1}$] agree with data-reported for uranium(VI) – sulfoxide adducts.

The reaction of $C_6H_5SOCH_2SOC_6H_5$ with two equivalents of [$UO_2(OO)_2.2H_2O$] yielded red colored products of the type [{$UO_2(OO)_2$}$_2$ $C_6H_5SOCH_2SOC_6H_5$]. IR spectra of all the compounds show that the broad peak observed for the H_2O molecules (ν_{OH} = 3200 – 3500 cm^{-1}) of starting compound [$UO_2(OO).2H_2O$] have been completely disappeared, indicating that the water molecules have been replaced completely by the bis(phenylsulfinyl) methane ligand. The spectra further show that there is no uncoordinated sulfoxide group in all the compounds. Since ν_{S-O} in the compounds has been shifted to lower frequencies compared to that of the free ligand, indicating the coordination of both the sulfoxide oxygen atoms to the uranyl group. The ^1H NMR spectra of all the compounds (Table 1) show that the –CH_2– protons of the

Table 1 The physical, analytical and spectral details for the compounds [$UO_2(OO)_2L$] and [$UO_2(OO)_2]_2L$

Compounds	m.p/°C	Solvents of crystallisation	Analysis (%) Found/ (Cacld) C	H	IR (ν in $cm^{-1)}$	^1H NMR (δ in ppm)
$PhSOCH_2SOPh$ (L)	185	Ethanol	59.4 (59.0)	4.7 (4.5)	1043 (br, S=O)	4.01 (s, 2H, CH_2); 7.52 – 7.71 (m, 10H, Ph)
[$UO_2(TTA)_2L$]	168	Benzene/ Dodecane	35. 3 (35.7)	2.2 (2.0)	1610 (br, C=O..M, TTA); 1040 (S=O,L); 1010 (S=O, L); 916 (O=U=O)	4.66 (s, br, CH_2, L); 6.78, 6.82 (s, CH, TTA); 7.26 – 8.25 (m, Ph + C_4H_3S, L + TTA)
[$UO_2(TTA)_2]_2L$	205	Benzene/ Dodecane	31. 9 (32. 0)	2.0 (1.7)	1610 (br, C=O..M, TTA); 1010 (S=O,L); 917 (O=U=O).	5.23 (s, br, CH_2, L); 6.77, 6. 82 (s, CH, TTA); 7.24 – 8.24 (m, Ph + C_4H_3S, L + TTA)
[$UO_2(BTA)_2L$]	173	Benzene/ Dodecane	41. 3 (41.0)	2.5 (2.6)	1620 –1595 (br, C=O..M, BTA) ; 1040 (S=O, L); 1008 (S=O, L); 918 (O=U=O).	4.69 (s, br, CH_2, L); 6.99 (s, CH, BTA); 7.33 – 8.54 (m, Ph , L +BTA)
[$UO_2(BTA)_2]_2L$	201	Benzene/ Dodecane	38. 5 (38.1)	2.6 (2.3)	1625 - 1598 (C=O..M, BTA); 1018 (S=O, L); 919 (O=U=O).	5.27 (s, br, CH_2, L); 6.97, 6.99 (s, CH, BTA); 7.37 – 8.54 (m, Ph , L + BTA)
[$UO_2(DBM)_2L$]	197	Chloroform/ Dodecane	52. 8 (52.5)	3.9 (3.5)	1590 (br, C=O..M, DBM); 1043 (S=O,L); 1009 (S=O, L); 903 (O=U=O).	4.43 (s, br, CH_2, L); 7.23 (s, CH, DBM); 7.30 – 8.46 (m, Ph , L + DBM)
[$UO_2(DBM)_2]_2L$	216	Chloroform/ Dodecane	59. 4 (59. 0)	4.7 (4.5)	1590 (br, C=O..M, DBM); 1009(S=O,L); 902 (O=U=O).	4.78 (s, br, CH_2, L); 7.23 (s, CH, DBM); 7.30 – 8.44 (m, Ph , L + DBM)

m = multiplet, s = singlet; br =broad.

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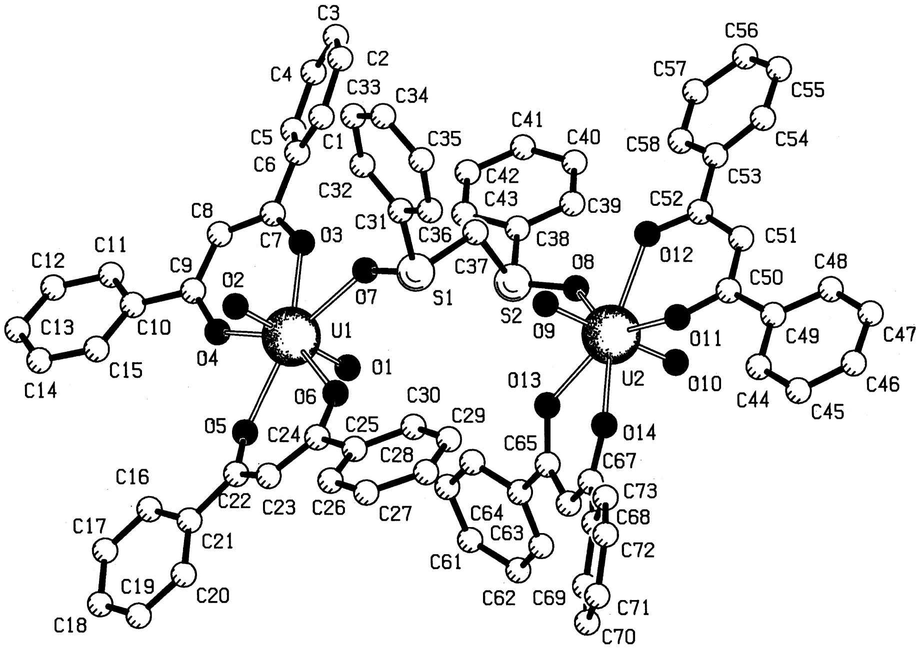

Fig. 2 The molecular structure of [$\{UO_2(DBM)_2\}_2.C_6H_5SOCH_2SOC_6H_5$].

$C_6H_5SOCH_2SOC_6H_5$ ligand are deshielded with respect to the free ligand, supporting the coordination of the sulfoxide oxygen atom with the uranyl group. The deshielding is greater in the 1:2 compounds compared to that of the 1:1 compounds, indicating clearly that the electron density transfer from ligand to metal on coordination is more in the former than the latter.

The structure of the compound [$\{UO_2(DBM)_2\}_2.C_6H_5SOCH_2SOC_6H_5$] is given in Fig. 2. The structure shows that the uranium atom is surrounded by seven oxygen atoms in a distorted pentagonal bi-pyramidal geometry. It shows further that the bis(phenylsulfinyl) ligand is a bridging bidentate and bonded through both of the sulfoxide oxygen atoms to two different uranyl bis(β-diketonate) units. The observed distances U1–O(S) [2.444 (3) Å], U2-O(S) [2.471(3) Å], U1-$O_{(DBM)}$ [2.344 (3) Å], U2-$O_{(DBM)}$ [2.341 (3)) Å], U1-$O_{(uranyl)}$ [1.769 (3) Å] and U2-$O_{(uranyl)}$ [1.779 (3) Å)] are within the accepted values.

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Techniques used: IR, ^{1}H NMR, Microanalysis, X-ray diffraction

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Table 2. Crystal and structural refinement details for [$\{UO_2(DBM)_2\}_2(C_6H_5SO)_2CH_2$].

Table 3. Selected interatomic bond distances and angles for [$\{UO_2(DBM)_2\}_2(C_6H_5SO)_2CH_2$]

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References cited in this synopsis

9 S. Karthikeyan, R.T. Paine and R.R. Rayan, *Inorg. Chim. Acta*, 1988, **144**, 135.
13 S. Kannan and G. Ferguson, *Inorg. Chem.*, 1997, **36**, 1724.
14 T.R. Musgrave and G.D. Kent, *J. Coord. Chem.*, 1972, **2**, 23.
15 M.A.A. Silva, M.H. Zain, P.C. Isolani, B. Wladislaw, L. Zinner and K. Zinner, *J. Coord. Chem.*, 1995, **36**, 311.
16 J.D. Ayala, L.B. Zinner, G. Vicentini, A.D. Pra and G. Bombieri, *Inorg. Chim. Acta*, 1993, **211**, 161.