SHORT PAPER

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Syntheses and characterisation of amide adducts of uranyl bis (β-diketonates) the molecular structure of $[UO_2(DBM)_2.C_4H_9CON(\mathit{3}\text{-}C_5H_{11})\ (\mathit{sec}\text{-}C_4H_9)]$[†]

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The first structurally characterised uranyl bis (β-diketonate)-amide adduct compound [$UO_2(DBM)_2$. C_4H_9CON ($\mathit{3}$-C_5H_{11}) (*sec*-C_4H_9)] (DBM = dibenzoylmethanate) shows that the amide ligand bonded through its amido oxygen atom to the uranyl group. The average bond distances for $U–O_{(uranyl)}$, $U–O_{(DBM)}$ and $U–O_{(amide)}$ are 1.778(5), 2.346(5) and 2.411(5)Å respectively.

Keywords: uranyl bis (β-diketonates), amide, adduct compound, X-ray structure

An enhancement in the solvent extraction separation of uranium (VI) ion from the nitric acid medium by using mixtures of β-diketones and amides has been reported.[1] The species responsible for these extraction have been isolated for some of the systems in solid state and characterised by the spectroscopic and elemental analysis methods.[2] However, there are no structural studies of these synergistic compounds to support the spectroscopic observations. As a part of our systematic work on the compounds of uranyl bis (β-diketonates) with neutral donor ligands,[3] we report here the first structurally characterised uranyl bis (β-diketonate)- amide adduct compound [$UO_2(DBM)_2$. $C_4H_9CON(\mathit{3}\text{-}C_5H_{11})$ (*sec*-C_4H_9)].

Results and discussion

Reaction of $[UO_2(OO)_2.\ 2H_2O]$ with one equivalent of N-*3*.pentyl, N-*sec*-butyl, pentanamide in chloroform yielded the adduct compounds of the type $[UO_2(OO)_2$. X] [where OO = TTA (thenoyltrifluoroacetonate) or DBM; X = amide]. IR spectra of both the compounds show that the OH absorption (at 3200 – 3500 cm^{-1}) for H_2O molecules of the starting compound $[UO_2(OO)_2.2H_2O]$ has completely disappeared. This indicates clearly that the water molecules from the starting compound $[UO_2(OO)_2.2H_2O]$ have been completely replaced by the amide ligand. Spectra further show that the ν_{CO} (1570 cm^{-1}) in the compounds has been shifted to lower frequencies compared to that of the free ligand (ν_{CO} = 1645 cm^{-1}), indicating the coordination of the amido-oxygen atom of the amide ligand to the uranyl group. The observed frequency differences $\Delta\nu_{CO}$ ($\Delta\nu = \nu_{\text{free ligand}} - \nu_{\text{compound}}$) agree well with structurally characterized compounds in which an amide ligand coordinates through its amido-oxygen atom [3e, 4] to the uranyl ion. The ^1H NMR spectra of both compounds show the expected peak multiplicities and integrations. The –CH- and $COCH_2$ protons of the amide ligand showed a down-field shift of *ca* 0.5 – 0.8 ppm in both compounds relative to the free ligand. This observation further supports the coordination of the amido-oxygen atom of the ligand to the uranyl group. The structure of one of the compounds $[UO_2(DBM)_2$. $C_4H_9CON(\mathit{3}\text{-}C_5H_{11})$ (*sec*-C_4H_9)] has been determined by single crystal X-ray diffraction methods which confirms our spectroscopic assignments.

The structure of the molecule [$UO_2(DBM)_2.C_4H_9CON$ ($\mathit{3}$-C_5H_{11}) (*sec*-C_4H_9)] with atomic numbering scheme is shown in Fig. 1, selected bond lengths and angles are given in Table 1. The uranium (VI) ion is surrounded by seven oxygen atoms (four of DBM ligand, two uranyl oxygen and one amide) to give a pentagonal bi-pyramidal geometry. The four oxygen atoms from DBM and one oxygen atom from amide form a planar pentagon. Two uranyl oxygen atoms occupy the apices. The average distances $U\text{-}O_{(uranyl)}$ [1. 778(5) Å], U-O $_{(diketonate)}$ [2.346(5) Å][3] and U-O $_{(amide)}$ [2.411(5)Å][4] are within usual range for these values.

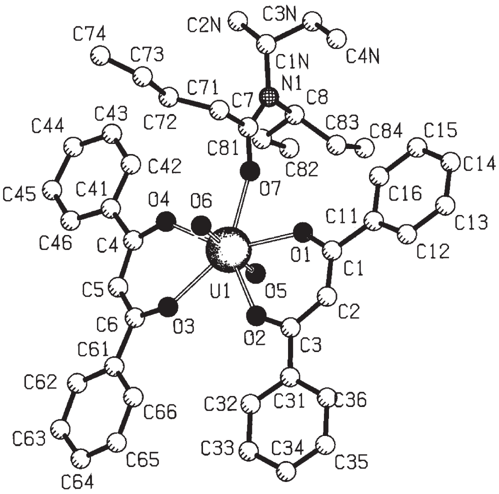

Fig. 1 The molecular structure of $[UO_2(DBM)_2$. C_4H_9CON ($\mathit{3}$-C_5H_{11}) (*sec*-C_4H_9)].

Experimental

Preparation of $[UO_2(DBM)_2.\ C_4H_9CON(3\text{-}C_5H_{11})\ (sec\text{-}C_4H_9)]$: Stoichiometric amounts of $[UO_2(DBM)_2.2H_2O$] and (N-*3*-pentyl, N-*sec*-butyl, pentanamide) were refluxed in chloroform (25 ml) for 15 min. The volume of solution was reduced to 5 ml, then layered with dodecane (2 ml). The solution on slow evaporation yielded the title compound. M.p. 175 °C. Anal. Calcd for $C_{44}H_{51}O_7NU$: C,56.0; H, 5.4; N, 1.5. Found: C, 55.9; H, 5.3; N, 1.4. IR (ν cm^{-1}, KBr): 1590 (CO, DBM); 1570 (CO, amide); 912 (O=U=O).

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

Table 1 Selected interatomic bond distances (Å) and angles (°) for the compound [$UO_2(DBM)_2$ $C_4H_9CON(3\text{-}C_5H_{11})$ (*sec*-C_4H_9)]

U1 – O1	2. 348(5)	U1 – O2	2.334(5)
U1 – O3	2.345(5)	U1 – O4	2.358(5)
U1 – O5	1.776(5)	U1 – O6	1.781(6)
U1 – O7	2.411(5)	C7 – O7	1.245(8)
C7 – N1	1.320(9)	N1 – C8	1. 467(10)
O5 – U1 – O6	179.5(3)	O3 – U1 – O4	70. 02(17)
O3 – U1 – O2	74.00(17)	O2 – U1 – O1	70.31 (18)
O1 – U1 – O7	73.49(18)	O4 – U1 – O7	72.30(17)
N1 – C7 – O7	120. 4 (7)	N1 – C7 – C71	121. 5 (7)
C71 – C7 – O7	118. 1 (7)	C8 – N1 – C1N	116. 0 (7)

Table 2 Crystal and structural refinement details for the compound [$UO_2(DBM)_2$ $C_4H_9CON(3\text{-}C_5H_{11})$ (*sec*-C_4H_9)]

Empirical formula	$C_{44}H_{51}O_7NU$
Formula weight	943.89
Crystal System	Monoclinic
Space Group	*P*21/*n*
a (Å)	13.353(3)
b (Å)	17.175(4)
c (Å)	17.779(4)
β (°)	97.47(2)
Volume (Å^3)	4042.6(16)
Z (formula unit)	4
F(000)	1880
Temperature (K)	293(2)
Calculated density (g/cm^3)	1.551
2θ Range for data collection (°)	2.04 to 24.98
Reflections collected/Unique	7414/7088(Rint =0.109)
Data/restraints/ parameters	7088/ 0 / 478
Goodness of fit on F^2	1.115
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0431$, w$R_2 = 0.0871$
R indices (all data)	$R_1 = 0.0847$, w$R_2 = 0.1096$

$W = 1/[\sigma^2(Fo^2) + (0.0483P)^2 + 7.0335P]$; $P = (Fo^2 + 2Fc^2)/3$

^{1}H NMR ($CDCl_3$, 300 MHz): 0.54(t, CH_3, amide); 0.81(t, CH_3, amide); 1.14 (t, CH_3, amide); 1.4 – 1.76 (m, CH_2, amide); 2.87 (br, CH_2CO, amide); 3.27 (br, CH, amide); 4.03 (br, CH, amide); 7.59 (br, C_6H_5 + CH, DBM); 8.45 (br, C_6H_5, DBM).

Preparation of [$UO_2(TTA)_2$. $C_4H_9CON(3\text{-}C_5H_{11})$ (sec-C_4H_9)]: This compound was prepared in a similar fashion as reported above. M.p. 160 °C . Anal. Calcd for $C_{30}H_{37}S_2F_6O_7NU$: C,38.3; H,3.9; N, 1.5. Found: C, 38.2; H, 3.8; N, 1.4. IR (ν cm^{-1}, KBr): 1610–1585 (br, CO, DBM); 1560 (CO, amide); 910 (O=U=O). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.65 (t, CH_3, amide); 0.89(t, CH_3, amide); 1.16 (t, CH_3, amide); 1.4–2.0 (m, CH_2, amide); 2.88 (br, CH_2CO, amide); 3.30 (br, CH, amide); 4.09 (br, CH, amide); 6. 78 (br, CH, TTA); 7.3–7.80 (m, C_4H_3S, TTA); 8.2 (br, CH, C_4H_3S, TTA).

X- ray crystallography: The X-ray diffraction data for the compound [$UO_2(DBM)_2$ $C_4H_9CON(3\text{-}C_5H_{11})$ (*sec*-C_4H_9)] was collected on an Enraf-Nonius CAD4 diffractometer fitted with graphite monochromated Mo–K_α radiation (λ = 0.71073 Å) at 293(2)°K. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-square procedures on F^2 using SHELXL-97.[5] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with geometrical constraints with the ideal bond lengths and angles were treated as riding atoms. The summary of crystallographic data, structural parameters and refinement details are given in Table 2.

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5 SHELXL-97, Automated Program for the structural refinements, Sheldrick (1997), University of Göttingen, Germany.