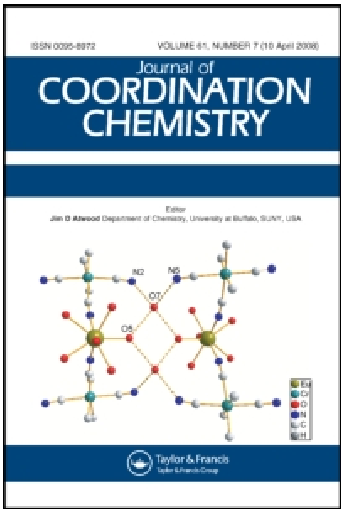

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Synthesis and structural studies of a bis(carbamoyl methyl) sulfoxide complex of uranyl nitrate

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Synthesis and structural studies of a bis(carbamoyl methyl) sulfoxide complex of uranyl nitrate

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A new tri-functional ligand $^{i}Bu_2NCOCH_2SOCH_2CON^{i}Bu_2$ was prepared and characterized. The coordination chemistry of this ligand with uranyl nitrate was studied with IR, ^{1}H NMR, electrospray mass–spectrometry, thermogravimetry, and elemental analysis. The structure of $[UO_2(NO_3)_2(^{i}Bu_2NCOCH_2SOCH_2CON^{i}Bu_2)]$ was determined by single-crystal X-ray diffraction. The uranium(VI) ion is surrounded by eight oxygens in a hexagonal bipyramidal geometry. Four oxygens from two nitrates and two oxygens from the ligand form a planar hexagon. The ligand is a bidentate chelate, bonding through sulfoxo and one of the carbamoyl groups to uranyl nitrate.

Keywords: Bis(carbamoyl methyl) sulfoxide; Coordination chemistry; Bidentate chelating mode; Uranium(VI); Crystal structure

1. Introduction

The coordination chemistry of lanthanides and actinides is very important for the development of new complexing ligands for the separation and purification of actinide ions from irradiated nuclear fuel, and also for the technology concerning the storage of highly radioactive waste materials [1–3]. Tri-functional ligands such as diglycolamide, 2,6-bis [bis(alkyl)phosphino)methyl] pyridine N,P,P′ trioxide [P(O)N(O)P(O)], 2,6-bis(N-alkyl acetamide) pyridine-N-oxide [C(O)N(O)C(O)], and bis(carbamoyl methyl) sulfoxide [BCMSO] (figure 1a–d) show excellent extraction properties for trivalent actinides when compared to tetra or hexavalent actinides; extensive solvent-extraction studies have been reported over the last 10 years [4–7]. The coordination chemistry of diglycolamide with lanthanide and actinide ions has been reported recently [8–10] showing that the ligand is tridentate chelating and bonds through both the carbamoyl

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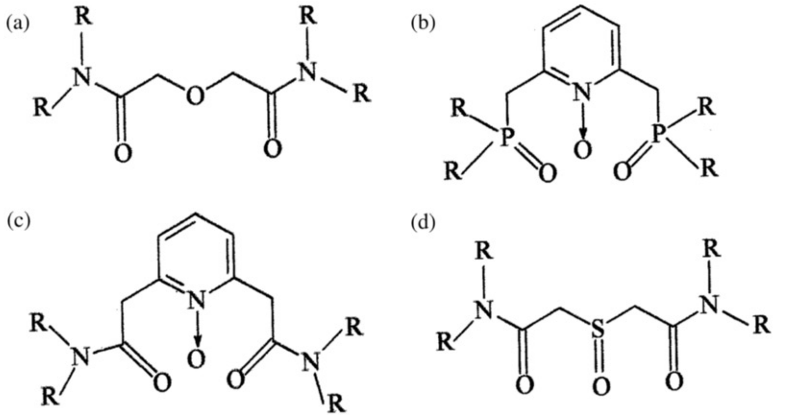

Figure 1. Ligands discussed herein. (a) diglycolamide, (b) P(O)N(O)P(O), (c) C(O)N(O)C(O) and (d) BCMSO.

and ethereal oxygens to the metal. The coordination chemistry of 2,6-bis[bis(alkyl) phosphino)methyl] pyridine N,P,P′ trioxide and 2,6-bis(N-alkyl acetamide) pyridine-N-oxide shows that they can be either tridentate chelating or bridging, chelating bidentate ligands [11, 12]. However, the coordination chemistry of bis(carbamoyl methyl) sulfoxide with any actinide or lanthanide has not been reported. As a continuation of our interest [13–17] in the coordination and separation chemistry of actinide ions, we report herein the synthesis and structure of bis(carbamoyl methyl) sulfoxide–uranyl nitrate.

2. Experimental

2.1. *Synthesis of [${}^iC_4H_9NCOCH_2SOCH_2CON^iC_4H_9$]*

To a solution of [$({}^iC_4H_9)_2NCOCH_2SCH_2CON({}^iC_4H_9)_2$] (15 g, 0.04 mol) in methanol (50 mL) a solution of 4.6 mL of 30% H_2O_2 (1.37 g, 0.04 mol) and SeO_2 (4.47 g, 0.04 mol) in methanol (50 mL) was added slowly with stirring. The solution was stirred for about 30 min and then 400 mL 10% NaCl solution was added. The viscous organic residue obtained was extracted with 100 mL of chloroform, dried over anhydrous sodium sulfate, and filtered. Removal of the solvent yielded a pasty solid which was re-dissolved in hot hexane and filtered. The solution on slow evaporation yielded a white solid, which was filtered and washed with cold hexane and dried. Yield: 9.5 g (61%). Elemental Anal. Calcd for [$({}^iC_4H_9)_2NCOCH_2SOCH_2CON({}^iC_4H_9)_2$]; $C_{20}H_{40}N_2O_3S$ (%): C, 61.9; H, 10.4; N, 7.2. Found (%): C, 61.2; H, 9.9; N, 6.9. IR (KBr, Nujol, $\nu\,\mathrm{cm}^{-1}$): 1654, 1625 (CO), 1049 (SO). ^{1}H NMR (25°C, $CDCl_3$, 500 MHz, δ in ppm): 0.90 (d, 6 Hz, 12H, CH_3), 0.93 (d, 6 Hz, 12H, CH_3), 1.93 (m, 6 Hz, 2H, CH), 2.04 (m, 6 Hz, 2H, CH), 3.00–3.23 (m, 8H, NCH_2), 3.8 (d, 2H, S(O)–CH_2–CO), 4.1 (d, 2H, S(O)–CH_2–CO).

Table 1. Important bond distances (Å) and angles (°) for **1**.

U(1)–O(11)	2.399(5)	U(1)–O(18)	2.397(6)
U(1)–O(71)	2.522(5)	U(1)–O(73)	2.539(5)
U(1)–O(81)	2.501(6)	U(1)–O(83)	2.517(6)
U(1)–O(1)	1.717(7)	U(1)–O(2)	1.716(7)
O(2)–U(1)–O(1)	179.3(2)	O(81)–U(1)–O(83)	50.9(2)
O(2)–U(1)–O(18)	87.5(2)	O(18)–U(1)–O(71)	64.7(2)
O(18)–U(1)–O(11)	69.7(2)	O(81)–U(1)–O(73)	60.6(2)
O(11)–U(1)–O(83)	64.1(2)	O(71)–U(1)–O(73)	50.3(2)

2.2. *Synthesis of [$UO_2(NO_3)_2(^iC_4H_9NCOCH_2SOCH_2CON\,^iC_4H_9)$]*

To a solution of $(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2$ (600 mg, 1.54 mmol) in chloroform, solid [$UO_2(NO_3)_2 \cdot 6H_2O$] (502 mg, 1 mmol) was added and stirred for a few minutes until all uranyl nitrate dissolved to give a clear solution. The solution was filtered and layered with iso-octane. The solution on slow evaporation deposited a pasty solid, which was washed in di-isopropyl ether to remove excess ligand and yield a fine yellow powder. The solution was filtered and the solid residue was washed in iso-propyl ether, hexane and dried. This crude product was crystallized from dichloromethane/iso-octane mixture as a yellow crystalline solid. Yield: 630 mg (81%). Elemental Anal. Calcd for [$UO_2(NO_3)_2(^iC_4H_9)_2NCOCH_2SOCH_2CON(^iC_4H_9)_2$]; $C_{20}H_{40}N_4O_{11}SU$ (%): C, 30.7; H, 5.1; N, 7.2. Found (%): C, 29.9; H, 4.8; N, 6.9. IR (KBr, Nujol, $\nu\,cm^{-1}$): 1656, 1591 (CO), 983 (SO), 943 (O=U=O). ^1H NMR (25°C, $CDCl_3$, 500 MHz, δ in ppm): 0.95–1.12 (m, 2H, CH_3), 1.87–2.18 (m, 4H, CH), 3.21–3.77 (m, 8H, NCH_2), 4.79 (q, 4H, S(O)–CH_2–CO).

2.3. *X-ray crystallography*

Data were measured at 150 K with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned at 50 mm from the CCD. Three-hundred and twenty-one frames were measured with a counting time of 10 s to give eight-thousand five-hundred and fifty-three independent reflections. Data analysis was carried out with the CrysAlis program [18]. The structure was solved using direct methods with the SHELXS97 program [19]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogens bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the carbon to which they are attached. An empirical absorption correction was carried out using the ABSPACK program [20]. The structure was refined to convergence on F^2 using SHELXXL97 [19]. Bond distances and angles are given in table 1 and crystal data and refinement parameters are given in table 2.

2.4. *Thermal analysis*

The simultaneous TG/DTA was recorded on Mettler TG/DTA instrument under a flow of air at 10°C min^{-1}.

Table 2. Crystal and structural refinement details for **1**.

Empirical formula	$C_{20}H_{40}N_4O_{11}SU$
Formula weight	782.65
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	8.8749(4)
b	25.8255(14)
c	13.1206(7)
β	99.961(5)
Volume (Å^3), Z	2961.9(3), 4
Calculated density ($g\,cm^{-3}$)	1.755
2θ Range for data collection (°)	2.70–30.0
Reflections collected/Unique	8553/5217
Data/restraints/parameters	8553/0/342
Goodness-of-fit on F^2	1.059
Final R indices $[I > 2\sigma(I)]$	0.0724
R indices (all data)	0.1268

2.5. *Electrospray mass spectrum*

ES–MS detection of positive ions was recorded in CH_2Cl_2 using a Micromass-Q-TOFMICRO instrument. The sample was introduced into the source with a syringe pump. Nitrogen was employed as both the drying and spraying gas with a source temperature of 90°C. The cone voltage was set to 30 V, the voltage applied on the capillary was 1162 kV and the sample solution flow rate was $5\,\mu L\,min^{-1}$. Spectrum was recorded from m/z of 100–1000.

3. Discussion

Reaction of bis(carbamoyl methyl) sulfide [$^iC_4H_9NCOCH_2SCH_2CON^iC_4H_9$] [17] with H_2O_2/SeO_2 in methanol yielded the corresponding bis(carbamoyl methyl) sulfoxide [$^iC_4H_9NCOCH_2SOCH_2CON^iC_4H_9$], quantitatively. The IR spectrum shows the presence of both the carbamoyl ($\nu_{CO} = 1654, 1625\,cm^{-1}$) and sulfoxo ($\nu_{SO} = 1049\,cm^{-1}$) groups in the synthesized ligand. The ^1H NMR spectrum shows the expected peak multiplicities and integration. The SO–CH_2–CO protons show two doublets due to their diastereotropic nature in agreement with the earlier reported results [7, 13]. C, H, and N analyses support the expected stoichiometry for the ligand.

Reaction of $[UO_2(NO_3)_2 \cdot 6H_2O]$ with the bis(carbamoyl methyl) sulfoxide in dichloromethane yielded $[UO_2(NO_3)_2(^iC_4H_9NCOCH_2SOCH_2CON^iC_4H_9)]$ (**1**). The IR spectrum of **1** shows that water from $[UO_2(NO_3)_2 \cdot 6H_2O]$ are completely replaced by the bis(carbamoyl methyl) sulfoxide ligand, bonded through sulfoxo and one carbamoyl group to the metal. The observed frequency differences for the sulfoxo ($\Delta\nu_{SO} = 66\,cm^{-1}$, where $\Delta\nu_{SO} = \nu_{SO(free\ ligand)} - \nu_{SO(complex)}$) and carbamoyl groups ($\Delta\nu_{CO} = 30–50\,cm^{-1}$, where $\Delta\nu_{CO} = \nu_{CO(free\ ligand)} - \nu_{CO(complex)}$) are consistent with direct bonding of sulfoxo and carbamoyl to uranyl. Similar differences are also observed in compounds of sulfoxides or amides with uranyl nitrate such as $[UO_2(NO_3)_2C_6H_5SOCH_2CON(C_4H_9)_4]$ [13], $[UO_2(NO_3)_2(^iPrO)_2POCH_2SO(p\text{-}MeC_6H_4)]$ [21] $[UO_2(NO_3)_2(^iC_3H_7CON\{^iC_4H_9\}_2)_2]$ [14], and $[UO_2(NO_3)_2(^iC_3H_7)_2\,NCOCH_2CON(^iC_3H_7)_2]$ [22]. ^1H NMR of

1 shows that the CH_2 protons are deshielded by *ca* 0.5–1.0 ppm with respect to the free ligand, indicating that the ligand is bonded to the metal center in solution also. C, H, and N analyses revealed that the metal to ligand ratio is 1 : 1. The structure of $[UO_2(NO_3)_2(^iBu_2NCOCH_2SOCH_2CON^iBu_2)]$ was determined using X-ray diffraction methods and confirms the spectral and analysis results.

The structure of **1** shows that bis(carbamoyl methyl) sulfoxide bonds to uranyl nitrate in a bidentate chelating fashion through the carbamoyl and sulfoxo oxygens. It shows further that one carbamoyl O(14) is uncoordinated. This structure is very similar to that reported for the uranyl nitrate–carbamoylmethyl sulfoxide compound $[UO_2(NO_3)_2(C_6H_5SOCH_2CON(C_4H_9)_2]$ [13], in which the carbamoylmethyl sulfoxide is bidentate chelating, bonding through both the carbomoyl and sulfoxo oxygens. The coordination number around uranium(VI) in **1** is eight in a hexagonal bipyramid. Four oxygens from two nitrates and two oxygens from bis(carbamoyl methyl) sulfoxide form the planar hexagon. The two uranyl oxygens occupy the axial positions. The r.m.s of the six fitted atoms is 0.0579 Å with the metal atom 0.023(3) Å from the plane. The observed bond distance of 2.399(5) Å between uranium and sulfoxo O(11) is slightly shorter than those reported in $[UO_2(NO_3)_2C_6H_5SOCH_2CON(C_4H_9)_2]$ [2.442(9) Å] [13] and $[UO_2(DBM)_2PhSOPh)]$ [2.427(4) Å] [23], but longer than those reported in $[UO_2(NO_3)_2(^iPrO)_2POCH_2SO(p\text{-}MeC_6H_4)]$ [2.36(2) Å] [21] and $[UO_2(DBM)_2PhCH_2SOCH_3)]$ [2.375(6) Å] [24]. The observed U–O(amide) bond distance U–O(18) of 2.397(6) Å is slightly shorter than the distances of 2.41(2) Å in $[UO_2(NO_3)_2(^iC_3H_7)_2NCOCH_2CON(^iC_3H_7)_2]$ [22], 2.426(8) Å in $[UO_2(NO_3)_2Ph\{EtO\}POCH_2CONEt_2]$, 2.404(5) Å in $[UO_2(NO_3)_2Ph_2POCH_2CONEt_2]$ [25], 2.442(9) Å in $[UO_2(NO_3)_2C_6H_5SOCH_2CON(C_4H_9)_2]$ [13] and comparable in magnitude with the values of 2.364(7)–2.377(9) Å observed in $[UO_2(NO_3)_2(C_5H_7N_2CH_2CO^iBu_2]$ [15]. The average U=O and U–O(NO_3) bond distances of 1.717(7) and 2.501(6)–2.539(5) Å, respectively, agree well with those found in previously reported uranyl nitrate compounds [13, 16, 17, 23–27]. As is apparent from figure 2, some isopropyl groups show high anisotropy, although no disorder model was found to be appropriate. There are no intermolecular distances less than the sum of van der Waal's radii.

3.1. *Thermal studies*

Thermogravimetric (TG) and differential thermal analyses (DTA) of **1** were carried out to find out the product of the decomposition reaction (Supplementary material). This compound decomposes in three steps to give U_3O_8 as the final product (identified from the powder X-ray diffraction pattern of the decomposition product) without any impurities. However, the decomposition product of phosphine oxide compounds of uranyl nitrate yielded the corresponding uranyl phosphate as a final product [28]. This observation clearly shows that the bis(carbamoyl methyl) sulfoxide ligands can be completely destroyed on incineration, as indeed can the amide ligands [15, 22].

3.2. *Electrospray–mass spectrometric study*

Electrospray–mass spectrum (ES–MS) of **1** was measured in methylene chloride (CH_2Cl_2) to establish the nature of compound formed in solution (Supplementary material). The spectrum shows many peaks and some of the peaks could be identified

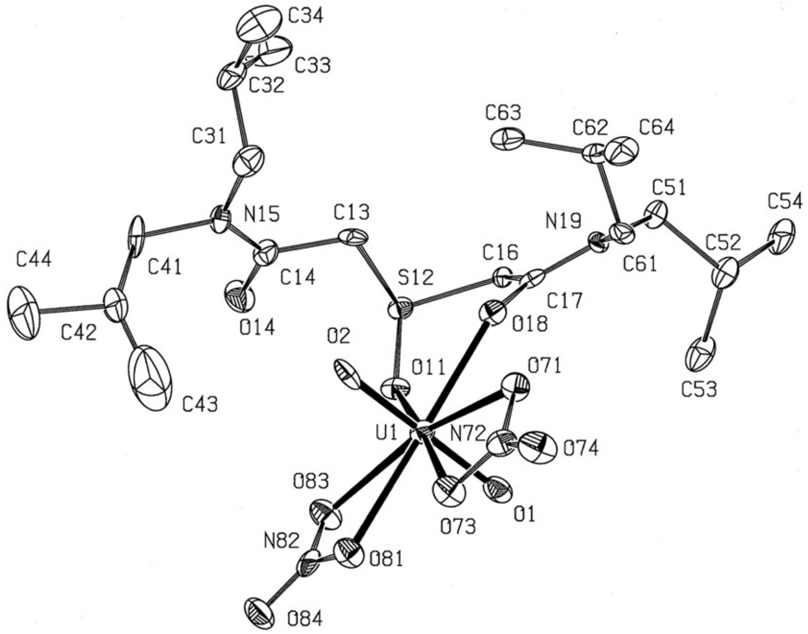

Figure 2. Molecular structure of **1** with ellipsoids at 50% probability.

without any doubt. The peaks at the *m*/*z* values of 726.12, 717.6 (100%), 523.42 and 389.3 are assigned to the species $[UO_2(NO_3)_2L - C_4H_9 + H]^+$, $[UO_2(NO_3)_2L - C_4H_9 - NO_3 + 3H_2O]^+$, $[UO_2L_2]^{2+}$, and $[LH]^+$ (where $L = {}^iC_4H_9NCOCH_2SOCH_2CON^iC_4H_9$), respectively. This study shows clearly that the ligand retains its bonding with the metal ion in solution [13].

4. Conclusions

The coordination chemistry of a new tri-functional ligand, bis(carbamoylmethyl) sulfoxide with uranyl nitrate shows that it is a bidentate chelating ligand, bonding through sulfoxo and one of carbamoyl oxygen. The ES–MS study in CH_2Cl_2 revealed that the ligand retains its bonding with uranyl ion in solution. The TG/DTA study shows that the ligand is completely incinerable on heating.

Supplementary materials

CCDC-762476 contains the supplementary crystallographic data for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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