Polyhedron 75 (2014) 81-87

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthetic, structural, extraction and theoretical studies of uranyl nitrate dithio-diglycolamide compounds



POLYHEDRON

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ARTICLE INFO

Article history: Received 27 January 2014 Accepted 6 March 2014 Available online 20 March 2014

Keywords: Dithioglycolamide Complex chemistry Uranyl nitrate Theoretical studies X-ray structure

ABSTRACT

Dithio-diglycolamide ligands of the types $[(CH_2SCH_2CONR_2)_2]$ (where $R = {}^iC_3H_7$, C_4H_9 , iC_4H_9 , C_8H_{17}) and $[C_7H_6(SCH_2CONR_2)_2]$ (where $R = {}^iC_4H_9$) were prepared and characterized. The complex chemistry of these ligands with uranyl nitrate was studied using IR, NMR and ESI-MS techniques and elemental analysis. The structures for two of the compounds, **2** and **4**, were determined by the X-ray diffraction method and revealed a bidentate chelating mode of bonding for the ligands in the solid state. The structures further show that the uranyl group is surrounded by six oxygen atoms in a hexagonal bi-pyramidal geometry. Theoretical studies were carried out to explain the relative stability of this chelating mode of ligand bonding. Extraction studies of U(VI), Pu(IV) and Am(III) ions from HNO₃ by one of the ligands, namely L⁴, in dodecane show appreciable extractions. The extracted metal ions could be back extracted quantitatively using 0.5 M HNO₃ or a mixture of 0.5 M HNO₃ and 0.5 M H₂C₂O₄.

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1. Introduction

A basic understanding of the coordination chemistry of the uranyl group is very important for the selective complexation and separation of this ion from acid media during reprocessing of irradiated advanced heavy water reactor (AHWR) nuclear fuel [1], seawater [2], nuclear plant effluents, biological and environmental samples [3,4]. The coordination chemistry of uranium has grown rapidly in recent years [5] due to the presence of new synthetic methods [6] and also due to the interesting properties, such as selective ion-exchange, mixed valency, ionic conductivity, enhanced fluorescence, magnetic ordering and non-linear optical properties, exhibited by its complexes [7]. Hydroxy pyridinone based ligands show selectivity for the uranyl ion from biological and environmental samples [4], whereas iso-butyramide based ligands show selectivity from nitric acid medium [8]. Many new extractants have been synthesized in recent years and their extraction and complex chemistry with the uranyl ion are well documented. The chemistry of the uranyl ion with bi-functional

ligands is of great interest, not only from the separation point of view, but also from the interesting properties exhibited in the solid state. It is reported that the nature of the spacer groups between the two functional groups play an important role in the solid state structure of the compounds formed. For example, in bi-functional amide (R₂NCO(CH₂)_nCONR₂) compounds of uranyl nitrate, the number of CH₂ groups bridging the amido groups decide the nature of the complex formed in the solid state [9]. When n = 1 or 2, the ligands always act as chelating, but with n = 3 or 4 they can act as either chelating or bridging, while with n = 5 or 6, they act exclusively as bridging ligands. Theoretical studies show that the modes of bonding for these ligands are energetically controlled. This is true in almost all reported bi-functional ligand uranyl nitrate compounds. For example, the solid state structures of compounds of carbamoyl methyl phosphonates [10a], carbamoyl methyl phosphine oxides [10b], malonamides [10c], carbamoyl methyl sulfoxide [10d], bi-phosphine oxides [10e], carbamoyl methyl pyrazole [10f] and carbamoyl pyrazole [10g] (where n = 1) with uranyl nitrate show that the ligands invariably act as chelating. The compounds of uranyl nitrate with thio-diglycolamide [11a], bis(carbamoyl methyl) sulfoxide [11b] and bis(carbamoyl methyl) sulfone [11c] (where n = 3) also show a bidentate chelating mode of bonding. However, the crystal structure of the uranyl nitrate, 1,2-phenylene bis(oxyacetamide) complex [12] shows a bidentate chelating mode of bonding, although the carbamoyl groups are separated by a six atom bridge



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(CH₂OC₆H₄OCH₂). This is very different from the bridging bidentate structure expected for a six atom CH₂ bridging ligand [9]. By replacing the CH₂ groups with oxygen atoms, the complexing properties of these bi-functional ligands in the solid state are significantly changed. The bi-functional dithio-glycolamide based ligands (Scheme 1) show selective extraction for the palladium ion [13a] from high level liquid waste and it has been proposed that they bond through both the thio-ether and amido groups to the metal centre [13b]. Since, these ligands have two amide groups, they are expected to show extraction for actinide(VI) and (IV) ions from nitric acid medium. However, as no systematic work on the extraction and complex chemistry of these ligands with actinide ions has so far been reported, we have studied and report herein the synthesis, structural and theoretical studies of dithio-glycolamide with uranyl nitrate and extraction studies with U(VI), Pu(IV) and Am(III) ions.

2. Experimental

2.1. General considerations

All reagents and solvents were of analytical grade and used as received. IR spectra were recorded as nujol mulls using a JASCO-610 FITR spectrometer. ¹H NMR spectra were recorded using a Bruker AMX-300 spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) are reported in hertz. Electrospray ionization mass spectrometric detection of positive ions in CH₂Cl₂ or CH₃COCH₃ was recorded using a MicrOTOF Q-II instrument. The samples were introduced into the source with the syringe pump. Nitrogen was employed as both the drying and spraying gas, with a source temperature of 180 °C. The cone voltage was set to 45 V, the voltage applied on the capillary was 1162 kV and the sample solution flow rate was 5 µL min⁻¹. Spectra were recorded from *m*/*z* of 100 to 1000.

2.2. Synthesis of L^1

To a methanolic solution (10 mL) of ethylene-1,2-dithiol (5.5 g, 0.059 mol), a methanolic solution (20 mL) of NaOH (4.7 g, 0.118 mol) was added slowly with stirring. The whole solution was stirred for 30 min. To this solution a solution of *N*,*N*-di-isopropyl carbamoyl methyl chloride (21 g, 0.118 mmol) in methanol (20 mL) was added slowly. The whole solution was stirred for 3 hours and then treated with 200 mL of 5% HCl solution. The organic layer formed was extracted with CHCl₃, dried over Na₂SO₄ and filtered. The solution on evaporation yielded a colorless crystalline solid in 75% yield. ¹H NMR (25 °C, CDCl₃) δ : 1.203 (d, 12H, CH₃, ⁱPr), 1.371 (d, 12H, CH₃, ⁱPr), 2.897 (s, 4H, -CH₂S-), 3.335 (s, 4H,



$$[L = L^1 (1); L = L^2 (2); L = L^3 (3); L = L^5 (4)]$$

Scheme 1. Synthesis of the ligands and their uranyl complexes.

2.3. Synthesis of L^2

This was prepared similarly to **L**¹ by taking ethylene-1,2-dithiol (5.5 g, 0.059 mol) and *N*,*N*-di-n-butyl carbamoyl methyl chloride (24.2 g, 0.118 mol), giving **L**² in 82% yield. ¹H NMR (25 °C, CDCl₃) δ : 0.916 (m, 12H, CH₃, Bu), 1.312 (m, 8H, NCCCH₂, Bu), 1.527 (m, 8H, NCCH₂, Bu), 2.921 (s, 4H, -CH₂S-), 3.271 (m, 8H, NCH₂, Bu) 3.324 (s, 4H, -SCH₂CO-). IR (cm⁻¹) *v*: 1637 (C=O). *Anal.* Calc. for C₂₂H₄₄N₂S₂O₂: C, 61.1; H, 10.2; N, 6.5. Found: C, 60.6; H, 9.8; N, 6.2%.

2.4. Synthesis of L^3

This was prepared similarly to **L**¹ by taking ethylene-1,2-dithiol (5.5 g, 0.059 mol) and *N*,*N*-di-isobutyl carbamoyl methyl chloride (24.2 g, 0.118 mol), giving **L**³ in 80% yield. ¹H NMR (25 °C, CDCl₃) δ : 0.834 (d, 12H, CH₃, ⁱBu), 0.874 (d, 12H, CH₃, ⁱBu), 1.875 (m, 2H, CH, ⁱBu), 1.976 (m, 2H, CH, ⁱBu), 2.884 (s, 4H, -CH₂S-), 3.078 (d, 4H, NCH₂, ⁱBu), 3.133 (d, 4H, NCH₂, ⁱBu), 3.317 (s, 4H, -SCH₂CO-). IR (cm⁻¹) *v*: 1632 (C=O). *Anal.* Calc. for C₂₂H₄₄N₂S₂O₂: C, 61.1; H, 10.2; N, 6.5. Found: C, 60.8; H, 9.7; N, 6.3%.

2.5. Synthesis of L⁴

This was prepared similarly to **L**¹ by taking ethylene-1,2-dithiol (3.4 g, 0.036 mol) and *N*,*N*-di-*n*-octyl carbamoyl methyl chloride (23 g, 0.72 mol), giving **L**⁴ in 85% yield. ¹H NMR (25 °C, CDCl₃) δ : 0.864 (br, 12H,CH₃, C₈H₁₇), 1.257 (br, 40H, CH₂, C₈H₁₇), 1.523 (m, 8H, NC-CH₂, C₈H₁₇), 2.910 (s, 4H, -CH₂S-), 3.233 (m, 8H, NCH₂, C₈H₁₇), 3.296 (s, 4H, -SCH₂CO-). IR (cm⁻¹) v: 1633 (C=O).

2.6. Synthesis of L⁵

This was prepared similarly to **L**¹ by taking tolyl-3,4-dithiol (3.04 g, 0.0195 mol) and *N*,*N*-diisobutyl carbamoyl methyl chloride (8 g, 0.39 mol), giving **L**⁵ in 81% yield. ¹H NMR (25 °C, CDCl₃) δ : 0.854 (m, 24H, CH₃, ⁱBu), 1.924 (m, 4H, CH, ⁱBu), 2.271 (s, 3H, – CH₃, tolyl), 3.130 (m, 8H, NCH₂, ⁱBu), 3.732 (s, 2H, –SCH₂CO–), 3.764 (s, 2H, –SCH₂CO–), 6.965 (dd, 1H, tolyl), 7.266 (d, 1H, tolyl), 7.389 (d, 1H, tolyl). IR (cm⁻¹) *v*: 1652 (C=O). *Anal.* Calc. for C₂₇H_{46-N₂S₂O₂: C, 65.6; H, 9.3; N, 5.7. Found: C, 65.3; H, 9.1; N, 5.7%.}

2.7. Synthesis of 1

To a solution of **L**¹ (250 mg, 0.67 mmol) in CH₂Cl₂ (20 mL), solid [UO₂(NO₃)₂·6H₂O] (335 mg, 0.66 mmol) was added and stirred for few minutes until all the [UO₂(NO₃)₂·6H₂O] dissolved to give a clear solution. This solution was filtered and layered with iso-octane. The solution on slow evaporation yielded a yellow crystalline solid, which was filtered, washed with hexane and dried. Yield: 84%. ¹H NMR (25 °C, CD₃COCD₃) δ : 1.551 (d, 12H,CH₃, ⁱPr), 1.663 (d, 12H, CH₃, ⁱPr), 2.955 (s, 4H, -CH₂S–), 3.824 (s, 4H, -SCH₂CO–), 4.034 (m,2H, NCH, ⁱPr), 4.509 (m, 2H, NCH, ⁱPr). IR (cm⁻¹) *v*: 1578 (C=O), 923 (O=U=O). *Anal.* Calc. for C₁₈H₃₆N₄S₂O₁₀U: C, 28.1; H, 4.7; N, 7.3. Found: C, 27.9; H, 4.4; N, 7.0%.

2.8. Synthesis of 2

This was prepared similarly to **1** by taking L^2 (259 mg, 0.60 mmol) and $[UO_2(NO_3)_2 \cdot 6H_2O]$ (300 mg, 0.59 mmol), giving **2** in 85% yield. ¹H NMR (25 °C, CDCl₃) δ : 0.803 (t, 6H, CH₃, Bu), 1.072 (t, 6H, CH₃, Bu), 1.272 (m, 4H, CH₂, Bu), 1.547 (m, 4H, CH₂,

Bu), 1.805 (m, 4H, CH₂, Bu), 1.924 (m, 4H, CH₂, Bu), 2.974 (s, 4H, – CH₂S–), 3.592 (s, 4H, –SCH₂CO–), 3.602 (t, 4H, NCH₂, Bu), 3.754 (t, 4H, NCH₂, Bu). IR (cm⁻¹) v: 1600 (C=O), 932 (O=U=O). *Anal.* Calc. for $C_{22}H_{44}N_4S_2O_{10}U$: C, 32.0; H,5.3; N, 6.8. Found: C, 31.6; H, 5.4; N, 6.7%.

2.9. Synthesis of 3

This was prepared similarly to **1** by taking **L**³ (258 mg, 0.60 mmol) and $[UO_2(NO_3)_2 \cdot 6H_2O]$ (300 mg, 0.59 mmol), giving **3** in 82% yield. ¹H NMR (25 °C, CDCl₃) δ : 0.928 (d, 12H, CH₃, ⁱBu), 1.210 (d, 12H, CH₃, ⁱBu), 2.279 (m, 2H, CH, ⁱBu), 2.459 (m, 2H, CH, ⁱBu), 3.434 (s, 4H, -CH₂S-), 3.440 (d, 4H, NCH₂, ⁱBu), 3.596 (8H, NCH₂ + -SCH₂CO-). IR (cm⁻¹) ν : 1570 (C=O), 930 (O=U=O). *Anal.* Calc. for C₂₂H₄₄N₄S₂O₁₀U: C, 32.0; H,5.3; N, 6.8. Found: C, 31.9; H, 5.2; N, 6.6%.

2.10. Synthesis of 4

This was prepared similarly to **1** by taking L^5 (250 mg, 0.50 mmol) and $[UO_2(NO_3)_2 \cdot 6H_2O]$ (251 mg, 0.50 mmol), giving **4** in 83% yield. ¹H NMR (25 °C, CD₃COCD₃) δ : 0.752 (m, 12H, CH₃, ⁱBu), 1.213 (m, 12H, CH₃, ⁱBu), 2.000 (br, 4H, CH, ⁱBu), 2.284 (s, 3H, CH₃, tolyl), 3.604 (br, 4H, NCH₂, ⁱBu), 3.958 (br, 4H, NCH₂, ⁱBu), 4.478 (br, 4H, -SCH₂CO-), 7.068 (br, 1H, tolyl), 7.443 (d, 1H, tolyl), 7.455 (d, 1H, tolyl). IR (cm⁻¹) ν : 1570 (C=O), 935 (O=U=O). *Anal.* Calc. for C₂₇H₄₆N₄S₂O₁₀U: C, 36.5; H,5.2; N, 6.3. Found: C, 36.1; H, 5.0; N, 6.1%.

2.11. Theoretical methods

Full geometry optimization for all the ligands and complexes has been carried out applying a popular non-local correlated hybrid density functional, namely, B3LYP. The crystal structures were taken as the initial geometry for optimization of the complexes for locating the minimum energy structure. Gaussian type atomic basis functions. 6-31 + G(d), were adopted for H. C. N. O and S atoms while for the U atom. SARC-ZORA [14a] basis sets were used for all the calculations. SARC-ZORA basis sets are segmented all-electron scalar relativistic basis sets in which the coefficients of contracted GTOs have been optimized for use with the ZORA scalar relativistic Hamiltonian. This particular basis set for U was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Pacific Northwest National Laboratory [14b]. Geometry optimization to locate the minimum energy structure was carried out applying a quasi-Newton-Raphson based algorithm. The energy of the systems was further improved by performing single point calculations at the MP2 level, adopting the same set of basis functions. These calculations have been performed applying the GAMESS suit of *ab initio* programs on a LINUX cluster platform [14c].

2.12. Solvent extraction studies

Distribution studies were performed using a solution of L^4 in dodecane with the required aqueous phase spiked with ²³³U, ²³⁹Pu or ²⁴¹Am tracers in a thermostated water bath for 1 h at 25 ± 0.1 °C. Assays of organic and aqueous phases were done in duplicate by alpha counting using a dioxane based liquid scintillator for ²³³U and ²³⁹Pu and direct γ counting for ²⁴¹Am. The distribution ratio (*D*) is defined as the ratio of the concentration of the metal ion in the organic phase to that in the aqueous phase.

2.13. Crystal structure determinations

Crystal data for 2 and 4 were measured on an Oxford Diffraction X-Calibur CCD System at 150(2) K with Mo K α radiation

($\lambda = 0.71073$ Å). The crystals were positioned 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the CRYSALIS program [15a]. The structures were solved using direct methods with the SHELXS97 program [15b]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in the geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they are attached. Empirical absorption corrections were refined to convergence on F^2 using SHELX197 [15b]. Selected crystallographic data for **2** and **4** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis of the dithio glycolamide ligands

The ligands L^1-L^5 were prepared in a manner similar to that reported [13] in the literature by reacting 1,2-ethane dithiol or 5-methyl-1,2-di-thiophenol with *N*,*N*'-dialkyl carbamoyl chloride (Scheme 1). The IR spectra of all the ligands show the presence of carbamoyl groups in the synthesized ligands. The ¹H NMR spectra of all the ligands show the expected peaks and integrations. The CHN analyses support the expected stoichiometries for the newly prepared ligands.

3.2. Synthesis of the 1,2-ethelene bis(thioglycolamide) uranyl nitrate complexes

The reaction of $[UO_2(NO_3)_2 \cdot 6H_2O]$ with the ligands L^1-L^3 yielded compounds 1-3 (Scheme 1). C, H and N analyses revealed that the ratio of uranyl nitrate to ligand is 1:1 in all the compounds. The IR spectra of 1-3 show that the water molecules from the starting compound $[UO_2(NO_3)_2 \cdot 6H_2O]$ are completely replaced by the ligand, which is bonded through the carbamoyl oxygen atom to the uranyl group. The observed frequency difference for the carbamoyl group ($\Delta v_{CO} = 37-62 \text{ cm}^{-1}$, where $\Delta v_{CO} = v_{CO}$ (free ligand) – $v_{CO(coordinated)}$) shows that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those observed for $[UO_2(NO_3)_2(N-cyclohexyl,2-pyrrolidone)_2]$ [16a], $[UO_2(NO_3)_2(1,3-dimethyl,2-imidazolidone)_2]$ [16b], $[UO_2(NO_3)_2(^iC_3H_7CON(^iC_4H_9)_2)_2]$ [8a], $[UO_2(NO_3)_2(^iC_3H_7)_2N$ COCH₂CON ($^iC_3H_7)_2$] [10c] and $[UO_2(NO_3)_2(C_{15}H_27N_3O)]$ [10f].

Table 1Crystal data for compounds 2 and 4.

Compound	2	4
Empirical formula	C ₂₂ H ₄₄ N ₄ O ₁₀ S ₂ U	$C_{27}H_{46}N_4O_{10}S_2U$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	ΡĪ
a (Å)	17.0993(9)	10.8372(9)
b (Å)	10.1195(4)	17.3889(12)
c (Å)	19.1525(11)	19.3630(14)
α (°)	90	78.941(6)
β (°)	108.337(8)	89.383(6)
γ (°)	90	82.011(6)
V (cm ³)	3145.8(3)	3545.9(5)
Ζ	4	4
$ ho_{ m calc} (m gcm^{-3})$	1.746	1.665
μ (mm ⁻¹)	5.347	4.750
Reflections collected/unique	9116/7336	19262/10579
Data/restrains/parameters	7336/0/356	10579/65/793
Goodness of fit (GOF) on F^2	1.116	0.962
Final R_1 indices $[I > 2\sigma(I)]$	0.0648	0.1085
wR ₂ indices (all data)	0.0877	0.1675

 $w=1/[\sigma^2(F_o^2)+(0.0352P)^2+17.6598P]$ for **2**, $w=1/[\sigma^2(F_o^2)+(0.1632P)^2+43.9344P]$ for **4**, where $P=(F_o^2+2F_o^2)/3.$

The ¹H NMR spectra of **1–3** show the expected peaks and integrations. All protons are deshielded with respect to the free ligand, indicating that the bonding between the ligand and the uranyl group persists in solution. The CH₂ group adjacent to the carbamoyl is more deshielded (ca. 0.4 ppm) compared to that of the CH₂ group attached to the S atom. The ESI-MS spectrum of **2** in acetone shows the presence of a peak at m/z of 764.2 [$UO_2(NO_3)L$]⁺], indicating that the metal ligand bond is retained in solution. It is apparent from the IR and NMR spectra that the ligand acts as a bidentate chelate and bonds through the carbamoyl groups to the uranyl group. The structure of **2** has been determined by the single crystal X-ray diffraction method, which confirms these spectral results.

3.3. Synthesis of 5-methyl-1,2-phenylene bis(thioglycolamide) uranyl nitrate complexes

The reaction of $[UO_2(NO_3)_2 \cdot 6H_2O]$ with the ligand L^5 yielded compound **4** (Scheme 1). C, H and N analyses revealed that the ratio of uranyl nitrate to ligand is 1:1. The IR spectrum of **4** shows that the water molecules from the starting compound $[UO_2(NO_3)_2 \cdot 6H_2O]$ are completely replaced by the ligand, which is bonded through the carbamoyl oxygen atom to the uranyl group. The observed frequency difference for the carbamoyl group ($\Delta v_{CO} = 63$ cm⁻¹, where $\Delta v_{CO} = v_{CO}$ (free ligand) – $v_{CO(coordinated)}$) shows that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those reported in the literature [10–12].

The ¹H NMR spectrum of **4** show the expected peaks and integrations and is broad due to a ligand exchange/disproportination reaction in solution [9]. The CH₂ group adjacent to the carbamoyl is deshielded compared to that observed in the free ligand. The ESI-MS spectrum of the compound in acetone shows a molecular ion peak at a m/z value of 826.33 [(UO₂L(NO₃)⁺], indicating that the ligand remains bonded to uranyl nitrate in solution. The spectrum further shows that the compound undergoes ligand exchange/disproportination in solution to give a mixture of $[UO_2L_2]$ $(m/z = 629.3, (UO_2L_2)^{2+})$ and $[UO_2L_3] (m/z = 876.4, (UO_2L_3)^{2+})$ ²⁺) species. It is apparent from the IR and NMR spectral results that the ligand acts as a bidentate chelating ligand and bonds through the carbamoyl groups to the uranyl group. The structure of **4** has been determined by the single crystal X-ray diffraction method, which confirms the spectral and analysis results.

3.4. Structures of $[UO_2(NO_3)_2(CH_2SCH_2CON\{C_4H_9\}_2)_2]$ (**2**) and $[UO_2(NO_3)_2C_7H_6(SCH_2CON \{C_4H_9\}_2)_2]$ (**4**)

The structure of **2** is shown in Fig. 1 and selected bond distances and angles are given in Table 2. The crystal structure of **4** consists of two crystallographically independent molecules and the



Fig. 1. The structure of $[UO_2(NO_3)_2(CH_2SCH_2CON\{C_4H_9\}_2)_2]$ (2).

Table 2

Important bond	lengths (Å)	and angles	(°) for 2 and 4.
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	2	4A	4B
U-01	1.746(5)	1.783(12)	1.774(11)
U-02	1.748(5)	1.773(12)	1.751(11)
U-071	2.507(5)	2.573(12)	2.561(14)
U-072	2.489(5)	2.544(11)	2.528(12)
U-081	2.518(5)	2.506(12)	2.499(14)
U-0 82	2.534(5)	2.497(11)	2.543(12)
U-020	2.382(5)	2.342(10)	2.342(10)
U-011	2.341(4)	2.370(11)	2.336(11)
01-U-02	177.7(2)	177.5(5)	176.8(5)
020-U-011	69.75(16)	71.1(3)	70.7(4)
081-U-082	49.93(16)	50.3(4)	49.7(4)
071-U-0 72	50.72(15)	50.0(4)	50.4(4)
072-U-081	60.46(16)	58.9(4)	59.4(4)
C19-O20-U	136.0(4)	149.3(11)	145.0(10)
C12-011-U	142.5(4)	138.0(10)	144.0(10)

structure of one of the molecules is shown in Fig. 2; selected bond distances and angles are given in Table 2. Although the observed R factors for **4** are relatively high compared to those obtained for **2**, the structure of **4** is sufficient to show the connectivity between the ligand and the metal ion in the solid state.

The structures of both **2** and **4** show that each uranium atom is surrounded by eight oxygen atoms in a hexagonal bi-pyramidal geometry. The two uranyl oxygen atoms occupy the axial positions. Four oxygen atoms of the two bidentate nitrate groups, together with two oxygen atoms of the bidentate dithio glycolamide ligand form the equatorial hexagonal plane. The UO₆ atoms in the equatorial plane show an r.m.s deviation of 0.029 Å for **2** and 0.047 and 0.069 Å for **4** in the two independent molecules.

This type of coordination is similar to that observed in the compounds of the bi-functional ligands malonamide, carbamoyl methyl phosphonate, carbamoyl methyl phosphine oxide, carbamoyl methyl sulfoxide and carbamoyl methyl pyrazole with uranyl nitrate, such as $UO_2(NO_3)_2(^iC_3H_7O)_2POCH_2CONEt_2$ [10a], [UO₂ $(NO_3)_2(C_6H_5)_2POCH_2CONEt_2$] [10b], [UO₂ $(NO_3)_2(C_6H_5)_2POCH_2CONEt_2$] [10b], [UO₂ $(NO_3)_2(C_1H_2rN_3-O)$] [10f] and [UO₂ $(NO_3)_2(C_3H_3N_2CON\{C_2H_5\}_2)$] [10g]. The average U–O(amide) distances 2.361(4) Å in **2** and 2.339(11) Å in **4** are comparable in magnitude with those of earlier reported uranyl nitrate–amide compounds, such as [UO₂ $(NO_3)(DMF)_2$] (2.397(6) Å) [17a], [UO₂ $(NO_3)_2$ (tetrabutylglutaramide)₂] (2.378(6) Å) [12], [UO₂ $(NO_3)_2$ (dibutyldecanamide)₂] (2.37(2) Å) [17b] and [UO₂ $(NO_3)_2(C_{15}H_2rN_3O)$] (2.364(7) Å) [10f]. The observed average U–O(NO₃) bond distances of 2.512(5) Å in **2** and 2.533(13) Å in **4**



Fig. 2. The structure of one of the two independent molecules in the asymmetric unit of 4.

are normal [10–12,16–18]. The angles subtended at the metal atom show that the uranium atom has a slightly distorted hexagonal bipyramidal geometry.

It is interesting to note from these structures that both these ligands act as bidentate chelating, though both the carbamoyl groups are separated by a six atoms bridge. It is reported that when carbamoyl groups are separated by more than five atoms, the ligands adopt the energetically more favored bridging bidentate mode of bonding rather than the less favored bidentate chelating mode of bonding [9]. The observed structures clearly reflect that the replacement of two of the CH_2 groups by sulfur atoms in **2** and **4** and two oxygen atoms in 1,2-phenylene bis(oxyacetamide) [12] changes the mode of bonding and hence the solid state structure. Theoretical studies were carried out to explain the stability of the mode of bonding for these ligands, compared with that of the analogous CH_2 bridged compounds.

3.5. Theoretical studies on dithio-diglycolamide uranyl nitrate compounds

Full geometry optimization of four ligands (Fig. 3 (a-d)) and their corresponding complexes (Fig. 4 (1-4)) has been carried out applying the B3LYP correlated non-local hybrid density functional. SARC-ZORA basis sets for U and Gaussian type atomic basis functions, 6-31 + G(d) for the H, C, N, O and S atoms were applied in all the calculations. Both all-cis and all-trans conformers of ligand **a** (all CH₂ group bridging), **b** (two of the CH₂ groups replaced with sulfur atoms), **c** (tolyl analogue of **a**) and **d** (tolyl analogue of **b**) were optimized to find the relative stability of the conformers. Note that even though the initial structures of the ligands considered were all cis or all trans conformers, after full optimization the structures turned out as shown in Fig. 3. It is predicted that in the case of ligand **a**, the all-trans conformer is more stable than the all-cis conformer by 5.5 kcal/mol, while for ligand **b**, the all-trans conformer is less stable by 7.5 kcal/mol. Note that for c and d invariably the cis conformers are the most stable structures. Based on the energies of the uranyl nitrate complexes with these four

ligands (all-*cis* conformer of ligands **a**–**b** and ligands **c**–**d**) and the energy of these complexes at the dissociation limit, the binding energies of the complexes were calculated and these are listed in Table 3 together with selected geometrical parameters. It is observed that the binding energies of these complexes should be similar and that the complex with ligand **a** should be the least stable. However, it is to be noted that the all-*cis* conformer of ligand **a** is less stable than its all-trans conformer, making it difficult to form a complex with uranyl nitrate as for ligand **a** the formation of bidentated complexes is only possible if the ligand is in its all-cis conformation. It is possible that the ligand in its all-trans conformation forms a complex with uranyl nitrate as a monodentate ligand. Formation of such complexes has been explored and the optimized structure of such complexes with ligands **a** and **b** are displayed in Fig. 5 (5–6). To satisfy the coordination of uranyl nitrate and these monodentated ligands, a solvent H₂O molecule is added to complete the equatorial coordination sphere. It is calculated that the monodentate ligand **a** forms a more stable complex than ligand **b** by 5.0 kcal/mol. This study clearly shows that the chelating mode of bonding for dithio based ligands is more stable energetically than the corresponding all CH₂ bridged ligand with uranyl nitrate. However, this result is reversed when bridging or monodentate modes of bonding are considered.

3.6. Extraction studies of U(VI), Pu(IV) and Am(III) with $\boldsymbol{L^4}$ from nitric acid medium

The extraction studies were carried out using the ligand L^4 in dodecane with U(VI), Pu(IV) and Am(III) ions in the tracer level (using ²³³U, ²³⁹Pu and ²⁴¹Am tracers) from nitric acid medium to assess the feasibility of using this ligand (0.2 M) for extraction purposes. Distribution ratios (D) for U(VI), Pu(IV) and Am(III) as a function of nitric acid concentration (Fig. 6) show clearly that U(VI) and Pu(IV) are extracted significantly from nitric acid at concentrations of 1–7 M. However, Am(III) did not show any appreciable extraction under the conditions studied. The observed distribution ratios follow the order: $D_{Pu(IV)} \gg D_{U(IV)} \gg D_{Am(III)}$ and are similar to those



Fig. 3. Optimized structure of the four ligands with selected distances in Å. Color code: red for O, deep blue for N, yellow for S and light blue for H atoms. (Color online.)



Fig. 4. DFT optimized structures of four complexes of uranyl nitrate and bi-dentate ligands with selected bond distances in Å and bond angles in degrees. Color code: red for O, deep blue for N, yellow for S and white for H atoms. (Color online.)

Table 3		
Relative stability of the ligands and	binding energies of	the complexes in kcal/mol.

System	Relative stability $(E_{all trans} - E_{all cis})$ in kcal/mol	Binding energy $(E_{\text{complex at eqm}} - E_{\text{complex at diss limit}})$ in kcal/mol
Ligand a	5.5	-
Ligand b	-7.5	-
Complex 1	-	57.25
Complex 2	-	61.05
Complex 3	-	59.7
Complex 4	-	61.9
Complex 5	-	42.8
Complex 6	-	37.8

observed for the monoamides, CMP, CMPO, CMSO or malonamide ligands with these metal ions [19,10d]. In order to establish the nature of the species extracted during the solvent extraction process, the distribution ratios for U(VI) were measured as a function of L^4 concentration. The plot of log D_U Vs log[HNO₃] (Fig. 7, Supporting information) shows a straight line with a slope close to two, indicating that two nitrates ions are involved in the extraction process. The plot of log D Vs log[L^4] for U(VI) shows (Fig. 8, Supporting information) a straight line with a slope equal to 1.35, indicating that the species extracted under the solvent extraction conditions are a mixture of [UO₂(NO₃)₂·L] and [UO₂(NO₃)₂·2L] [20,10d].



Fig. 5. DFT optimized structures of two complexes of uranyl nitrate and the monodentate ligands **a** and **b** with selected bond distances in Å. Color code: red for O, deep blue for N, yellow for S, sky blue for U and light blue for H atoms. (Color online.)



Fig. 6. Distribution ratio vs. [HNO₃] for U(VI), Pu(IV) and Am(III) ions with 0.2 M L⁴ in dodecane.

4. Conclusions

The complex chemistry of dithio-diglycolamide ligands with uranyl nitrate shows a chelating mode of bonding for these ligands. The dioctyl based ligand shows an appreciable extraction for uranyl and plutonium(IV) ions from the nitric acid medium. The extracted ions could be stripped back quantitatively using 0.5 M HNO₃ or a mixture of 0.5 M HNO₃ + 0.5 M $H_2C_2O_4$, respectively. Theoretical studies clearly revealed that the chelating mode of bonding for these ligands is more energetically favorable than monodentate or bridging bidentate modes of bonding.

Acknowledgements

We wish to thank Dr. S.K. Aggarwal, Associate Director, Radiochemistry and Isotope Group and Head, Fuel Chemistry Division for his support. We also wish to thank IIT, Bombay for ESI-MS spectra, the National NMR facility TIFR, Mumbai for NMR spectra, Dr. V.K. Jain, Head, Chemistry Division, BARC for NMR spectra and C, H, N analysis, EPSRC, United Kingdom and the University of Reading, United Kingtom for funds for the diffractometer.

Appendix A. Supplementary data

CCDC 980352 and 980353 contain the supplementary crystallographic data for compounds 2 and 4, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.03.015.

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