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

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ABSTRACT

Dithio-diglycolamide ligands of the types [\(\text{CH}_2\text{SCH}_2\text{CONR}_2\)] \(_2\) (where \(R = \text{C}_7\text{H}_5\), \(\text{C}_6\text{H}_5\), \(\text{C}_6\text{H}_5\) \(\text{C}_6\text{H}_5\)) and [\(\text{C}_6\text{H}_4\text{SCH}_2\text{CONR}_2\)] \(_2\) (where \(R = \text{C}_6\text{H}_5\)) 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 HNO\(_3\) by one of the ligands, namely L\(_1\), in dodecane show appreciable extractions. The extracted metal ions could be back extracted quantitatively using 0.5 M HNO\(_3\) or a mixture of 0.5 M HNO\(_3\) and 0.5 M H\(_2\)C\(_2\)O\(_4\).

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 pyridine 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 (\(R_2\text{NCO(CHO)}_2\)) \(_2\) compounds of uranyl nitrate, the number of CH\(_2\) 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 phosphate oxides [10b], malonamides [10c], carbamoyl methyl sulfoxide [10d], bi-phosphate 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 tri-oxyacetalimide [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.
(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 FTIR 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 CH₂COCH₃ 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 L¹

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 Na₂S₂O₇ 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

Scheme 1. Synthesis of the ligands and their uranyl complexes.
Bu), 1.805 (m, 4H, CH₂, Bu), 1.924 (m, 4H, CH₂, Bu), 2.974 (s, 4H, –CH₂S–), 3.592 (s, 4H, –SO₂CH₂CO–), 3.602 (t, 4H, NCH₂, Bu), 2.754 (t, 4H, NCH₂, Bu), IR (cm⁻¹): 1600 (C=O), 932 (O=U=O). Anal. Calc. for C₂₂H₄₆N₄O₁₀S₂: 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 L¹ (258 mg, 0.50 mmol) and [UO₂(NO₃)₂·6H₂O] (300 mg, 0.59 mmol), giving 3 in 82% yield. ¹H NMR (25 °C, CDCl₃) δ: 0.928 (d, 12H, CH₃, Bu), 1.210 (d, 12H, CH₃, Bu), 2.279 (m, 2H, CH, Bu), 2.459 (m, 2H, CH, Bu), 3.434 (s, 4H, –CH₂S–), 7.455 (d, 1H, tolyl). IR (cm⁻¹): 36.1; H, 5.0; N, 6.1%. Calc. for C₂₂H₄₄N₄O₁₀S₂: C, 32.0; H, 5.0; N, 6.1%. Anal. Calc. for C₂₂H₄₄N₄O₁₀S₂: C, 32.0; H, 5.3; N, 6.8. Found: C, 31.6; H, 5.4; N, 6.7%.

2.10. Synthesis of 4

This was prepared similarly to 1 by taking L² (250 mg, 0.50 mmol) and [UO₂(NO₃)₂·6H₂O] (251 mg, 0.50 mmol), giving 4 in 83% yield. ¹H NMR (25 °C, CD₂COCD₃) δ: 0.752 (m, 12H, CH₃, Bu), 1.213 (m, 12H, CH₃, Bu), 2.000 (br, 4H, CH, Bu), 2.284 (s, 3H, CH₃ tolyl), 3.604 (br, 4H, NCH₂, Bu), 3.958 (br, 4H, NCH₂, Bu), 4.478 (br, –SCH₂CO–), 7.068 (br, 1H, tolyl), 7.443 (d, 1H, tolyl), 7.455 (d, 1H, tolyl), IR (cm⁻¹): 1570 (C=O), 935 (O=U=O). Anal. Calc. for C₂₂H₄₆N₄O₁₀S₂U: 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 L⁴ 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 Kα radiation (λ = 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 CRYSTALS 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 carried out using the ABSPACK program [15c]. The structures were refined to convergence on Fl using SHELXL97 [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 L¹–L⁵ 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 [UO₂(NO₃)₂·6H₂O] with the ligands L¹–L⁵ 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 [UO₂(NO₃)₂·6H₂O] are completely replaced by the ligand, which is bonded to the carbamoyl oxygen atom to the uranyl group. The observed frequency difference for the carbamoyl group (ΔνCO = 37–62 cm⁻¹), where ΔνCO = ν(CO (free ligand) – ν(CO(coordinated)) shows that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those observed for [UO₂(NO₃)₂(N-cyclohexyl-2-pyrrrolidone)] [16a], [UO₂(NO₃)₂(1,3-dimethyl-2-imidazolidone)₁₆b], [UO₂(NO₃)₂(C₅H₄CON(C₆H₂O₂)₈] [16a], [UO₂(NO₃)₂(C₇H₇)₂NCOCH₂CON(C₅H₄)H₂] [10c] and [UO₂(NO₃)₂(C₂H₂NO)] [10f].

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₂H₄₆N₄O₁₀S₂U</td>
<td>C₂₂H₄₆N₄O₁₀S₂U</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>Pt</td>
</tr>
<tr>
<td>a (Å)</td>
<td>17.0993(9)</td>
<td>10.8372(9)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.1195(4)</td>
<td>17.3889(12)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>19.1525(11)</td>
<td>19.3630(14)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>89.383(6)</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>89.383(6)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>108.337(8)</td>
<td>108.337(8)</td>
</tr>
<tr>
<td>V (cm³)</td>
<td>3145.8(3)</td>
<td>3545.9(5)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>μ(μm⁻¹)</td>
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<td>1.665</td>
</tr>
<tr>
<td>μ(mm⁻¹)</td>
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<td>4.750</td>
</tr>
<tr>
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<td>19262/10579</td>
</tr>
<tr>
<td>Data/restrains/parameters</td>
<td>356</td>
<td>793</td>
</tr>
<tr>
<td>Goodness of fit (GOF) on F²</td>
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<td>0.71073</td>
</tr>
<tr>
<td>R₁ (I &gt; 2σ(I))</td>
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<td>0.0648</td>
</tr>
<tr>
<td>wR₁ (all data)</td>
<td>0.1675</td>
<td>0.1675</td>
</tr>
</tbody>
</table>

w = 1/[σ²(I)] for 2, w = 1/[σ²(I)] for 4, where F = (F² + 2F²)/3.

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 CRYSTALS 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 carried out using the ABSPACK program [15c]. The structures were refined to convergence on Fl using SHELXL97 [15b]. Selected crystallographic data for 2 and 4 are summarized in Table 1.
The $^1$H 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 CH$_2$ group adjacent to the carbamoyl is more deshielded (ca. 0.4 ppm) compared to that of the CH$_2$ 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$_3$)$_2$L)$_2$], 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$_3$)$_2$(CH$_2$SCH$_2$CON{C$_4$H$_9$}$_2$)]$^2^+$ (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$_3$)$_2$(CH$_2$SCH$_2$CON{C$_4$H$_9$}$_2$)$_2$]·6H$_2$O] 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 ($\Delta$νCO = 63 cm$^{-1}$, where $\Delta$νCO = νCO (free ligand) − νCO (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 $^1$H NMR spectrum of 4 show the expected peaks and integrations and is broad due to a ligand exchange/disproportionation reaction in solution [9]. The CH$_2$ 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 m/z value of 826.3 (UO$_2$(NO$_3$)$_2$(CH$_2$SCH$_2$CON{C$_4$H$_9$}$_2$)$_2$ $^+$). The observed R$_{cd}$, 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$_3$)$_2$(CH$_2$SCH$_2$CON{C$_4$H$_9$}$_2$)$_2$]·6H$_2$O] 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 ($\Delta$νCO = 63 cm$^{-1}$, where $\Delta$νCO = νCO (free ligand) − νCO (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].

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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 CH2 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 CH2 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 bidentate 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 L4 from nitric acid medium

The extraction studies were carried out using the ligand L4 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)} > D_{U(IV)} > D_{Am(III)} and are similar to those
observed for the monoamides, CMP, CMPO, CMSO or malonamide ligands with these metal ions \cite{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 concentration. The plot of log \( D_U \) Vs log[HNO\(_3\)] (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 \( D_U \) 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 \([UO_2(NO_3)_2\text-L]\) and \([UO_2(NO_3)_2\text-2L]\) \cite{20,10d}.

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

<table>
<thead>
<tr>
<th>System</th>
<th>Relative stability ((E_{\text{all trans}} - E_{\text{all cis}})) in kcal/mol</th>
<th>Binding energy ((E_{\text{complex at eqm}} - E_{\text{complex at diss limit}})) in kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand a</td>
<td>5.5</td>
<td>–</td>
</tr>
<tr>
<td>Ligand b</td>
<td>–7.5</td>
<td>–</td>
</tr>
<tr>
<td>Complex 1</td>
<td>–</td>
<td>57.25</td>
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<tr>
<td>Complex 2</td>
<td>–</td>
<td>61.05</td>
</tr>
<tr>
<td>Complex 3</td>
<td>–</td>
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</tr>
<tr>
<td>Complex 4</td>
<td>–</td>
<td>61.9</td>
</tr>
<tr>
<td>Complex 5</td>
<td>–</td>
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</tr>
<tr>
<td>Complex 6</td>
<td>–</td>
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</tr>
</tbody>
</table>

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.)

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.)
4. Conclusions

The complex chemistry of dithio-diglycolamide ligands with uranyl nitrate shows a chelating mode of bonding for these ligands. The diocetyl 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 H₂C₂O₄ respectively. Theoretical studies clearly reveal that the chelating mode of bonding for these ligands is more energetically favorable than monodentate or bridging bidentate modes of bonding.

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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.

References


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