

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 $\text{R} = \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_6\text{H}_5, \text{C}_8\text{H}_{17}$) and $[\text{C}_7\text{H}_6(\text{SCH}_2\text{CONR}_2)_2]$ (where $\text{R} = \text{C}_4\text{H}_9$) 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 HNO_3 by one of the ligands, namely **L**⁴, 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 $\text{H}_2\text{C}_2\text{O}_4$.

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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-butylamide 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 ($\text{R}_2\text{NCO}(\text{CH}_2)_n\text{CONR}_2$) 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 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 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 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 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 *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,

-SCH₂CO-), 3.355 (m, 2H, CH, ⁱPr), 3.962 (m, 2H, CH, ⁱPr). IR (cm⁻¹) ν: 1624 (C=O). Anal. Calc. for C₁₈H₃₆N₂S₂O₂: C, 57.4; H, 9.6; N, 7.4. Found: C, 57.1; H, 9.4; N, 7.2%.

2.3. Synthesis of L²

This was prepared similarly to L¹ 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 L² 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, NCCCH₂, Bu), 2.921 (s, 4H, -CH₂S-), 3.271 (m, 8H, NCH₂, Bu) 3.324 (s, 4H, -SCH₂CO-). IR (cm⁻¹) ν: 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 L³

This was prepared similarly to L¹ 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 L³ 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) ν: 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 L¹ 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 L⁴ 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) ν: 1633 (C=O).

2.6. Synthesis of L⁵

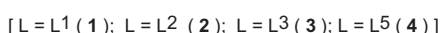
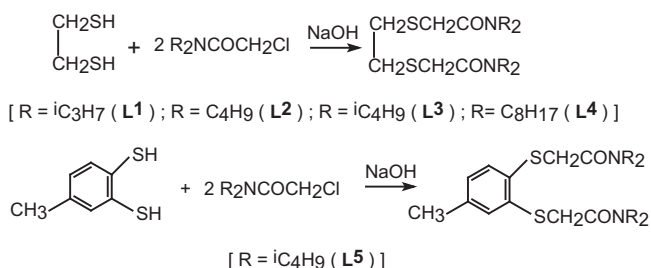
This was prepared similarly to L¹ by taking tolyl-3,4-dithiol (3.04 g, 0.0195 mol) and *N,N*-diisobutyl carbamoyl methyl chloride (8 g, 0.39 mol), giving L⁵ in 81% yield. ¹H NMR (25 °C, CDCl₃) δ: 0.854 (m, 24H, CH₃, ⁱBu), 1.924 (m, 4H, CH, ⁱBu), 2.271 (s, 3H, -CH₃, tolyl), 3.130 (m, 8H, NCH₂, ⁱBu), 3.732 (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) ν: 1652 (C=O). Anal. Calc. for C₂₇H₄₆N₂S₂O₂: 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 L¹ (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) ν: 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 L² (259 mg, 0.60 mmol) and [UO₂(NO₃)₂·6H₂O] (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,



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

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