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Article

Lanthanum(III) and Uranyl(VI) Diglycolamide Complexes: Synthetic Precursors and Structural Studies Involving Nitrate Complexation

Shanmugaperumal Kannan, Morgan A. Moody, Charles L. Barnes, and Paul B. Duval*

Department of Chemistry, University of Missouri-Columbia, 601 South College Avenue, Columbia, Missouri 65211

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The synthesis and structural characterization of lanthanum(III) and uranyl(VI) complexes coordinated by tridentate diglycolamide (DGA) ligands $O(CH_2C(O)NR_2)_2$ [R = *i*-Pr (L^1), *i*-Bu (L^2)] are described. Reaction of L with $UO_2Cl_2(H_2O)_n$ forms the uranyl(VI) *cis*-dichloride adducts UO_2Cl_2L [L = L^1 (**1a**), L^2 (**1b**)], while reaction of excess L with the corresponding metal nitrate hydrate produces $[LaL_3][La(NO_3)_6]$ [L = L^1 (**2a**), L^2 (**2b**)] for lanthanum and $UO_2(NO_3)_2L$ [L = L^1 (**3a**), L^2 (**3b**)] for uranium. Compounds **2b** and **3a** have been structurally characterized. The solid-state structure of the cation of **2b** shows a triple-stranded helical arrangement of three tridentate DGA ligands with approximate D_3 point-group symmetry, while the counteranion consists of six bidentate nitrate ligands coordinated around a second La center. The solid-state structure of **3a** shows a tridentate DGA ligand coordinated along the equatorial plane perpendicular to the O=U=O unit as well as two nitrate ligands, one bidentate and oriented in the equatorial plane and the other monodentate and oriented parallel to the uranyl unit with the oxygen donor atom situated above the mean equatorial plane. Ambient-temperature NMR spectra for **3a** and **3b** indicated an averaged chemical environment of high symmetry consistent with fluxional nitrate hapticity, while spectroscopic data obtained at −30 °C revealed lower symmetry consistent with the slow-exchange limit for this process.

Introduction

Diglycolamide (DGA) molecules (Chart 1), particularly those with long-chain alkyl (e.g., *n*-octyl) amide substituents, have attracted increasing attention in the DIAMEX process for selectively extracting trivalent actinide and lanthanide ions into aliphatic *n*-dodecane solvents.[1–6] Advantages of diglycolamide ligands include ease of synthesis, milder stripping requirements, and chemical compositions consisting of fully incinerable elements (i.e., no P or S present) that adhere to the CHON principle.[7]

However, solvent extraction entails a complex interplay involving the organic solvent and its impact on the ability of an extracting agent to bind metal(s) effectively, influencing the stoichiometry, coordination mode, stability, and solubility of the resulting coordination complex(es).

Structural studies can offer valuable insight into the correlation of these parameters to the relative compatibility between a particular ligand design and the coordination sphere of the metal ion. However, despite the promising results exhibited by diglycolamide extractants for f-element separations, very few structural characterizations, including only studies on La,[8] the lanthanides Ce and Yb,[9] and the actinide Np,[10] have been reported. Of these, only the lanthanide study was conducted in the presence of nitrate ion,[9] which is expected to be an important participant in the separation chemistry, given the nitric acid conditions in the nuclear waste stream.

In this study we have targeted two systems, La(III) and uranyl(VI), that have shown anomalous results in f-element extraction studies on which structural characterization might shed light. For example, a curious drop-off in the abilities

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* To whom correspondence should be addressed. E-mail: duvalp@missouri.edu.

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of DGA ligands to extract lanthanum as opposed to the other lanthanides has been observed,[9] while uranyl(VI) extraction has consistently been found to be relatively poor compared with that of spherical trivalent metal ions. In both instances, the extent to which nitrate ion influences the coordination chemistry and thus the extraction efficiency remains unclear. While long-chain hydrocarbon substituents offer greater solubilities upon complexation and hence more effective extraction into common organic solvents such as *n*-dodecane, use of smaller hydrocarbon groups (i.e., *i*-Pr, *i*-Bu) is more conducive to characterization by single-crystal X-ray crystallography. In addition to the structural results, we report here a modified high-yield synthesis of these DGA ligands.

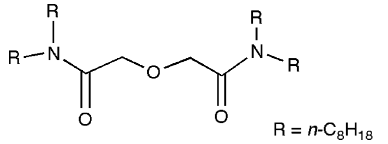
Experimental Section

General Considerations. All of the reactions were conducted on the benchtop. Tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled over sodium benzophenone ketyl. Acetonitrile and anhydrous methanol were distilled over CaH_2. ^1H NMR spectra (referenced to a nondeuterated impurity in the solvent) were recorded using a Bruker AMX-250 or -300 spectrometer. Chemical shifts (δ) are reported in parts per million, and coupling constants (J) are reported in hertz. Infrared spectra were obtained as mulls (in a mixture of type NVH and type B immersion oils pressed between KBr plates) using a Thermo Nicolet Nexus 670 FTIR spectrometer. UV−vis spectra were obtained as THF and acetonitrile solutions on a Hewlett-Packard 8452A diode-array spectrophotometer. Elemental analyses were performed by Desert Analytics. Diglycolyl chloride, diisopropylamine, diisobutylamine, $La(NO_3)_3 \cdot 6H_2O$, and $UO_2(NO_3)_2 \cdot 6H_2O$ (Aldrich) and UO_3 (Pfaltz & Bauer) were used as received.

Synthesis of the Diglycolamides ($NR_2C(O)CH_2)_2O$ [R = *i*-Pr (L^1), *i*-Bu (L^2)]. In a modification of existing synthetic procedures,[9,11] a solution of diisopropyl amine (9.0 mL, 0.069 mol) and triethylamine (10 mL, 0.72 mol) in benzene (50 mL) was added slowly to a solution of diglycolyl chloride (5.0 g, 0.029 mol) in benzene (100 mL) with stirring. The reaction mixture was stirred for 2 h and then treated with 100 mL of a 5% HCl solution. The organic layer was separated, dried over sodium sulfate, and filtered. Removal of the solvent in vacuo yielded a pasty solid, which was redissolved in 10 mL of hexane and filtered. A white solid was obtained upon slow evaporation of the hexane solution. Yield for L^1: 6.0 g (69%). A similar procedure provided L^2 in 82% yield. ^1H NMR for L^2 (25 °C, $CDCl_3$): δ 0.86 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 0.89 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 1.89 [m, 2H, $CH(CH_3)_2$], 2.00 [m, 2H, $CH(CH_3)_2$], 3.03 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 3.20 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 4.35 (s, 4H, OCH_2). IR (cm^{-1}): ν(C=O) 1653.

Synthesis of $UO_2Cl_2L^1$ (1a). The orange residue produced upon evaporation of a solution of UO_3 (200 mg, 0.70 mmol) in HCl (2 mL) was redissolved in 5 mL of methanol and added slowly with stirring to a solution of L^1 (250 mg, 0.833 mmol) in methanol (5 mL). The yellow precipitate was filtered, washed with ether, and dried. Yield: 420 mg (94%). ^1H NMR (25 °C, DMSO-d_6): δ 1.11 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 1.30 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 3.43 [m, 2H, $CH(CH_3)_2$], 3.91 [m, 2H, $CH(CH_3)_2$], 4.08 (s, 4H, OCH_2). IR (cm^{-1}): ν(U=O) 923, ν(C=O) 1605.

Chart 1



Synthesis of $UO_2Cl_2L^2$ (1b). This compound was prepared similarly to **1a**, using UO_3 (200 mg, 0.70 mmol) and L^2 (400 mg, 1.12 mmol). The yellow product was recrystallized from 1,2-dichloroethane/methanol/DME. Yield: 450 mg (92%). ^1H NMR (25 °C, DMSO-d_6): δ 0.78 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 0.81 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 1.87 [m, 4H, $CH(CH_3)_2$], 3.03 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 3.07 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 4.19 (s, 4H, OCH_2). IR (cm^{-1}): ν(U=O) 923, ν(C=O) 1605. Anal. Calcd for $C_{20}H_{40}Cl_2N_2O_5U$: C, 34.44; H, 5.78; N, 4.02. Found: C, 30.91; H, 5.08; N, 3.61.

Synthesis of $[La(L^1)_3][La(NO_3)_6]$ (2a). Solid $La(NO_3)_3 \cdot 6H_2O$ (200 mg, 0.46 mmol) was slowly added to a CH_2Cl_2 solution of L^1 (300 mg, 1.00 mmol) with stirring, giving a clear, colorless solution within minutes. Stirring for an additional 2 h deposited a white solid product that was filtered, washed with CH_2Cl_2, and dried. The product was recrystallized from methanol/1,2-dichloroethane. Yield: 320 mg (89%). ^1H NMR (25 °C, $CDCl_3$): δ 1.27 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 1.41 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 3.73 [m, 4H, $CH(CH_3)_2$], 4.73 (s, 4H, OCH_2). IR (cm^{-1}): ν(C=O) 1604. Anal. Calcd for $C_{48}H_{96}La_2N_{12}O_{27}$: C, 37.17; H, 6.24; N, 10.84. Found: C, 36.68; H, 5.83; N, 10.65.

Synthesis of $[La(L^2)_3][La(NO_3)_6]$ (2b). Solid $La(NO_3)_3 \cdot 6H_2O$ (200 mg, 0.46 mmol) was slowly added with stirring to a solution of L^2 (400 mg, 1.12 mmol) in 1,2-dichloroethane, generating a clear, colorless solution within minutes. The reaction mixture was layered with heptane and allowed to stand for 12 h, yielding colorless crystals that were filtered, washed with hexanes, and dried. Yield: 350 mg (88%). ^1H NMR (25 °C, CD_3OD): δ 0.90 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 0.97 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 2.09 [m, 4H, $CH(CH_3)_2$], 3.03 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 3.07 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 4.81 (s, 4H, OCH_2). IR (cm^{-1}): ν(C=O) 1603. Anal. Calcd for $C_{60}H_{120}La_2N_{12}O_{27}$: C, 41.91; H, 7.03; N, 9.78. Found: C, 41.72; H, 6.83; N, 9.56.

Synthesis of $UO_2(NO_3)_2L^1$ (3a). Solid $UO_2(NO_3)_2 \cdot 6H_2O$ (502 mg, 1.00 mmol) was added slowly with stirring to a solution of L^1 (600 mg, 2.0 mmol) in chloroform. The reaction mixture was filtered and allowed to stand for 12 h in a closed vial, during which time a yellow crystalline solid was deposited. This product was filtered, washed with chloroform, dried, and recrystallized from methanol/1,2-dichloroethane. Yield: 650 mg (94%). ^1H NMR (25 °C, CD_3OD): δ 1.47 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 1.85 [d, 12H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 4.06 [m, 4H, $CH(CH_3)_2$], 5.70 (s, 4H, OCH_2). IR (cm^{-1}): ν(U=O) 936, ν(C=O) 1606.

Synthesis of $UO_2(NO_3)_2L^2$ (3b). This compound was prepared similarly to **1a**, using $UO_2(NO_3)_2 \cdot 6H_2O$ (502 mg, 1.00 mmol) and L^2 (800 mg, 2.2 mmol). Yield: 700 mg (93%). ^1H NMR (25 °C, CD_2Cl_2): δ 1.07 [d, 24H, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 2.27 [m, 2H, $CH(CH_3)_2$], 2.38 [m, 2H, $CH(CH_3)_2$], 3.41 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 3.84 [d, 4H, $^3J_{HH}$ = 7 Hz, $CH_2CH(CH_3)_2$], 5.69 (br s, 4H, OCH_2). IR (cm^{-1}): ν(U=O) 942, ν(C=O) 1602. Anal. Calcd for $C_{20}H_{40}N_4O_{11}U$: C, 32.00; H, 5.37; N, 7.46. Found: C, 36.52; H, 5.96; N, 7.47.

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Table 1. Summary of X-ray Crystallographic Data

	2b	3a
empirical formula	$C_{68}H_{136}La_2Cl_8N_{12}O_{27}$	$C_{16}H_{32}N_4O_{11}U$
formula weight	2115.31	649.49
space group	rhombohedral, *R*3*c* (No. 161)	orthorhombic, *Pbca* (No. 61)
a (Å)	14.4936(3)	11.8894(5)
b (Å)	14.4936(3)	16.0816(6)
c (Å)	82.795(3)	25.2065(10)
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	90
V (Å^3)	15062.2(7)	4819.5(3)
Z	6	8
ρ_{calc} (g cm^{-3})	1.399	1.914
T (K)	173(2)	173(2)
μ (mm^{-1})	1.123	6.796
θ range (deg)	1.48−27.13	1.62−27.17
total reflections	33839	33063
unique reflections	7425	5347
parameters	354	297
R1, wR2[a]	0.0583, 0.0948	0.0530, 0.0576
max, min peaks (e Å^{-3})	1.334, −1.111	0.903, −0.810
GOF	1.023	1.047

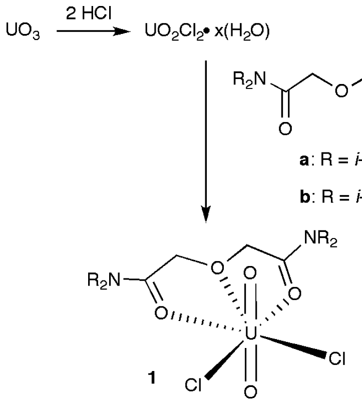
[a] Values of R1 are based on selected data having $F > 2\sigma(F)$; values of wR2 are based on all of the data.

X-ray Crystallographic Data. Single crystals of **2b** and **3a** suitable for X-ray analysis were obtained from heptane and methanol/1,2-dichloroethane, respectively. Single crystals were placed in degassed hydrocarbon oil and mounted on a glass fiber. Intensity data were obtained at −100 °C on a Bruker SMART CCD area detector system using the ω scan technique with Mo Kα radiation from a graphite monochromator. Intensities were corrected for Lorentz and polarization effects. Equivalent reflections were merged, and absorption corrections were made using the multiscan method. Space groups, lattice parameters, and other relevant information are given in Table 1. The structures were solved by direct methods with full-matrix least-squares refinement using the SHELX package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and included in the refinement using a riding model with fixed isotropic U. The final difference map contained no features of chemical significance.

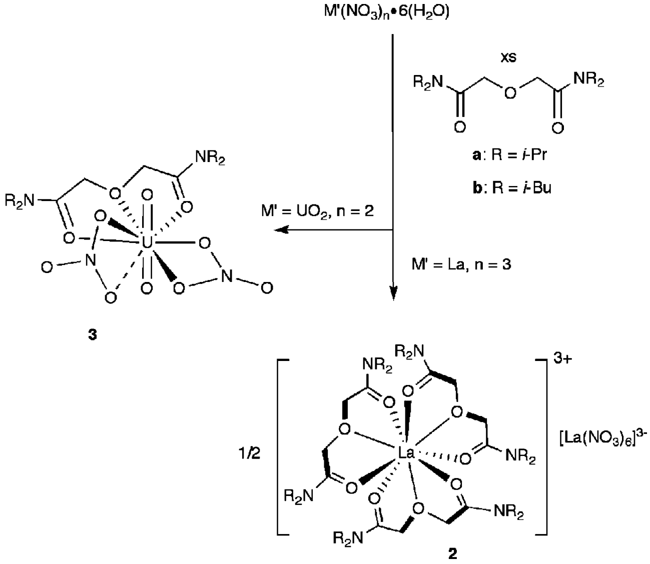
Results and Discussion

Synthesis of Uranyl(VI) Chloride Diglycolamide Complexes. We recently reported a simple synthetic route to anhydrous uranyl(VI) *cis*-dihalide complexes coordinated by a neutral tridentate dicarboxamide ligand.[12] As an extension of this chemistry to analogous derivatives coordinated by tridentate DGA ligands, we have modified the existing synthetic methodologies to yield diglycolamide compounds having the general formula $(NR_2C(O)CH_2)_2O$ [R = *i*-Pr (L^1), *i*-Bu (L^2)]. Reaction of commercially available diglycolyl chloride with the appropriate secondary amine in benzene followed by workup in hexane provides these chelating ligands in excellent yields. Addition of a methanol solution of $UO_2Cl_2 \cdot xH_2O$ to a DGA ligand L precipitates the *cis*-dihalide adduct UO_2Cl_2L (**1**) as an air-stable yellow solid (Scheme 1).

Scheme 1



Scheme 2



Compounds **1a** and **1b** are soluble in methanol. Their ^{1}H NMR spectra showed two sets of peaks assignable to chemically distinct resonances for each amide substituent and chemical equivalence between the two sides of the DGA ligand, as observed in the free ligand and consistent with the averaged C_{2v} point-group symmetry shown in Scheme 1. The wavenumber of the C=O bond stretch in these uranyl complexes was red-shifted approximately 50 cm^{-1} with respect to that of the free ligand, reflecting increased electron donation that was also observed in the analogous nitrate derivatives **3a** and **3b** (see below).

Synthesis and Structural Characterization of Lanthanum Nitrate Diglycolamide Complexes. Reaction of the metal nitrate hydrates with excess DGA produces the corresponding metal complexes, as shown in Scheme 2.

We considered whether the anomalously low D values previously reported by the Scott group[9] for complexes of L^1 with La as opposed to the other lanthanides might reflect the capability of lanthanum to accommodate an expanded coordination sphere (D is the distribution ratio, the relative concentration of an extracted species in the organic versus the aqueous phase). For example, previous structural analyses[9] of DGA complexes of Ce and the much-smaller lanthanide Yb revealed that both exhibit nine-coordinate geometries in which the metal is sterically saturated with three tridentate DGA ligands. However, a separate study[8]

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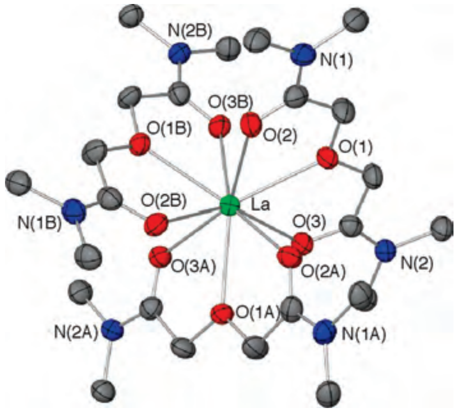

Figure 1. Thermal ellipsoid drawing of the cation of **2b**, showing the atom-labeling scheme used in Table 2. Displacement ellipsoids are shown at 50% probability. For clarity, only the α-carbon atoms of the *i*-Bu groups are shown.

Table 2. Bond Lengths (Å) and Angles (deg) in **2b** and **3a**

2b		3a	
La(1)−O(1)	2.580(3)	U(1)−O(1)	2.393(3)
La(1)−O(2)	2.501(3)	U(1)−O(2)	2.592(3)
La(1)−O(3)	2.496(3)	U(1)−O(3)	2.402(3)
La(2)−O(4)	2.647(3)	U(1)−O(4)	2.543(3)
La(2)−O(5)	2.663(3)	U(1)−O(5)	2.522(3)
La(2)−O(7)	2.603(3)	U(1)−O(7)	2.963(3)
La(2)−O(8)	2.711(3)	U(1)−O(8)	2.528(3)
O(2)−C(2)	1.244(5)	U(1)−O(10)	1.748(3)
O(3)−C(12)	1.258(5)	U(1)−O(11)	1.758(3)
N(1)−C(2)	1.336(5)	O(1)−C(1)	1.257(5)
N(2)−C(12)	1.328(5)	O(3)−C(10)	1.248(5)
		N(3)−O(4)	1.257(5)
O(2)−La(1)−O(3)	121.28(10)	N(4)−O(8)	1.239(5)
La(1)−O(2)−C(2)	128.2(3)	N(1)−C(1)	1.321(5)
La(1)−O(3)−C(12)	127.4(3)	N(2)−C(10)	1.321(5)
O(2)−La(1)−O(2A)	85.73(10)		
O(2)−La(1)−O(3A)	81.17(10)	O(10)−U(1)−O(11)	174.04(14)
O(2)−La(1)−O(3)	121.28(10)	O(1)−U(1)−O(10)	90.05(12)
La(1)−O(2)−C(2)	128.2(3)	O(2)−U(1)−O(10)	94.35(12)
La(1)−O(3)−C(12)	127.4(3)	O(3)−U(1)−O(10)	86.49(13)
O(2)−La(1)−O(2A)	85.73(10)	O(4)−U(1)−O(10)	86.59(12)
		O(5)−U(1)−O(10)	89.47(12)
		O(8)−U(1)−O(10)	111.75(13)
		O(8)−U(1)−O(11)	74.11(13)
		U(1)−O(8)−N(4)	708.73(10)
		U(1)−O(5)−N(3)	97.4(2)
		U(1)−O(4)−N(3)	97.0(2)
		O(1)−U(1)−O(3)	118.54(10)

reported a 10-coordinate geometry in which the larger La center is coordinated by two diglycolamide ligands and three picrate ions (one bidentate and two monodentate).

Single crystals suitable for X-ray crystallography were obtained for **2b**. A thermal ellipsoid drawing of its structure is shown in Figure 1, and selected bond distances and bond angles are listed in Table 2. The $[La(L^2)_3]^{3+}$ cation comprises a nine-coordinate La center wrapped by three tridentate DGA ligands in a D_3-symmetric triple-stranded helix in which the central ether donors [O(1)] of the DGA ligands adopt the capping positions of a twisted tricapped trigonal prismatic geometry. As with most chiral compounds built up from achiral ligands, crystals of **2b** consist of a racemic mixture wherein enantiomers are inverted by a glide plane along the *c* axis in space group *R*3*c*. The lanthanum−amide bond distances of 2.501(3) and 2.496(3) Å for La(1)−O(2) and La(1)−O(3), respectively, are both within the normal range, as is the La(1)−O(1) bond distance of 2.580(3) Å between La and the central ether oxygen donors.[13]

The nine-coordinate triple-helical geometry observed for the cation in **2b** is similar to that reported for analogous lanthanide complexes coordinated by three semirigid tridentate ligands[14] and the same as that reported for both the Ce and Yb DGA derivatives.[9] However, unlike the case of the Ce and Yb compounds, where the three nitrate anions required for charge balance reside loosely within the secondary coordination sphere of the $[Ln(L^1)_3]^{3+}$ cation, in **2b** these groups are incorporated into a homoleptic 12-coordinate $[La(NO_3)_6]^{3-}$ counteranion, a familiar motif in the nitrate coordination chemistry of the larger early lanthanides.[15] Thus, 2 equiv of lanthanum nitrate hydrate is consumed for every 3 equiv of DGA, a result that was consistently reproduced in both chlorinated (chloroform, methylene chloride) and hydrocarbon solvents, even when an excess of DGA was used. The large $[La(NO_3)_6]^{3-}$ ion is known to cocrystallize with large cationic complexes[15] and may be responsible for the anomalous extraction results that have been observed for La compared with the other lanthanides.[9]

NMR spectra obtained for **2a** and **2b** showed chemical equivalence between the two sides and the two faces of the DGA ligand, consistent with averaged D_{3h} point-group symmetry and indicative of rapid P/M interconversion of the chiral triple-helical geometry on the NMR time scale (P/M refers to the right-hand and left-hand isomers, respectively, of chiral helicates). This flexibility has been noted with most nine-coordinate triple-helical lanthanide complexes bound by three tridentate ligands.[14]

Synthesis and Structural Characterization of Uranyl(VI) Nitrate Diglycolamide Complexes. In contrast to the effectiveness displayed by diglycolamide ligands in extracting large spherical trivalent ions, which reflects a well-matched nine-coordinate metal center encapsulated by three tridentate ligands as seen in the solid-state structure of **2b**, relatively poor selectivity has been observed with the linear uranyl(VI) ion. This apparent mismatch likely stems from stereochemical incompatibility of the diglycolamide ligand (and its relatively large bite angle) with the equatorial coordination plane of the uranyl dioxo group. It should be noted that structural characterization of an analogous Np(V) DGA complex has shown that two DGA ligands are indeed capable of occupying the slightly more expanded equatorial region belonging to the larger neptunyl(V) center.[10] For the slightly smaller uranyl(VI) center, this fit is less likely, although solution data have suggested that a 2:1 DGA/metal stoichiometry may be possible.[6] This poses a dilemma: With only a single DGA ligand, the remaining equatorial sites must be saturated with bidentate nitrate ligands; however, one nitrate does not suffice, and steric constraints likely do not permit two.[16] This awkward misfit contrasts with the

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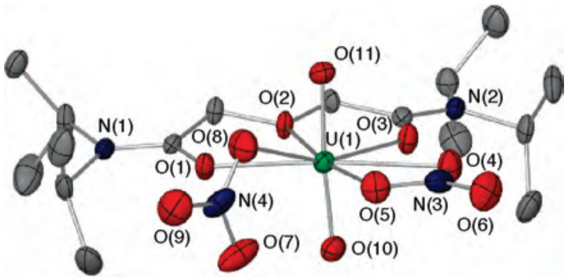

Figure 2. Thermal ellipsoid drawing of **3a**, showing the atom-labeling scheme used in Table 2. Displacement ellipsoids are shown at 50% probability.

coordinative synergy between two bidentate nitrate groups and two tributylphosphate ligands in the uranyl equatorial plane that allows this species to be effectively extracted during the PUREX process[17] and provided the impetus for our interest in characterizing the structure of a uranyl diglycolamide complex with nitrate coordination.

Indeed, an unusual twist in nitrate coordination was observed here in an evident steric response to accommodate coordination of one diglycolamide ligand. Addition of uranyl nitrate to a chloroform solution of the DGA ligand L^1 precipitated the adduct UO$_2$(NO$_3$)$_2$L^1 (**3a**) as an air-stable yellow solid (Scheme 2). Single crystals of **3a** suitable for X-ray crystallography were obtained from a mixture of methanol and 1,2-dichoroethane. The structure of **3a** is shown in Figure 2, and selected bond distances and bond angles are listed in Table 2. The uranyl(VI) center is coordinated in the equatorial plane by one tridentate diglycolamide ligand, one bidentate nitrate group, and one monodentate nitrate donor; the latter nitrate binding mode is much less common in nitrate coordination chemistry.[16,18] All of the equatorial donor atoms are approximately coplanar except for the η^1-bound nitrate oxygen atom [O(8)], which is conspicuously situated 20° above the mean equatorial plane. Distortion from idealized equatorial coordination has been reported with increasing frequency in uranyl(VI) coordination chemistry,[19–21] but to the best of our knowledge, this is the first example displayed by a nitrate ligand.[16] In this instance, the elevated location of O(8) above the equatorial plane is part of a steric response that directs this nitrate ligand into the least-congested orientation, namely, perpendicular to the equatorial plane, which in turn positions O(7) below the equatorial plane, resulting in a long-range (~2.9 Å) interaction with the uranium atom. This quasi-bidentate nitrate group is thus oriented parallel to the dioxo unit, which in turn is tilted slightly away, generating a modest distortion of the O(10)−U−O(11) bond angle to 174.0(1)°. The U−O(amide) bond distances of 2.393(3) and 2.402(3) Å for U(1)−O(1) and U(1)−O(3), respectively, are significantly longer than those we have reported for other uranyl amide complexes[22] and toward the long end of the range of structurally characterized examples.[23]

Ambient-temperature ^{1}H NMR spectra obtained for **3a** and **3b** showed equivalent resonances for the two sides of the DGA ligand, indicating a higher symmetry than is present in the solid-state structure of **3a**, where the inequivalent amide oxygen donors O(1) and O(2) are situated adjacent to the monodentate and bidentate nitrate groups, respectively. Fluxional hapticity of the two nitrate ligands could have generated averaged chemical environments for these groups in the ambient-temperature NMR spectra. When the temperature was decreased to −30 °C, the NMR spectra showed a lower symmetry (i.e., separate resonances for each methylene group in the ligand backbone) consistent with that observed in the solid-state structure, suggesting the slow-exchange limit is attained for fluxional nitrate coordination at this lower temperature.

Conclusions

Structural characterization of La(III) and uranyl(VI) DGA complexes containg nitrate coordination revealed features in their respective coordination spheres that may hint at the origin of some of the anomalous behavior that has been reported for these metals in separation studies. For example, the lanthanum complex **2b** possesses a triple-stranded helical [La(L^2)$_3$]$^{3+}$ cation similar to that previously observed in structurally characterized Ce and Yb derivatives, but this cation is associated with a homoleptic [La(NO$_3$)$_6$]$^{3-}$ counteranion regardless of metal/ligand stoichiometry. Meanwhile, the equatorial region of the uranyl(VI) complex **3a** contains one DGA unit and two nitrate ligands, one of which is coordinated in an unusual quasi-bidentate mode that is oriented parallel to the dioxo group.

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Supporting Information Available: X-ray crystallographic files in CIF format for **2b** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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