Coordination of Lanthanide Nitrates with *N,N,N′,N′*-Tetramethylsuccinamide

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Two compound classes have been identified from the reaction of trivalent lanthanide nitrates with tetramethyl-succinamide (TMSA). The nature of these Ln−TMSA compounds has been examined in the solid phase by thermogravimetric analysis (TGA) and single-crystal X-ray diffraction and in solution by infrared spectroscopy. Isostructural, 10-coordinate compounds with a 2:1 TMSA:Ln stoichiometry were found for the lanthanides La and Ce. Single-crystal X-ray diffraction analysis of the Ln−TMSA nitrate compounds, Ln = La and Ce, reveals a polymeric structure with each metal center containing one chelating bidentate succinamide and two bridging bidentate succinamides. For the remaining lanthanides Pr, Nd, Gd, Yb, and Lu, a series of isostructural, 9-coordinate compounds containing a 3:2 TMSA:Ln ratio were formed. Single-crystal X-ray diffraction analysis of the Ln−TMSA products, Ln = Ce, Pr, Nd, Gd, and Yb, reveals these compounds to be dimeric, with each metal center containing one chelating bidentate succinamide and two bridging bidentate succinamides. The solution stoichiometries were examined in acetonitrile−water mixtures and support the stoichiometries observed in the solid-state structures. Cerium nitrate appears to be a special (and transitional) lanthanide in its reaction with TMSA. Although infrared and TGA analyses indicate a 2:1 ligand-to-metal product, crystals for both the 2:1 and 3:2 compounds were isolated. No evidence for such multiple forms was found with any of the other lanthanides.

Introduction

The potential application of diamide compounds as selective extractants for use in nuclear fuel reprocessing has attracted much recent research interest. First identified and examined for this purpose by Siddell in the 1960s,[1−3] their extraction behavior with f-block metal ions has been extensively reinvestigated by Musikas[4−13] and others.[14−23] Most of the diamides studied to date are either *N,N,N′,N′*-tetraalkylmalonamide, $R_1R_2NC(O)(CH_2)_nC(O)NR_1R_2$, $n = 1$, or closely related derivatives. As a result of this interest in malonamides, some work describing malonamide coordination chemistry with f-block metal ions has been reported and several crystal structures of malonamides with lanthanides and actinides have been published.[19,24−27] However, other types of diamides also have been studied as potential f-block metal ion extractants, e.g., compounds such as *N,N,N′,N′*-tetraalkylsuccinamide ($n = 2$) or *N,N,N′,N′*-tetraalkylglutaramide ($n = 3$), in which the amide functionalities are spaced farther apart.[8,20−22] Yet only one crystal structure containing a tetraalkylsuccinamide with an f-block metal ion, that of $UO_2(NO_3)_3$(tetrabutylsuccinamide),[28] and only one crystal structure of a tetraalkylglutaramide with an f-block metal ion, $[UO_2(NO_3)_3$(tetrabutylglutaramide)$]_x$,[29] have been reported.

In this report, we describe the first solid-state structures of tetramethylsuccinamide (TMSA) with lanthanide nitrates as determined by thermogravimetric analysis (TGA), infrared (IR)

spectroscopy, and single-crystal X-ray diffraction. We have also performed infrared spectroscopic studies to evaluate whether these solid-state structures are maintained in solution.

Experimental Section

Materials and Methods. The hydrated lanthanide nitrates La(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Pr(NO₃)₃·6H₂O, Nd(NO₃)₃·6H₂O, Gd(NO₃)₃·5−6H₂O, Yb(NO₃)₃·5H₂O, and Lu(NO₃)₃·5H₂O were obtained from in-house stocks listed as 99.9% pure. All other reagents were of reagent grade and were obtained from Aldrich Chemical Co. (Milwaukee, WI).

IR spectroscopic measurements were carried out on a Nicolet 750 Fourier transform infrared (FT-IR) spectrometer at a resolution of 1 cm⁻¹. Proton (¹H) and ¹³C{¹H} NMR spectra were obtained using a 500 CMX Infinity (Chemagnetics) spectrometer at a nominal frequency of 500 MHz (¹H) or 126 MHz (¹³C). Samples were dissolved in CDCl₃, and the reported chemical shifts are relative to added tetramethylsilane.

Gas chromatography/mass spectroscopy data (GC/MS) were obtained using a Hewlett-Packard 5890 series II gas chromatograph and 5972 mass spectrometer. The column used was a 30 m × 0.25 mm i.d. 0.25 μm DB-5MS film obtained from J&W Scientific, Folsom, CA. Ultrahigh-purity helium was used as the carrier gas. For each measurement, the GC oven conditions started with an initial temperature of 40 °C for 4 min, were then increased at 8 °C/min to a temperature of 300 °C, and then were held at 300 °C, for the duration of the measurement.

The mass axis was calibrated using perfluorotributylamine (PFBTA). Standard 70 eV electron impact mass spectra were collected and stored by the HP Chemstation software.

Ligand Preparation. Tetramethylsuccinamide was prepared by the action of dimethylamine upon succinyl chloride in diethyl ether as described previously for the preparation of tetramethylmalonamide[30] and was purified by vacuum sublimation (95 °C bath, 20 mTorr vacuum) onto a liquid-nitrogen-cooled coldfinger. A crystalline white solid was obtained, with an uncorrected melting point of 83.5−84.5 °C (lit. 84.5−85.5 °C).[31] Crystals suitable for X-ray analysis were obtained by sublimation. IR (KBr; cm⁻¹): 2961 (w), 2929 (w), 1633 (s). GC/MS (retention time 21.4 min): *m/e* 172 (parent peak), 128 (100%), 100, 72. ¹H NMR (CDCl₃): δ 2.65 (s, 2H), 2.93 (s, 3H), 3.04 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 28.33, 35.53, 37.17, 172.18. The estimated purity of the TMSA is greater than 99%.

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Table 1. Summary of Crystallographic Parameters for Representative Compounds

compound	**1**	**4**	**7**
empirical formula	$C_8H_{16}N_2O_2$	$C_{24}H_{48}N_{12}Nd_2O_{24}$	$C_{16}H_{32}LaN_7O_{13}$
fw	172.23	1177.22	669.40
temp, K	173(2)	173(2)	173(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	7.6199(4)	8.720(2)	11.5604(1)
b, Å	5.5366(2)	15.783(4)	16.7875(2)
c, Å	11.4331(6)	15.863(5)	13.8918(2)
α, deg	90	90	90
β, deg	107.307(2)	98.61(2)	104.712(1)
γ, deg	90	90	90
V, Å^3	460.50(4)	2158(1)	2607.60(5)
Z	2	2	4
density, Mg m^{-3}	1.242	1.811	1.705
abs coeff, mm^{-1}	0.090	2.476	1.712
no. of reflns collected	2742	13 412	16 354
no. of independent reflns	1068 ($R_{int} = 0.0069$)	5042 ($R_{int} = 0.0197$)	6066 ($R_{int} = 0.0383$)
no. of obsd reflns	885 [$I > 2\sigma(I)$]	4385 [$I > 2\sigma(I)$]	4643 [$I > 2\sigma(I)$]
range of rel transm factors	0.96−0.91	0.96−0.74	0.97−0.71
data/restraints/parameters	1054/0/58	5038/0/287	6066/0/343
goodness-of-fit on F^2	1.123	1.028	0.954
final R indices [$I > 2\sigma(I)$]	R1 = 0.0382	R1 = 0.0182	R1 = 0.0282
	wR2 = 0.1031	wR2 = 0.0448	wR2 = 0.0559
R indices (all data)	R1 = 0.0489	R1 = 0.0237	R1 = 0.0469
	wR2 = 0.1169	wR2 = 0.0484	wR2 = 0.0614

Reaction of Lanthanide Nitrate Complexes with TMSA. A solution containing at least a 10% stoichiometric excess of TMSA in 5 mL of methanol was added to a well-stirred solution composed of 0.5 g of hydrated trivalent lanthanide nitrate in 10 mL of methanol. The resulting solution was then heated to boiling and concentrated to ca. 5 mL total volume. For the lanthanides Pr−Lu, precipitates formed during this time. These solids were isolated by filtration and then washed with methanol. The compounds were further purified by crystallization as described below. For the lanthanides Ce and La, the reaction solutions were then allowed to evaporate to dryness at room temperature and then crystallized as described below. Product yields were quantitative.

The compounds were crystallized typically by placing about 75 mg of sample in 3 mL of a polar organic solvent such as methanol, acetonitrile, or nitromethane and heating gently to facilitate dissolution. Addition of approximately 10 vol % water was required to dissolve the Pr through Lu products. Samples crystallized either after slow cooling of the heated solution or from solvent−diethyl ether mixtures using vapor diffusion techniques. A summary of the key bands found in the IR spectra of these complexes (KBr; in cm^{-1}) is provided in the Supporting Information.

Thermogravimetric Analysis. Thermogravimetric analyses of a series of crystalline lanthanide nitrate−TMSA salts were run on Seiko 320 series thermogravimetric and differential scanning calorimeters. Thermolysis was carried out in a flow of oxygen to 1000 °C in preheated (1000 °C) platinum pans at a scan rate of 1 °C/min. Under these conditions, reproducible, positive shifts in the thermal baseline were calibrated to 0.05 ± 0.01 mg. Three trials were run for each sample.

IR Spectroscopic Titrations. A standard solution cell with CaF$_2$ windows and a path length of 0.015 mm was used for all solution experiments. Ligand-to-Ln(NO$_3$)$_3$·xH$_2$O ratios (Ln = La and Ce) of 0.5:1.0, 1.0:1.0, 1.5:1.0, 2.0:1.0, and 3.0:1.0 were prepared by dissolving the appropriate quantity of TMSA in 1.0 mL of a 2.68×10^{-2} M CH$_3$-CN stock solution of the Ln(NO$_3$)$_3$ salt. The solution was vortex-stirred at room temperature and then allowed to stand for 1 h. Due to the poor solubility of the Ln(NO$_3$)$_3$·xTMSA compounds (Ln = Pr through Lu) in CH$_3$CN solutions, their solution IR spectra could not be measured under these conditions. However, solutions of the lanthanide nitrate−TMSA compounds could be prepared using 99.7% acetonitrile−0.3% water as the solvent. Careful subtraction of a reference spectrum containing 0.3% water in acetonitrile allowed reliable spectra of these solutions to be obtained even in the OH stretching region.

X-ray Crystallography. The X-ray data for all complexes were collected on a Siemens CCD area detector-equipped diffractometer with Mo Kα ($\lambda = 0.710\,73$ Å) radiation. Diffraction data were collected at −100 °C by using a stream of nitrogen gas. The geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atom with $B = 1.2U_{eqv}(C)$. Refinement

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Table 2: Thermogravimetric Analysis of Trivalent Lanthanide Nitrate − Tetramethylsuccinamide Compounds

| compound	metal oxide	residual weight, mg			error, % 1.5:1/2.0:1
		found	calcd for 1.5:1.0	calcd for 2.0:1.0	
La(NO$_3$)$_3$·xTMSA	La$_2$O$_3$	3.91	4.66	3.92	16/0.2
Ce(NO$_3$)$_3$·xTMSA	CeO$_2$	5.17	5.86	5.11	12/1.1
Pr(NO$_3$)$_3$·xTMSA	Pr$_6$O$_{11}$	3.59	3.61	3.09	0.5/14
Nd(NO$_3$)$_3$·xTMSA	Nd$_2$O$_3$	5.00	4.98	4.34	0.4/15
Eu(NO$_3$)$_3$·xTMSA	Eu$_2$O$_3$	4.46	4.44	3.87	0.50/15
Gd(NO$_3$)$_3$·xTMSA	Gd$_2$O$_3$	6.14	6.09	5.32	1.0/15
Yb(NO$_3$)$_3$·xTMSA	La$_2$O$_3$	6.45	6.44	7.41	0.62/13
Lu(NO$_3$)$_3$·xTMSA	Lu$_2$O$_3$	3.93	3.88	3.4	0.8/16

Scheme 1. Pathways of Ligand Loss from TMSA−Lanthanide Nitrate Compounds upon Thermolysis: (A) Ligand Desorption; (B) Imide Formation
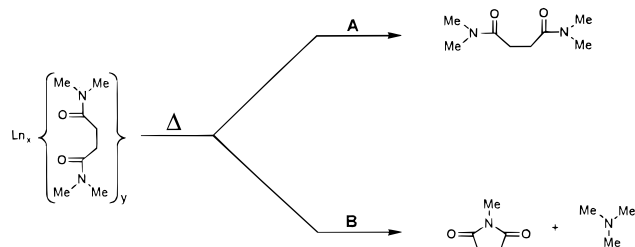
of non-hydrogen atoms was carried out with anisotropic temperature factors. A summary of the crystallographic parameters for one member of each series is reported in Table 1.

Results and Discussion

Thermogravimetric Analysis. The composition of the bulk crystallized solids following the reaction of lanthanide nitrates with excess TMSA can be conveniently obtained by heating the compounds and monitoring the accompanying weight changes with the assumption that the solids convert solely to the stable, nonvolatile lanthanide oxides. Crystallized samples from the reaction of TMSA with the lanthanide(III) nitrates where Ln = La, Ce, Pr, Nd, Gd, Yb, and Lu were examined by TGA in flowing oxygen up to 1000 °C. No weight loss was observed until 200 °C for any of these compounds. Weight loss did begin after 200 °C and was essentially complete by 400 °C. In most cases, weight reductions corresponding to TMSA loss/decomposition were observed first, followed by weight losses corresponding to nitrate decomposition. However, for several samples, these events were concomitant. After the samples were heated to 1000 °C under flowing oxygen, the values of the residual weights, which were assumed to contain only the stable metal oxides M$_2$O$_3$ (M = La, Nd, Gd, Yb, Lu), M$_6$O$_{11}$ (M = Pr), and MO$_2$ (M = Ce),[32] could be used to calculate the ligand-to-metal ratios initially present. Table 2 shows the agreement between the experimental results and the calculated residual weights assuming either a 2:1 or a 3:2 ligand-to-metal ratio in the initial sample. These results clearly indicate that a 2:1 TMSA-to-metal ratio is present in the lanthanum and cerium compounds and that products with a 3:2 TMSA:Ln ratio are formed with all other lanthanides.

By routing the oxygen flow through an infrared spectrometer, we could examine the TMSA structure at the time of ligand removal from the solid. Scheme 1 outlines the proposed behavior of TMSA upon thermolysis of these lanthanide nitrate−TMSA compounds. Two major pathways involving TMSA removal are observed. The first pathway (A in Scheme 1) is identified by
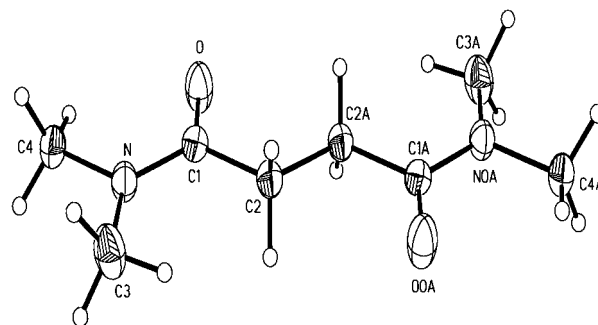
Figure 1. ORTEP illustration of *N,N,N′,N′*-tetramethylsuccinamide (**1**).

Table 3. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) in **1**

Bond Distances			
O−C(1)	1.231(2)	N−C(4)	1.460(2)
N−C(1)	1.349(2)	C(1)−C(2)	1.520(2)
N−C(3)	1.454(2)	C(2)−C(2A)	1.523(2)

Bond Angles			
C(1)−N−C(3)	124.6(1)	N−C(1)−C(2)	117.3(1)
C(1)−N−C(4)	120.1(1)	O−C(1)−C(2)	120.9(1)
O−C(1)−N	121.6(1)	C(1)−C(2)−C(2A)	111.5(1)

Torsion Angles	
N−C(1)−C(2)−C(2A)	172.2(1)
C(1)−C(2)-C(2A)−C(1A)	180.0

the IR band at 1674 cm^{-1} characteristic of free TMSA in the gas phase and is assigned to simple loss of the bound, intact, TMSA ligand from the complex. The second pathway (B in Scheme 1) is defined by an IR band in the carbonyl stretching region at 1736 cm^{-1} and by bands in the C−H stretching region at 2826 and 2779 cm^{-1}. The 1736 cm^{-1} band has been assigned to *N*-methylsuccinimide by independent measurement of the IR spectrum with authentic *N*-methylsuccinimide under comparable conditions, and the 2826 and 2779 cm^{-1} bands are assigned to trimethylamine by comparison with its literature spectrum.[33] By characterization of the thermolysis products, pathway B can be identified as involving the cyclization of the TMSA to *N*-methylsuccinimide with elimination of trimethylamine and desorption of both fragments. Such cyclizations of diamides and amic acids upon thermolysis to form imides are known.[34]

Crystal Structures. TMSA. The structure of the uncomplexed TMSA molecule (**1**) is shown in Figure 1. The all-anti configuration of the backbone is the expected configuration for succinamides[35] but differs from the conformations observed with tetraalkylmalonamides.[19,35] However, in both cases, the carbonyl groups on the amides are oriented ca. 180° from each other, presumably to minimize dipole−dipole interactions. Although the backbone in **1** is all-anti, with a C(1)−C(2)−C(2A)−C(1A) angle of 180°, the carbonyl groups are slightly twisted by ca. 7.5° with respect to the carbon backbone, as evidenced by the N−C(1)−C(2)−C(2A) and O−C(1)−C(2)−C(2A) torsion angles (Table 3).

The bond lengths and angles in **1** appear unexceptional. The C(1)−O bond length of 1.231(2) Å and the C(1)−N bond length of 1.349(2) Å are well within the typical C−O bond lengths of 1.23(1) Å and C−N bond lengths of 1.34(2) Å found in *N,N*-dialkylacetamides.[36] As expected, the amide functional group

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Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in **4**

		Bond Distances				
Nd−O(1)	2.381(2)	O(4)−N(4)	1.263(2)	N(2)−C(4)	1.326(3)
Nd−O(2)	2.369(1)	O(5)−N(4)	1.266(2)	N(2)−C(8)	1.462(3)
Nd−O(3)	2.368(1)	O(6)−N(4)	1.219(2)	N(2)−C(7)	1.464(3)
Nd−O(4)	2.552(2)	O(7)−N(5)	1.265(2)	N(3)−C(9)	1.326(3)
Nd−O(5)	2.545(2)	O(8)−N(5)	1.272(2)	N(3)−C(11)	1.462(3)
Nd−O(7)	2.563(2)	O(9)−N(5)	1.217(2)	N(3)−C(12)	1.462(3)
Nd−O(8)	2.510(2)	O(10)−N(6)	1.264(2)	C(1)−C(2)	1.510(3)
Nd−O(10)	2.544(2)	O(11)−N(6)	1.275(2)	C(2)−C(3)	1.530(3)
Nd−O(11)	2.548(2)	O(12)−N(6)	1.218(2)	C(3)−C(4)	1.509(3)
O(1)−C(1)	1.251(2)	N(1)−C(1)	1.328(3)	C(9)−C(10)	1.512(3)
O(2)−C(4)	1.256(2)	N(1)−C(6)	1.459(3)	C(10)−C(10A)	1.515(4)
O(3)−C(9)	1.262(2)	N(1)−C(5)	1.467(3)		

		Bond Angles				
O(8)−Nd−O(11)	76.86(5)	O(1)−Nd−O(4)	99.94(6)	C(4)−N(2)−C(8)	119.0(2)
O(10)−Nd−O(11)	50.42(5)	O(8)−Nd−O(4)	113.16(6)	C(4)−N(2)−C(7)	124.5(2)
O(5)−Nd−O(11)	119.82(6)	O(10)−Nd−O(4)	68.76(6)	C(8)−N(2)−C(7)	116.3(2)
O(3)−Nd−O(4)	149.16(5)	O(5)−Nd−O(4)	49.69(5)	C(9)−N(3)−C(11)	121.2(2)
O(2)−Nd−O(4)	122.24(5)	O(11)−Nd−O(4)	70.15(5)	C(9)−N(3)−C(12)	123.2(2)
O(1)−Nd−O(4)	99.94(6)	O(3)−Nd−O(7)	128.81(5)	C(11)−N(3)−C(12)	115.3(2)
O(8)−Nd−O(4)	113.16(6)	O(2)−Nd−O(7)	76.90(5)	O(6)−N(4)−O(4)	121.9(2)
O(10)−Nd−O(4)	68.76(6)	O(1)−Nd−O(7)	141.79(6)	O(6)−N(4)−O(5)	122.3(2)
O(5)−Nd−O(4)	49.69(5)	O(8)−Nd−O(7)	50.24(5)	O(9)−N(5)−O(7)	122.2(2)
O(11)−Nd−O(4)	70.15(5)	O(10)−Nd−O(7)	128.16(5)	O(9)−N(5)−O(8)	121.5(2)
O(3)−Nd−O(7)	128.81(5)	O(5)−Nd−O(7)	74.28(6)	O(7)−N(5)−O(8)	116.3(2)
O(2)−Nd−O(7)	76.90(5)	O(11)−Nd−O(7)	86.24(6)	O(12)−N(6)−O(10)	122.0(2)
O(1)−Nd−O(7)	141.79(6)	O(4)−Nd−O(7)	70.78(6)	O(12)−N(6)−O(11)	121.3(2)
O(8)−Nd−O(7)	50.24(5)	C(1)−O(1)−Nd	148.24(14)	O(10)−N(6)−O(11)	116.7(2)
O(10)−Nd−O(7)	128.16(5)	C(4)−O(2)−Nd	136.08(13)	O(1)−C(1)−N(1)	120.9(2)
O(5)−Nd−O(7)	74.28(6)	C(9)−O(3)−Nd	155.62(13)	O(1)−C(1)−C(2)	121.1(2)
O(11)−Nd−O(7)	86.24(6)	N(4)−O(4)−Nd	97.12(12)	N(1)−C(1)−C(2)	118.1(2)
O(4)−Nd−O(7)	70.78(6)	N(4)−O(5)−Nd	97.38(12)	C(1)−C(2)−C(3)	114.2(2)
C(1)−O(1)−Nd	148.24(14)	N(5)−O(7)−Nd	94.83(11)	C(4)−C(3)−C(2)	114.8(2)
C(4)−O(2)−Nd	136.08(13)	N(5)−O(8)−Nd	97.18(12)	O(2)−C(4)−N(2)	120.2(2)
O(8)−Nd−O(11)	76.86(5)	N(6)−O(10)−Nd	96.57(11)	O(2)−C(4)−C(3)	119.6(2)
O(10)−Nd−O(11)	50.42(5)	N(6)−O(11)−Nd	96.06(11)	N(2)−C(4)−C(3)	120.1(2)
O(5)−Nd−O(11)	119.82(6)	C(1)−N(1)−C(6)	120.5(2)	O(3)−C(9)−N(3)	121.6(2)
O(3)−Nd−O(4)	149.16(5)	C(1)−N(1)−C(5)	122.9(2)	O(3)−C(9)−C(10)	120.4(2)
O(2)−Nd−O(4)	122.24(5)	C(6)−N(1)−C(5)	116.4(2)	N(3)−C(9)−C(10)	118.0(2)
C(9)−C(10)−C(10A)	111.8(2)				

	Torsional Angles		
N(1)−C(1)−C(2)−C(3)	−176.7(2)	N(3)−C(9)−C(10)−C(10A)	−179.4(2)
C(1)−C(2)−C(3)−C(4)	−73.5(2)	C(9)−C(10)−C(10A)−C(9A)	180.0
C(2)−C(3)−C(4)−N(2)	−82.5(2)		

is planar: its component atoms N, C(1), O, and C(2) are coplanar to within 0.002 Å.

Examination of the Cambridge Structural Database[37] indicates that TMSA is only the third diamide with an unsubstituted ethane bridge. The all-anti conformation found in TMSA is also observed in the other two reported diamides, succinamide and *N,N′*-bis(2,2,6,6-tetramethylpiperidyl-4)succinic acid diamide dihydrate.[38,39]

Ln₂(TMSA)₃(NO₃)₆; Ln = Ce, Pr, Nd, Gd, Yb. With most of the lanthanide nitrates, the isolated TMSA−Ln nitrate compounds possess structures with a 3:2 ligand-to-metal stoichiometry. Crystal structures have been obtained with the lanthanides cerium (**2**), praseodynium (**3**), neodymium (**4**), gadolinium (**5**), and ytterbium (**6**); all are isostructural. A representative structure is shown for the neodymium complex, **4**, in Figure 2. Selected bond lengths, bond angles, and torsional angles in **4** are given in Table 4.

These compounds are dimeric; each 9-coordinate metal is surrounded by three bidentate nitrates, one bidentate chelating succinamide, and one bridging bidentate succinamide. This
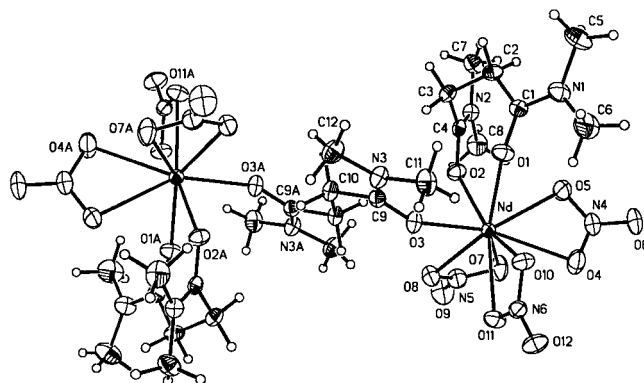
Figure 2. ORTEP illustration of Nd₂(NO₃)₆(TMSA)₃ (**4**).

structure is distorted from either of the two major polyhedra expected for a 9-coordinated complex: a tricapped trigonal prism and a monocapped square antiprism.[40] It appears to be best described as a tricapped trigonal prism: one trigonal face is defined by one of each of the three nitrate oxygen atoms [O(4), O(7), and O(11)], the second trigonal face is defined by the three amide oxygens atoms [O(1), O(2), and O(3)], and each square face is capped by the other bound nitrate oxygen atoms [O(5), O(8), and O(10)]. The short O···O length, 2.15(1) Å, of the nitrate anion is the major cause of the observed distortion from a regular trigonal prism geometry.

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No unusual features are associated with the bidentate nitrate anions, with an average O···O distance of 2.152(8) Å, an average M−O(nitrate) bond length of 2.54(2) Å, and an average O···Nd···O angle of 50.1(3)°. The M−O(nitrate) bond length in **4** is slightly shorter than that in reported Nd(NO$_3$)$_3$−malonamide structures, but this shortening is consistent[41] with the smaller Nd crystal radius expected for the lower 9-coordination found in **4** as compared to the 10-coordination found in Nd(NO$_3$)$_3$−malonamide structures.[19]

The bridging TMSA is remarkably similar in structure to the uncomplexed ligand. The all-anti conformation is maintained with the torsional angles of the succinamide backbone being within 1° of 180° and with the carbonyl groups again oriented 180° from each other. The planarity of the amide functionality is unchanged by lanthanide coordination. The slight shortening of the amide carbonyl bond length to 1.262(2) Å and the slight lengthening of the carbonyl carbon to nitrogen bond length to 1.326(3) Å are consistent with the trends observed upon coordination of simple *N,N*-dialkylacetamides to lanthanide ions.[36]

The M−O(amide) bond length of 2.368(1) Å is appreciably shorter than that observed in the Nd(NO$_3$)$_3$−malonamide structures,[19] which is again consistent with the expected decrease in bond length accompanying the lower coordination number of the Nd−succinamide compound. The M−O−C angle of 155.6(1)° is consistent with the angles observed for simple *N,N*-dialkylacetamides coordinated to lanthanide ions [152(8)°].[36]

Structural features of the chelating TMSA ligand have many similarities to and some differences from the bridging TMSA ligand. The conformation around the amide group remains all-anti; however, as shown in Table 4, the conformer of the chelating ligand does differ from the free or bridging ligand by changing, through two bond rotations, to a gauche conformation. The C(1)−C(2)−C(3)−C(4) torsion angle has changed from ca. 180° in the uncomplexed or bridging ligand to ca. −74° and the C(2)−C(3)−C(4)−N(2) torsion angle has changed from ca. 180° in the uncomplexed or bridging ligand to ca. −83° in its chelated conformation. This rotation greatly reduces the O(amide) to O(amide) distance from 4.924 Å in the bridging succinamide to 2.985 Å in the chelating ligand. The O···O distance of 2.985 Å is slightly longer than that observed in other metal succinamides [2.746 Å found in UO$_2$(NO$_3$)$_3$(tetrabutylsuccinamide)[28] and 2.857 Å found in SnBr$_4$(*N,N'*-diethylsuccinamide)[42] as well as the range of O···O distances (2.803−2.828 Å) found in Nd−malonamide structures.[19]

The planarity of the amide has been slightly altered, with the nitrogen residing 0.035 Å above the plane formed by the three adjacent carbon atoms. The amide carbonyl carbon to oxygen bond has shortened slightly [1.251(2) and 1.256(2) Å] compared to that of the bridging amide, and the carbonyl carbon to nitrogen bond length either is the same or has slightly lengthened [1.326(3) and 1.328(3) Å].

The M−O(amide) bond distances [2.381(2) and 2.369(1) Å] are the same as or slightly longer than that observed in the bridging succinamide fragment. However, the M−O−C angles are markedly less at only 148.2(1) and 136.1(1)° and approach the range of M−O−C angles found in Nd−malonamides (127−139.8°).[19]

The isostructural compounds **2**−**6** span most of the lanthanide series. Despite the changes in metal ion size from Ce to Yb, little difference in amide ligand structure is observed. As

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Table 5. Comparison of M−O Bond Lengths (Å) for Ln(NO$_3$)$_3$·*x*TMSA

Ln(NO$_3$)$_3$·2TMSA[a]

	La	Ce
O$_1$	2.485(2)	2.459(2)
O$_2$	2.509(2)	2.477(2)
O$_3$	2.468(2)	2.4442(14)
O$_4$	2.436(2)	2.412(2)
O$_5$	2.798(2)	2.815(2)
O$_6$	2.654(2)	2.625(2)
O$_8$	2.630(2)	2.602(2)
O$_9$	2.684(2)	2.663(2)
O$_{11}$	2.747(2)	2.734(2)
O$_{12}$	2.660(2)	2.636(2)

Ln(NO$_3$)$_3$·1.5TMSA[b]

	Ce	Pr	Nd	Gd	Yb
O$_1$	2.415(2)	2.405(2)	2.381(2)	2.334(2)	2.259(2)
O$_2$	2.402(2)	2.3809(14)	2.3686(14)	2.316(2)	2.242(2)
O$_3$	2.401(2)	2.385(2)	2.3680(14)	2.319(2)	2.248(2)
O$_4$	2.597(2)	2.575(2)	2.552(2)	2.500(2)	2.426(2)
O$_5$	2.584(2)	2.560(2)	2.545(2)	2.507(2)	2.476(2)
O$_7$	2.604(2)	2.587(2)	2.563(2)	2.509(2)	2.441(2)
O$_8$	2.547(3)	2.527(2)	2.510(2)	2.465(2)	2.406(2)
O$_{10}$	2.585(2)	2.561(2)	2.544(2)	2.495(2)	2.437(2)
O$_{11}$	2.587(3)	2.564(2)	2.548(2)	2.409(2)	2.418(2)

[a] O$_1$, O$_2$ are bidentate TMSA atoms, and O$_3$, O$_4$ are bridging TMSA atoms. O$_5$−O$_{12}$ are bidentate nitrate atoms. [b] O$_1$, O$_2$ are bidentate TMSA atoms, and O$_3$ is a bridging TMSA atom. O$_4$−O$_{11}$ are bidentate nitrate atoms.
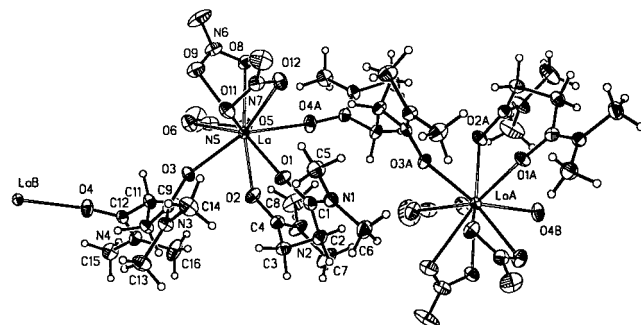

Figure 3. ORTEP illustration of [La(NO$_3$)$_3$(TMSA)$_2$]$_n$ (**7**).

summarized in Table 5, the M−O(amide) bond distances do decrease by ca. 0.15−0.16 Å upon going from Ce to Yb and the O···O distance in the chelating succinamide decreases by ca. 0.08 Å. These changes, however, are not manifested in any dramatic changes in ligand orientation. The torsion angles in compounds **2** and **6** are the same to within 2° in all cases, indicating that the ligands can adapt to changing metal size with only minor perturbations in conformation.

[Ln(TMSA)$_2$(NO$_3$)$_3$]$_n$; Ln = La, Ce. Compounds with a 2:1 TMSA-to-lanthanide stoichiometry were obtained for lanthanum (**7**) and cerium (**8**). Their structures have been determined by X-ray crystallography. The compounds are isostructural; the structure for the lanthanum complex, **7**, is shown in Figure 3. Selected bond lengths, bond angles, and torsional angles for **7** are given in Table 6.

The larger size of these early lanthanides allows expansion to a 10-coordinate environment. These compounds are polymeric; the metal is surrounded by (1) three bidentate nitrates, (2) one bidentate chelating succinamide, and (3) two bridging bidentate succinamides. In this structure, the oxygen atoms bound directly to the lanthanide form a highly irregular polyhedron.

Table 6. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in **7**

Bond Distances

La−O(1)	2.485(2)	O(4)−La(B)	2.436(2)	N(2)−C(8)	1.463(4)
La−O(2)	2.509(2)	O(5)−N(5)	1.247(2)	N(2)−C(7)	1.477(4)
La−O(3)	2.468(2)	O(6)−N(5)	1.276(3)	N(3)−C(9)	1.330(4)
La−O(4A)	2.436(2)	O(7)−N(5)	1.228(3)	N(3)−C(14)	1.467(3)
La−O(5)	2.798(2)	O(8)−N(6)	1.266(3)	N(3)−C(13)	1.472(3)
La−O(6)	2.654(2)	O(9)−N(6)	1.266(3)	N(4)−C(12)	1.328(4)
La−O(8)	2.630(2)	O(10)−N(6)	1.231(3)	N(4)−C(10)	1.460(3)
La−O(9)	2.684(2)	O(11)−N(7)	1.231(3)	N(4)−C(15)	1.462(4)
La−O(11)	2.747(2)	O(12)−N(7)	1.269(3)	C(1)−C(2)	1.515(3)
La−O(12)	2.660(2)	O(13)−N(7)	1.233(3)	C(2)−C(3)	1.547(4)
O(1)−C(1)	1.254(3)	N(1)−C(1)	1.330(3)	C(3)−C(4)	1.513(4)
O(2)−C(4)	1.253(3)	N(1)−C(6)	1.464(3)	C(9)−C(10)	1.514(4)
O(3)−C(9)	1.255(3)	N(1)−C(5)	1.464(3)	C(10)−C(11)	1.532(4)
O(4)−C(12)	1.255(3)	N(2)−C(4)	1.333(4)	C(11)−C(12)	1.506(4)

Bond Angles

O(4A)−La−O(3)	152.84(7)	O(1)−La−O(11)	71.51(6)	C(8)−N(2)−C(7)	115.1(3)
O(4A)−La−O(1)	79.06(7)	O(2)−La−O(11)	134.67(6)	C(9)−N(3)−C(14)	121.0(2)
O(3)−La−O(1)	79.98(6)	O(8)−La−O(11)	96.53(6)	C(9)−N(3)−C(13)	123.5(2)
O(4A)−La−O(2)	80.74(7)	O(6)−La−O(11)	117.77(7)	C(14)−N(3)−C(13)	115.4(2)
O(3)−La−O(2)	76.65(7)	O(12)−La−O(11)	47.14(6)	C(12)−N(4)−C(16)	124.4(2)
O(1)−La−O(2)	72.63(6)	O(9)−La−O(11)	62.59(6)	C(12)−N(4)−C(15)	120.7(2)
O(4A)−La−O(8)	74.73(6)	O(4A)−La−O(5)	69.58(7)	C(16)−N(4)−C(15)	114.9(2)
O(3)−La−O(8)	131.73(6)	O(3)−La−O(5)	113.35(6)	O(7)−N(5)−O(6)	121.2(3)
O(1)−La−O(8)	141.44(6)	O(1)−La−O(5)	130.98(6)	O(5)−N(5)−O(6)	117.5(2)
O(2)−La−O(8)	128.78(6)	O(2)−La−O(5)	66.02(6)	O(10)−N(6)−O(8)	120.6(3)
O(4A)−La−O(6)	115.02(7)	O(8)−La−O(5)	63.45(6)	O(10)−N(6)−O(9)	121.7(3)
O(3)−La−O(6)	77.12(6)	O(6)−La−O(5)	46.50(7)	O(8)−N(6)−O(9)	117.6(2)
O(1)−La−O(6)	149.87(6)	O(12)−La−O(5)	125.70(6)	O(13)−N(7)−O(12)	121.7(3)
O(2)−La−O(6)	83.17(6)	O(9)−La−O(5)	94.68(6)	O(13)−N(7)−O(11)	121.3(3)
O(8)−La−O(6)	68.36(6)	O(11)−La−O(5)	157.09(6)	O(12)−N(7)−O(11)	117.0(2)
O(4A)−La−O(12)	73.78(7)	C(1)−O(1)−La	158.3(2)	O(1)−C(1)−N(1)	120.3(3)
O(3)−La−O(12)	117.55(6)	C(4)−O(2)−La	134.9(2)	O(1)−C(1)−C(2)	120.3(3)
O(1)−La−O(12)	76.65(6)	C(9)−O(3)−La	157.7(2)	N(1)−C(1)−C(2)	119.4(2)
O(2)−La−O(12)	143.13(6)	C(12)−O(4)−La(B)	165.8(2)	C(1)−C(2)−C(3)	111.4(2)
O(8)−La−O(12)	69.21(6)	N(5)−O(5)−La	94.9(2)	C(4)−C(3)−C(2)	114.3(2)
O(6)−La−O(12)	131.74(6)	N(5)−O(6)−La	101.2(2)	O(2)−C(4)−N(2)	120.1(3)
O(4A)−La−O(9)	120.13(7)	N(6)−O(8)−La	98.1(2)	O(2)−C(4)−C(3)	120.2(3)
O(3)−La−O(9)	86.94(6)	N(6)−O(9)−La	95.5(2)	N(2)−C(4)−C(3)	119.6(3)
O(1)−La−O(9)	134.03(6)	N(7)−O(11)−La	95.7(2)	O(3)−C(9)−N(3)	121.7(20)
O(2)−La−O(9)	145.92(6)	N(7)−O(12)−La	100.0(2)	O(3)−C(9)−C(10)	120.6(2)
O(8)−La−O(9)	48.10(6)	C(1)−N(1)−C(6)	124.0(2)	N(3)−C(9)−C(10)	117.6(2)
O(6)−La−O(9)	63.96(7)	C(1)−N(1)−C(5)	119.0(2)	C(9)−C(10)−C(11)	111.4(2)
O(12)−La−O(9)	70.95(6)	C(6)−N(1)−C(5)	116.1(2)	C(12)−C(11)−C(10)	110.0(2)
O(4A)−La−O(11)	117.93(6)	C(4)−N(2)−C(8)	120.4(3)	O(4)−C(12)−N(4)	120.9(2)
O(3)−La−O(11)	70.63(6)	C(4)−N(2)−C(7)	124.3(3)	O(4)−C(12)−C(11)	118.3(2)
N(4)−C(12)−C(11)	120.7(3)				

Torsional Angles

N(1)−C(1)−C(2)−C(3)	151.4(3)	N(3)−C(9)−C(10)−C(11)	174.6(3)
C(1)−C(2)−C(3)−C(4)	82.6(3)	C(9)−C(10)−C(11)−C(12)	−168.2(2)
C(2)−C(3)−C(4)−N(2)	80.7(3)	C(10)−C(11)−C(12)−N(4)	−100.0(3)
O(1)−C(1)−C(2)−C(3)	−28.0(4)	O(3)−C(9)−C(10)−C(11)	−5.2(4)
C(2)−C(3)−C(4)−O(2)	−99.4(3)	C(10)−C(11)−C(12)−O(4)	79.6(3)

In the chelating succinamide ligand, the planarity of the amide functionality has again altered slightly from that of the free ligand, with deviations from the mean plane of the amide of 0.058 Å for N(1) and 0.022 Å for N(2). The amide carbonyl carbon to oxygen bond distances [1.253(3) and 1.254(3) Å] and the carbonyl carbon to nitrogen bond lengths [1.330(3) and 1.333(4) Å] are similar to those observed in the 3:2 structure.

The M−O(amide) bond distances [2.485(2) and 2.509(2) Å] differ slightly; however, the M−O−C angles are markedly different at 158.3(2) and 134.9(2)°, similar to the bond angle difference observed in the 3:2 structure.

The conformational changes in the chelating succinamide from the uncomplexed ligand are also similar to those observed in the 3:2 structure; again, the succinamide changes from the all-anti conformation of the uncomplexed ligand to a gauche conformation, primarily by two C−C rotations at the C(2)−C(3) and C(3)−C(4) bonds. This is manifested in the changes from 180° in the dihedral angles along the succinamide backbone: C(5)−N(1)−C(1)−C(2) = −169.2°; N(1)−C(1)−C(2)−C(3) = 151.4°; C(1)−C(2)−C(3)−C(4) = 82.6°; C(2)−C(3)−C(4)−N(2) = 80.7°; C(3)−C(4)−N(2)−C(8) = −175.4°.

With the bridging succinamide ligand, the amide functionality again remains planar with deviations from the mean plane of the amide of 0.001 Å for N(3) and 0.003 Å for N(4). The amide carbonyl carbon to oxygen bond distances [1.255(3) Å in each instance] and the carbonyl carbon to nitrogen bond lengths [1.330(3) and 1.328(3) Å] are effectively the same as those observed in the 3:2 structure.

The M−O(amide) bond distances [2.468(2) and 2.436(2) Å] are significantly less than those lengths found in the chelating succinamide in the same molecule. However, the M−O−C angles at 157.7(2) and 165.8(2)° are similar to the longer of the two angles present in the bridging succinamide at 158.3-(2)° and are comparable to the bond angle observed with the bridging succinamide in the 3:2 structures.

The conformations found with the bridging succinamides in these 2:1 compounds are perhaps their most interesting feature; they differ in detail from both the uncomplexed ligand (and so with the bridging succinamide found in the 3:2 structure) and the conformers found with the chelating succinamides. Here the succinamide changes from the all-anti conformation of the uncomplexed ligand to a single gauche conformation, primarily
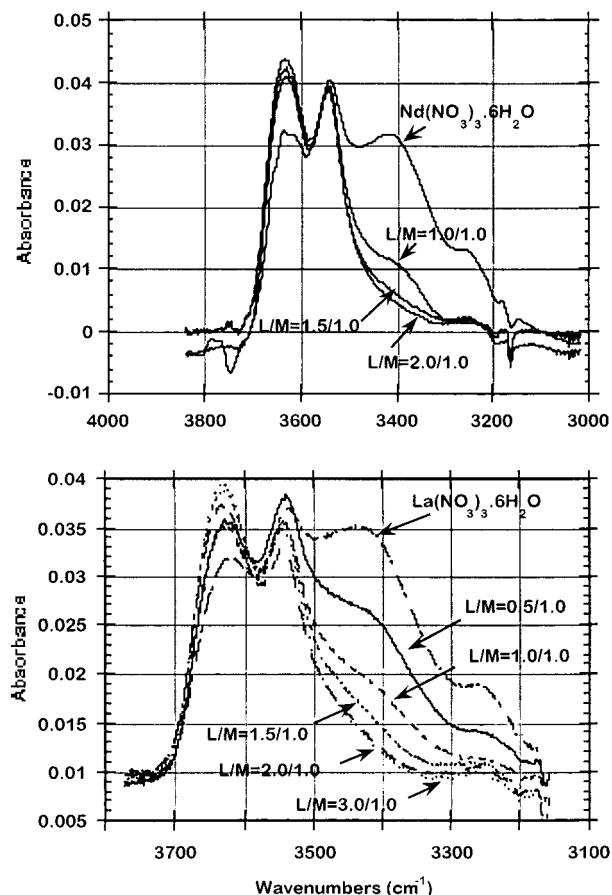
Figure 4. IR spectra of TMSA reactions with La(NO$_3$)$_3$ (bottom) and Nd(NO$_3$)$_3$ (top) in anhydrous CH$_3$CN as a function of ligand-to-metal ratio.

by a single C−C rotation at the C(11)−C(12) bond. This is revealed by the dihedral angles along the succinamide backbone: C(15)−N(4)−C(12)−C(11) = −178.8°; N(4)−C(12)−C(11)−C(10) = 100.0°; C(12)−C(11)−C(10)−C(9) = 168.2°; C(11)−C(10)−C(9)−N(3) = −174.6°; C(10)−C(9)−N(3)−C(14) = 178.5°. This type of conformer deviation from an all-anti configuration has also been observed in the bridging glutaramide ligand found in [UO$_2$(NO$_3$)$_3$(tetrabutylglutaramide)]$_x$.[29]

Infrared Spectroscopic Analysis. Although the solid-state stoichiometries and structures of the TMSA−lanthanide nitrate compounds have been established by TGA and X-ray crystal structure analysis, the question remains as to whether these stoichiometries correspond to the compositions of the TMSA−lanthanide nitrate compounds in solution. To address the question, the substitution of Ln(NO$_3$)$_3$−aquo complexes by TMSA in acetonitrile−water was followed by FT-IR examination of the O−H and amide stretching frequencies at 3600−3200 and 1650−1570 cm^{-1}, respectively, as a function of changing ligand-to-metal ratios. The amide carbonyl and O−H stretching frequencies for the coordinated ligand and H$_2$O were used as a simple, qualitative diagnostic of the M−L solution stoichiometry.

Figure 4 shows the progressive loss of coordinated water[43] as a function of increasing ligand concentration for La(NO$_3$)$_3$, which forms a 2:1 TMSA:Ln compound in the solid state, and Nd(NO$_3$)$_3$, which forms a 3:2 TMSA:Ln compound in the solid state. Clearly, the ligand-to-metal ratio at the point where all

coordinated water has been removed from the metal corresponds to the stoichiometry found in the solid-state structures. Changes in the carbonyl region are complex until the ligand-to-metal ratio observed in the solid-state structure is met, but in all cases, no free ligand is observed until the ligand:lanthanide ratio exceeds that found in the solid-state structures. In addition, at the ligand:lanthanide ratio found in the solid-state structures, their solution IR spectra resemble their solid IR spectra (KBr pellet). Together, these IR experiments indicate that the basic features of these compounds observed in the solid state also are present in solution.

Shifts in the ν(C=O) band to lower energies are often taken as an indication of the strength of the metal−amide interaction. The single amide carbonyl band present in uncomplexed TMSA splits into two or three bands upon coordination to lanthanide nitrates. Although a 30−40 cm^{-1} decrease from the uncomplexed TMSA band is observed for the low-energy amide resonance, the higher energy amide carbonyl band is either similar to or even higher in energy than that found for the uncomplexed ligand. Identical results were obtained when the solid samples were measured either as KBr pellets or as Fluorolube mulls, eliminating the possible contribution of matrix effects. The reason for the observed increase in the ν(C=O) frequency is unknown, although it should be noted that similar behavior has been observed in the IR spectra of tetramethyl-malonamide−lanthanide nitrate compounds.[44,45]

Summary and Conclusions

The coordination chemistry of TMSA with lanthanide nitrates has been examined with a variety of lanthanides that span the entire lanthanide series. The ligand-to-metal stoichiometries of these compounds have been established by TGA and confirmed by selected single-crystal X-ray structure determinations. The nature of these compounds in solution was examined by IR spectroscopic titrations, and the major structural features observed in the solid state appear to be maintained in solution.

This study provides the first X-ray structural data on the TMSA molecule itself and on lanthanide−TMSA compounds and is only the third report concerning any metal−succinamide structure. For TMSA itself, an all-anti configuration was found, consistent with previous observations and indicating that the anti configuration is likely the preferred conformation for compounds with the succinamide backbone. Upon complexation with the larger metal ions La and Ce, compounds with a 2:1 TMSA-to-metal stoichiometry are formed; with the later, smaller lanthanides, compounds with a 3:2 stoichiometry are found. Interestingly, reaction of TMSA with cerium(III) nitrate appears to give, on the basis of both TGA analysis of the isolated product and IR spectroscopic titration, a product with a 2:1 ligand-to-metal stoichiometry. However, single-crystal X-ray structure determinations found material with 3:2 as well as 2:1 stoichiometry. This indicates that the size of Ce(III), although favoring the 2:1, 10-coordinate structure, is very close to the point of transition between 9- and 10-coordination. All smaller lanthanide ions prefer the 3:2, 9-coordinate structure. Structural changes in the coordination chemistry have been documented by performing single-crystal X-ray diffraction analyses on compounds that span the bulk of the lanthanide series. Interestingly, the amide contribution to the metal−amide oxygen bond distance appears quite consistent. Although the size of the metal−amide oxygen bond distance changes from 2.475 Å (**7**)

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(44) Vicentini, G.; Perrier, M. *Inorg. Nucl. Chem.* **1969**, *5*, 957−962.
(45) Vicentini, G. *J. Inorg. Nucl. Chem.* **1972**, *34*, 669−672.

to 2.250 Å (**6**), subtraction of the appropriate metal radius[41] reveals that the average amide contribution to the metal−oxygen bond distance (23 measurements) is a consistent 1.068 ± 0.006 Å.

The TMSA ligand has been shown to be quite versatile, with three identified binding conformers. In the 3:2 structures, the free ligand conformation is maintained while acting as a bridging, bidentate ligand and a bidentate, chelating conformer is also adopted in the same molecule. A comparison of the two conformers shows that TMSA alters to its chelating form primarily by two, ca. 80°, rotations, one involving the $C(sp^3)−C(sp^3)$ bonds in the ethane backbone and the other involving the $C(sp^3)−C(sp^2)$ bond between the ethane backbone and the carbonyl carbon. In the 2:1 structure, a similar chelating conformer is observed but the bridging, bidentate ligand adopts a new conformation that differs from the uncomplexed ligand conformation by a single, ca. 90°, rotation about the $C(sp^3)−C(sp^2)$ bond. By a comparison of the free ligand conformation and the bidentate chelate conformation within the same molecule, the degree and type of conformational reorganization required for chelation are made apparent.

Supporting Information Available: Lists of crystallographic experimental details, final fractional coordinates, thermal parameters, bond distances, bond angles, torsion angles, and least-squares planes and a table summarizing key infrared frequencies for compounds **1**−**8**. This material is available free of charge via the Internet at http://pubs. acs.org.

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