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Coordination of Lanthanide Triflates and Perchlorates with *N*,*N*,*N*′,*N*′-Tetramethylsuccinamide

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Compounds formed from the reaction of *N*,*N*,*N*′,*N*′-tetramethylsuccinamide (TMSA) with trivalent lanthanide salts possessing the poorly coordinating counteranions triflate ($CF_3SO_3^-$) and perchlorate (ClO_4^-) have been prepared and examined. Structural features of these Ln−TMSA compounds have been studied in the solid phase by thermogravimetric analysis, infrared spectroscopy, and, in selected cases, by single-crystal X-ray diffraction and in solution by infrared spectroscopy. Eight-coordinate compounds, $[Ln(TMSA)_4]^{3+}$, derived from coordination of four succinamide ligands to the metal ion could be formed with all lanthanides examined (Ln = La, Pr, Nd, Eu, Yb, Lu). Structural analyses by single-crystal X-ray diffraction were performed for the lanthanide triflate salts $Ln(C_8H_{16}N_2O_2)_4(CF_3SO_3)_3$: Ln = La, compound **1**, monoclinic, $P2_1/n$, $a = 11.0952(2)$ Å, $b = 19.2672(2)$ Å, $c = 24.9759(3)$ Å, $\beta = 90.637(1)°$, $Z = 4$, $D_{calcd} = 1.586$ g cm^{-3}; Ln = Nd, compound **2**, monoclinic, $C2/c$, $a = 24.6586(10)$ Å, $b = 19.3078(7)$ Å, $c = 11.1429(4)$ Å, $\beta = 90.450(1)°$, $Z = 4$, $D_{calcd} = 1.603$ g cm^{-3}; Ln = Eu, compound **3**, monoclinic, $C2/c$, $a = 24.4934(2)$ Å, $b = 19.3702(1)$ Å, $c = 11.1542(1)$ Å, $\beta = 90.229(1)°$, $Z = 4$, $D_{calcd} = 1.617$ g cm^{-3}; Ln = Lu, compound **5**, monoclinic, $C2/c$, $a = 24.2435(4)$ Å, $b = 19.6141(2)$ Å, $c = 11.2635(1)$ Å, $\beta = 90.049(1)°$, $Z = 4$, $D_{calcd} = 1.626$ g cm^{-3}. X-ray analysis was also carried out for the perchlorate salt: Ln = Eu, compound **4**, triclinic, $P\bar{1}$, $a = 10.9611(2)$ Å, $b = 14.6144(3)$ Å, $c = 15.7992(2)$ Å, $\alpha = 106.594(1)°$, $\beta = 91.538(1)°$, $\gamma = 90.311(1)°$, $Z = 2$, $D_{calcd} = 1.561$ g cm^{-3}. In the presence of significant amounts of water, 7-coordinate compounds with mixed aquo−TMSA cation structures $[Ln(TMSA)_3(H_2O)]^{3+}$ (Ln = Yb) and $[Ln(TMSA)_2(H_2O)_3]^{3+}$ (Ln = La, Pr, Nd, Eu, Yb) have been isolated with structural determinations by single-crystal X-ray diffraction obtained for the following species: $Yb(C_8H_{16}N_2O_2)_3(H_2O)(CF_3SO_3)_3$, compound **6**, monoclinic, $P2_1/n$, $a = 8.9443(3)$ Å, $b = 11.1924(4)$ Å, $c = 44.2517(13)$ Å, $\beta = 93.264(1)°$, $Z = 4$, $D_{calcd} = 1.735$ g cm^{-3}; $Yb(C_8H_{16}N_2O_2)_3(H_2O)(ClO_4)_3$, compound **7**, monoclinic, Cc, $a = 19.2312(6)$ Å, $b = 11.1552(3)$ Å, $c = 19.8016(4)$ Å, $\beta = 111.4260(1)°$, $Z = 4$, $D_{calcd} = 1.690$ g cm^{-3}; $Yb(C_8H_{16}N_2O_2)_2(H_2O)_3(CF_3SO_3)_3$, compound **8**, triclinic, $P\bar{1}$, $a = 8.6719(1)$ Å, $b = 12.2683(2)$ Å, $c = 19.8094(3)$ Å, $\alpha = 75.815(1)°$, $\beta = 86.805(1)°$, $\gamma = 72.607(1)°$, $Z = 2$, $D_{calcd} = 1.736$ g cm^{-3}. Unlike in the analogous nitrate salts, only bidentate binding of the succinamide ligand to the lanthanide metal is observed. IR spectroscopy studies in anhydrous acetonitrile suggest that the solid-state structures of these Ln−TMSA compounds are maintained in solution.

Introduction

The use of diamides as selective extractants for the actinides and lanthanides relevant to nuclear fuel reprocessing is an area of active research.[1−11] One area of particular interest concerns the molecular structures of the extracted species. Both solution structural studies and single-crystal solid-state structural work have been performed in an attempt to better understand the structure/reactivity patterns of diamide complexation to f-block metal ions.[12] Most of this research has focused on the malonamides, molecules where the two amide functional groups are attached to a single sp^3 carbon. The succinamides, where the two amide functional groups are attached in a 1,2-fashion to an ethane bridge, have also been examined as potential actinide complexing agents; although few structural studies of the succinamides with f-block metal ions are known.

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Over the past few years, our group has studied amides and diamides and their interactions with f-block metal ions.[5,11,13−18] As part of this investigation, we recently described the coordination of *N*,*N*,*N*′,*N*′-tetramethylsuccinamide (TMSA, $Me_2NC(O)CH_2CH_2C(O)NMe_2$) with a number of lanthanide nitrates.[17] In that report, we found that the succinamide ligand formed compounds possessing both 3:2 and 2:1 TMSA:Ln^{3+} stoichiometries. These compounds contain both bridging and chelating modes of coordination for TMSA, with the three nitrate counteranions being bound to the metal in a bidentate fashion.

Previous studies[19−23] with the diamide *N*,*N*,*N*′,*N*′-tetramethylmalonamide (TMMA, $Me_2NC(O)CH_2C(O)NMe_2$) used a combination of elemental analysis, infrared (IR) spectroscopy, conductance measurements, and single-crystal X-ray diffraction structure analyses to conclude that with the poorly coordinating counteranions hexafluorophosphate (PF_6^-) and perchlorate (ClO_4^-), compounds are formed with diamide-to-metal ratios higher that those found with their analogous nitrate salts. Unlike the nitrate salts, no evidence was found for anion binding to the metal's primary coordination sphere. In the presence of sufficient molar quantities of TMSA, a lack of anion binding to the metal also might be expected. This would leave further coordination sites available for additional TMSA binding as compared to the nitrate salt. However, because of the differing coordination types and numbers found in our prior study of the nitrate salts, the number and type of diamide coordination expected for TMSA in such systems was uncertain. This prompted an investigation into the coordination chemistry of TMSA with lanthanide salts containing relatively poorly coordinating counteranions. In this report, we describe the products formed from the reaction of lanthanide triflates and perchlorates with TMSA. The products' structures and the nature of the metal−ligand interactions have been examined in the solid state by thermogravimetric analysis (TGA), IR spectroscopy, and single-crystal X-ray diffraction. We have also performed infrared spectroscopic studies in anhydrous and in wet organic solvents to evaluate whether the observed solid-state structures are maintained in solution.

Experimental Section

Materials and Methods. $La(SO_3CF_3)_3\cdot xH_2O$, $Pr(SO_3CF_3)_3\cdot xH_2O$, $Nd(SO_3CF_3)_3\cdot xH_2O$, $Eu(SO_3CF_3)_3\cdot xH_2O$, $Yb(SO_3CF_3)_3\cdot xH_2O$, $La(ClO_4)_3\cdot 6H_2O$, and $Ce(ClO_4)_3\cdot 6H_2O$ were obtained from Alfa/Aesar Chemicals and used without further purification. Aqueous solutions of $Nd(ClO_4)_3$ and $Yb(ClO_4)_3$ (40 wt %) and solid $Lu(SO_3CF_3)_3\cdot xH_2O$ were obtained from Aldrich Chemical Co. TMSA was prepared as previously described.[17] Thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were run on a Seiko Series 320 calorimeter. Samples were run under a dry O_2 purge and with a temperature ramp of 1 °C/min. Volatile materials evolved from the TGA experiment were monitored by tandem Fourier transform infrared spectroscopy (FT-IR). All infrared data were collected on a Nicolet 750 FT-IR spectrometer.

Infrared data were collected to monitor the reaction of TMSA with $Ln(SO_3CF_3)_3\cdot xH_2O$ or $La(ClO_4)_3\cdot xH_2O$ dissolved in CH_3CN. In these experiments, 0.0269 mmol of the lanthanide hydrate was stirred in 1 mL of CH_3CN at room temperature over a stoichiometric range of TMSA, such that TMSA:Ln = 0.5−5.0. Spectra were collected on each sample using a 0.015 mm path length cell outfitted with either CaF_2 (when using mixed organic/aqueous solvents) or NaCl plates (when using anhydrous CH_3CN as the solvent).

Preparation of $Ln(TMSA)_4(SO_3CF_3)_3$ (Ln = La, Pr, Nd, Eu, Yb, Lu). A solution containing 4 equiv of TMSA in ethanol was added with stirring to a solution composed of 0.1 g of $Ln(SO_3CF_3)_3$ in 5.0 mL of ethanol. Evaporation of the solvent at room temperature left a crude oil. When the oil was triturated with a 5-fold excess volume of diethyl ether, the product formed as a powder in near-quantitative yield. Crystalline needles were obtained from absolute ethanol by vapor diffusion with diethyl ether at 5 °C.

Preparation of $Ln(TMSA)_4(ClO_4)_3$ (Ln = La, Ce, Nd, Yb). Either as a methanolic solution ($La(ClO_4)_3\cdot 6H_2O$, $Ce(ClO_4)_3\cdot 6H_2O$) or as a 40 wt % aqueous solution ($Nd(ClO_4)_3$, $Yb(ClO_4)_3$), 0.1 mmol of the $Ln(ClO_4)_3$ was added to a stirred solution composed of 0.42 mmol of TMSA dissolved in 1.0 mL methanol. (*Warning! Perchlorate salts are potentially explosive. They should be handled in small quantities and with caution.*) Then 1.5 mL (9 mmol) of triethyl orthoformate was added, and the solution volume was slowly reduced with heating to approximately 0.5 mL total volume. At this point, a solid precipitated. The solution was cooled, the liquid was decanted, the residual solid was washed with ether three times and dried under vacuum, and then the solid was redissolved in a minimum of warm ethanol. Small, clear crystals precipitated from solution upon sitting overnight at 5 °C.

Preparation of $Ln(TMSA)_2(H_2O)_3(SO_3CF_3)_3$ (Ln = La, Pr, Nd, Eu, Yb, Lu). Two milliliters of a 0.1 mM $Ln(SO_3CF_3)_3$ solution in methanol was combined with 2.0 equiv of TMSA. In the case of the lanthanum and praseodymium salts the solution volume was reduced to 1.5 mL, placed in contact with diethyl ether vapor, and refrigerated. Fine needles precipitated from solution over a 3 day period in 20% yield. With the lanthanides Nd, Eu, and Yb, this approach did not yield a crystalline product. With these lanthanides, the reaction solvents were evaporated to yield crude oils. The oils then were triturated with a 5:1 excess volume of diethyl ether to form pastes. Excess diethyl ether was decanted off, and the residual pastes were left exposed to the atmosphere; these pastes solidified upon standing overnight. The solids were further washed in diethyl ether, air-dried, and dissolved in 0.5 mL of 2-propanol. Solids precipitated from these solutions after cooling to 5 °C in 20−40% yield. Crystallization of the solids was accomplished from an 2-propanol solution in contact with diethyl ether vapor at 5 °C. The solids were air-dried at room temperature before infrared and thermal analyses were performed.

Preparation of $Ln(TMSA)_2(H_2O)_3(ClO_4)_3$ (Ln = Ce, Yb). The combination of 0.2 g of $Ln(ClO_4)_3(H_2O)_x$ with 2.0 equiv of TMSA in methanol followed by solvent evaporation was performed and yielded oily residues. The residues then were triturated with diethyl ether and air-dried overnight to form pastes. Recrystallization of the pastes was difficult; however, crystalline material was obtained by contacting 0.2 g of solid in 2.0 mL of wet methanol (3% water) with 2-propanol vapor at 5 °C. Yields of crystalline materials were around 20%. The crystalline solids were then air-dried at room temperature before infrared and thermal analysis.

Preparation of $Ln(TMSA)_3(H_2O)(CF_3SO_3)_3$ (Ln = Yb, Lu) and $Yb(TMSA)_3(H_2O)(ClO_4)_3$. These compounds were occasionally isolated during attempts to prepare the 4:1 complexes as described above in the absence of added triethyl orthoformate (perchlorate salt).

X-ray Crystallography. The following conditions were used to prepare single crystals for analysis by X-ray diffraction: $La(TMSA)_4(CF_3SO_3)_3$ (**1**), slow cooling of a saturated ethanol solution; $Nd(TMSA)_4(CF_3SO_3)_3$ (**2**), vapor diffusion of diethyl ether into an acetonitrile solution; $Eu(TMSA)_4(CF_3SO_3)_3$ (**3**), vapor diffusion of diethyl ether into a 2-propanol solution; $Eu(TMSA)_4(ClO_4)_3$ (**4**), vapor diffusion of

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Table 1. Crystallographic Data for Compounds 1 − 8

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
empirical formula	$C_{35}H_{64}F_9LaN_8O_{17}S_3$	$C_{35}H_{64}F_9NdN_8O_{17}S_3$	$C_{35}H_{64}F_9EuN_8O_{17}S_3$	$C_{32}H_{64}Cl_3EuN_8O_{20}$	$C_{35}H_{64}F_9LuN_8O_{17}S_3$	$C_{27}H_{50}F_9YbN_6O_{16}S_3$	$C_{24}H_{50}Cl_3YbN_6O_{19}$	$C_{19}H_{38}F_9YbN_4O_{16}S_3$
fw	1275.03	1280.36	1288.08	1139.22	1311.09	1154.95	1006.09	1018.75
temp, K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	Cc (No. 9)	$P\bar{1}$ (No. 2)
a, Å	11.0952(2)	24.6586(10)	24.4934(2)	10.9611(2)	24.2435(4)	8.9443(3)	19.2312(6)	8.6719(1)
b, Å	19.2672(2)	19.3078(7)	19.3702(1)	14.6144(3)	19.6141(2)	11.1924(4)	11.1552(3)	12.2683(2)
c, Å	24.9759(3)	11.1429(4)	11.1542(1)	15.7992(2)	11.2635(1)	44.2517(13)	19.8016(4)	19.8094(3)
α, deg	90	90	90	106.594(1)	90	90	90	75.815(1)
β, deg	90.637(1)	90.450(1)	90.229(1)	91.538(1)	90.049(1)	93.264(1)	111.4260(1)	86.805(1)
γ, deg	90	90	90	90.311(1)	90	90	90	72.607(1)
V, Å^3	5338.8(1)	5305.0(3)	5291.98(7)	2424.37(7)	5356.0(1)	4422.8(3)	3954.4(2)	1949.48(5)
Z	4	4	4	2	4	4	4	2
density, ρ_{calcd}, g cm^{-3}	1.586	1.603	1.617	1.561	1.626	1.735	1.690	1.736
abs coeff, μ, cm^{-1}	10.20	12.00	14.07	15.38	20.62	2.364	2.648	2.667
R1^a ($I > 2\sigma(I)$/ all data)	0.0428/ 0.0625	0.0591/ 0.1195	0.0601/ 0.0756	0.0450/ 0.0713	0.0239/ 0.0279	0.0525/ 0.0631	0.0393/ 0.0399	0.0843/ 0.0885
wR2^b ($I > 2\sigma(I)$/ all data)	0.0901/ 0.1070	0.1236/ 0.1643	0.1545/ 0.1762	0.0934/ 0.1136	0.0603/ 0.0676	0.0958/ 0.1015	0.1036/ 0.1067	0.2142/ 0.2237

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

diethyl ether into an acetonitrile solution; $Lu(TMSA)_4(CF_3SO_3)_3$ (**5**), vapor diffusion of diethyl ether into a 2-propanol solution; $Yb(TMSA)_3(H_2O)(CF_3SO_3)_3$ (**6**), slow cooling of a saturated ethanol solution; $Yb(TMSA)_3(H_2O)(ClO_4)_3$ (**7**), slow cooling of a saturated methanol solution; $Yb(TMSA)_2(H_2O)_3(CF_3SO_3)_3$ (**8**), vapor diffusion of diethyl ether into an ethanol solution.

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 $B = 1.2U_{eqv}(C_{methylene})$ or $1.5U_{eqv}(C_{methyl})$. Non-hydrogen atoms were refined with anisotropic temperature factors. The crystallographic parameters are summarized in Table 1.

Interestingly, although **1**−**3** and **5** all initially appeared to be isostructural, the La derivative (**1**) did not exhibit systematic absences consistent with a *C*-centered Bravais lattice. Thus, **1** was solved in the primitive space group $P2_1/n$, necessitating the refinement of the entire formula unit. The heavier, smaller lanthanide analogues **2**, **3**, and **5** were successfully solved and refined in the higher symmetry $C2/c$, but this required that one anion be disordered across a 2-fold axis. The S2 anion in these compounds was indeed observed to be disordered, and the disorder was successfully modeled with each atom in this anion (S2, O8−10, C18, F4−F6) fractionally off the 2-fold axis. Each of these atoms was refined at 50% occupancy.

Although complex **6** appeared to exhibit some minor disorder of one anion (S3), it was not possible to resolve a stable disorder model. It was estimated that the maximum disorder present does not exceed 10% and that several atomic positions would be common to both models. Thus, the refinement in one ordered orientation actually proceeded smoothly with only one large residual peak unaccounted for.

Compound **7** never produced high-quality single crystals, and the refinement of this complex suffered from weak data. Most of this can be attributed to the high thermal motion normally observed for perchlorate salts. It was not possible to refine a disorder model for the anions. In the final refinement of this complex several atoms could not be refined anisotropically and were refined isotropically only. These atoms include O2, O7, C1, C4, C9, C10, and C17.

Complex **8** exhibited very high thermal motion of the anions compared to the Yb cation complex. The thermal parameters suggested rotational disorder about the S−C bond, but again this was not resolvable into reasonable disorder models. The high thermal motion of the anions led to higher than normal final residuals for this complex; however, the key features of the cation appear to be reasonably well resolved.

Results

Thermal Decomposition Behavior of $Ln(SO_3CF_3)_3$ Hydrates and Their TMSA Salts. The thermal behavior of hydrated lanthanide triflates has been reported previously.[24,25] However, because of some inconsistencies in the assignments of specific thermal events, and since the as-received triflate salts contained varying amounts of water, we briefly examined the thermal behavior of simple hydrated lanthanide triflates. TGA, DTA, and DSC scans were run at a 1 °C/min scan rate, from 25 to 1100 °C, under an O_2 purge with the offgases being examined by FT-IR. To establish a baseline for the TMSA−Ln complexes, each hydrated system was examined in triplicate.

The lanthanide triflates, having the approximate composition $Ln(SO_3CF_3)_3 \cdot 9H_2O$, begin losing water below 25 °C and are completely dehydrated below 200 °C. The anhydrous $Ln(SO_3CF_3)_3$ decomposes between 350 and 600−700 °C with evolution of SO_2 and COF_2 to give LnF_3. Further small weight losses are observed from 700 to 1100 °C for each LnF_3 compound and are presumed to be associated with the formation of lanthanide oxyfluorides and finally the stable lanthanide oxide.

Crystalline $Ln(TMSA)_4(SO_3CF_3)_3$ compounds show no weight loss up to 150−200 °C. Near 180 °C, DTA and DSC indicate a sharp endothermic phase change consistent with melting of the TMSA complex. Above this melting temperature, the TGA shows a continuous weight loss up to 325 °C. Tandem TGA-IR analysis of the volatile material indicates that this loss corresponds to removal of TMSA. Above 325 °C, exothermic cyclization of tetramethylsuccinnamide to the *N*-methylsuccinimide with concomitant loss of trimethylamine is observed. Such behavior has been previously observed during thermolysis of other lanthanide−TMSA salts.[17] This event is followed by stepwise losses and decomposition of triflate anion as described above for pure $Ln(SO_3CF_3)_3$. At 600 °C, the observed weight was consistently 4−12% higher than the theoretical LnF_3 weight. This deviation dropped to a minimum of between 0.4 and 2% at 700 °C for each complex. The agreement between the observed and calculated weights for the oxide at 1100 °C was within 2% for all compounds examined (Table 2). This indicates

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Table 2. TGA Results for TMSA−Ln Triflate Compounds

compd	exptl wt (mg) of Ln_2O_3 at 1100 °C	theor wt (mg)	diff (%)	exptl wt (mg) of LnF_3 at 700 °C	theor wt (mg)	diff (%)
$La(TMSA)_4(CF_3SO_3)_3$	2.20	2.23	1.3	2.30	2.31	0.43
$Pr(TMSA)_4(CF_3SO_3)_3$	1.89	1.92	1.5	2.40	2.39	0.42
$Nd(TMSA)_4(CF_3SO_3)_3$	3.76	3.80	1.0	2.23	2.16	3.2
$Eu(TMSA)_4(CF_3SO_3)_3$	3.49	3.53	1.1	3.17	3.10	2.2
$Yb(TMSA)_4(CF_3SO_3)_3$	2.53	2.54	0.4	2.97	3.08	3.5
$Lu(TMSA)_4(CF_3SO_3)_3$	4.50	4.58	1.7	2.35	2.31	1.7
$Yb(TMSA)_3(H_2O)(CF_3SO_3)_3$	2.54	2.52	0.8	3.08	3.06	0.65
$Lu(TMSA)_3(H_2O)(CF_3SO_3)_3$	2.79	2.68	3.7	3.20	3.14	1.9
$Pr(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	2.99	3.20	6.5	3.72	3.68	1.09
$Nd(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	3.17	3.13	1.2	3.75	3.72	0.81
$Eu(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	2.62	2.67	1.8	3.17	3.10	2.26
$Yb(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	2.54	2.52	0.86	2.94	3.06	4.08
$Lu(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	4.39	4.35	0.92	6.09	6.06	0.50

Table 3. Further TGA Results for Mixed Ln−TMSA−Aquo Compounds

compd	exptl wt at 200 °C	theor wt at 200 °C	diff (%)
$Yb(TMSA)_3(H_2O)(CF_3SO_3)_3$	15.14	15.24	0.70
$Pr(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	16.97	17.10	0.76
$Nd(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	17.32	17.40	0.46
$Eu(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	14.00	13.93	0.50
$Yb(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	15.14	15.49	2.26
$Lu(TMSA)_2(H_2O)_3(CF_3SO_3)_3$	25.28	25.27	0.04
$Yb(TMSA)_3(H_2O)(ClO_4)_3$	14.30	14.21	0.63
$Ce(TMSA)_2(H_2O)_3(ClO_4)_3$	10.13	10.14	0.10
$Yb(TMSA)_2(H_2O)_3(ClO_4)_3$	13.29	13.21	0.61

that the overall stoichiometry can be obtained by monitoring the weight change resulting from the conversion either to LnF_3 at 700 °C or to Ln_xO_y at 1100 °C.

The weight loss corresponding to dehydration of $Ln(TMSA)_x(H_2O)_y(SO_3CF_3)_3$ compounds occurs in one step at temperatures between 30 and 60 °C for La, Pr, Nd, Eu, and Yb. The compound $Lu(TMSA)_2(H_2O)_3(SO_3CF_3)_3$ shows well-resolved, two-step water losses at about 26 °C and at 82 °C. From this point on, further decomposition events are similar to those of the $Ln(TMSA)_4(SO_3CF_3)_3$ compounds described above. The results in Table 3 monitor the loss of water measured between 25 and 150 °C. Typical weight loss uncertainties in this range were generally below 1% for the two trials run for each compound listed. From the dehydrated species at 150 °C, the number of ligands was determined by ascribing the weight loss to 700 °C to the formation of the LnF_3 compound as described above. For the large weight loss associated with the mass of two, three, or four ligands, the agreement between the calculated and observed weight losses is good, with discrepancies typically below 2%.

Thermal Decomposition of $Ln(ClO_4)_3$ Hydrates and Their TMSA Salts. $La(ClO_4)_3{\cdot}6H_2O$ and $Ce(ClO_4)_3{\cdot}6H_2O$ begin losing water below 25 °C and are completely dehydrated below 200 °C. Other $Ln(ClO_4)_3$ hydrates were available only as aqueous solutions and so were not investigated thermally. Perchlorate decomposition began near 450 °C, was exothermic, and in most cases, resulted in the ejection of sample from the sample pan.

For crystalline $Ln(TMSA)_4(ClO_4)_3$ compounds, no weight loss occurred up to 220 °C. Decomposition began with loss of TMSA and continued with decomposition of perchlorate and formation of the oxide near 450 °C. Concomitant ejection of sample from the sample pan was again observed with this exothermic decomposition. Therefore, mass changes from this point were highly variable and therefore unreliable. Use of the results from the TGA analyses of the perchlorate salts was therefore restricted to the analysis of the mass changes from 25 to 200 °C.

Table 4. Infrared Data (cm^{-1}) for TMSA−Ln Perchlorate Complexes

	ν(M-OC)		$\nu(ClO_4^-)$	
compd	KBr	CH_3CN	KBr	CH_3CN
$La(TMSA)_4(ClO_4)_3$	1615	1614	1092	1100
$Ce(TMSA)_4(ClO_4)_3$	1615	1614	1092	1100
$Nd(TMSA)_4(ClO_4)_3$	1614 1625 (sh)	1615	1092	1100
$Yb(TMSA)_4(ClO_4)_3$	1619.5 1634 (sh)	1614 1646	1089	1101
$Yb(TMSA)_3(H_2O)(ClO_4)_3$	1616	1614	1150 1167 (sh) 1089	1102
$Ce(TMSA)_2(H_2O)_3(ClO_4)_3$	1613	1609.7	1146 1110 1090	1102

For the perchlorate compound $Yb(TMSA)_3(H_2O)(ClO_4)_3$, TGA shows a one-step weight loss corresponding to one water at temperatures between 30 and 60 °C (Table 3). With $Ce(TMSA)_2(H_2O)_3(ClO_4)_3$ as well, the weight loss corresponding to thermal displacement occurred in one step at temperatures between 30 and 60 °C. On the other hand, $Yb(TMSA)_2(H_2O)_3(ClO_4)_3$ was observed to lose water in two steps, one near 60 °C and the other near 110 °C. The results in Table 3 list the weight loss of water measured between 25 and 150 °C. Typical weight loss discrepancies in this range were below 1%.

Infrared Spectra of $Ln(ClO_4)_3$ Hydrates and Their TMSA Salts. The infrared spectra of lanthanide perchlorate hydrates and of the $Ln(TMSA)_4(ClO_4)_3$ compounds show little change as the lanthanide is varied. With these 4:1 TMSA adducts, the vibrations at 3200−3400 cm^{-1} characteristic of metal-coordinated water[26] were not observed. Key bands and their assignments are summarized in Table 4.

The infrared spectra of the $Ln(TMSA)_2(H_2O)_3(ClO_4)_3$ adducts dissolved in anhydrous CH_3CN do show the metal-coordinated water band in the 3200−3400 cm^{-1} region. The presence of metal-coordinated water has little influence on the perchlorate band at 1003 cm^{-1}. The amide region is quite similar to that observed with the 4:1 complexes.

At the concentrations examined, water-related bands were not observed in the infrared spectrum of the $Yb(TMSA)_3(H_2O)(ClO_4)_3$ dissolved in anhydrous CH_3CN. The amide region appears quite similar to that observed with the other Ln−TMSA perchlorate compounds.

Infrared Spectra of $Ln(SO_3CF_3)_3$ Hydrates and Their TMSA Salts. The infrared spectra of $Ln(TMSA)_x(H_2O)_y(SO_3$-

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(26) Nakamoto, K. *Infrared and RAMAN Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley-Interscience: New York, 1978.

$CF_3)_3$ ($x = 2-4$, $y = 0-3$) compounds, like those of the analogous perchlorate salts, are characterized by the carbonyl vibration around 1615 cm^{-1}. Another feature of the spectrum for the triflate compounds is the collapse from a complex band structure in the region between 1130 and 1360 cm^{-1} to a single strong band near 1270 cm^{-1} and a weak band near 1225 cm^{-1} as the compound's TMSA to Ln ratio increases. For the 3:1 and 4:1 TMSA:Ln adducts, the vibrations at 3200−3400 cm^{-1} characteristic of metal-coordinated water[15] cannot be observed. However, for the $Ln(TMSA)_2(H_2O)_3(SO_3CF_3)_3$ species, bands due to coordinated water in the 3200−3400 cm^{-1} region are observed. Key bands and their assignments are summarized in Table 5.

Table 5. Infrared Data (cm^{-1}) for TMSA−Ln Triflate Complexes

	ν(M−OC)		$\nu_i(CF_3SO_3^-)$	
compd	KBr	CH_3CN	KBr	CH_3CN
$La(TMSA)_4(CF_3SO_3)_3$	1615 1620 (sh)	1614	1032 (s) 1267 (s)	1032 1272 (s)
$Pr(TMSA)_4(CF_3SO_3)_3$	1622 (sh) 1614	1613	1030 (s) 1034 (sh) 1267 (s)	1032 (s) 1041 (sh) 1272 (s)
$Nd(TMSA)_4(CF_3SO_3)_3$	1615	1614	1031 (s) 1042 (sh) 1267 (s)	1031 (s) 1041 (sh) 1272 (s)
$Eu(TMSA)_4(CF_3SO_3)_3$	1617	1617	1032 (s) 1034 (sh) 1267 (s)	1031 (s) 1034 (sh) 1272 (s)
$Yb(TMSA)_4(CF_3SO_3)_3$	1617	1615	1032 (s) 1038 (sh) 1267 (s)	1032 (s) 1272 (s)
$Lu(TMSA)_4(CF_3SO_3)_3$	1617	1615	1032 (s) 1038 (sh) 1267 (s)	1032 (s) 1272 (s)
$Yb(TMSA)_3(H_2O)$-$(CF_3SO_3)_3$		1616		1138 (sh) 1154 (w) 1225 (w) 1237 (vw) 1272 (s)
$La(TMSA)_2(H_2O)_3$-$(CF_3SO_3)_3$	1615 1667 (w)	1612	1304 1282 1267 1225 1229 1160 1031 1026 (sh)	1307 (w) 1271 (s) 1238 1223 1157 1032
$Pr(TMSA)_2(H_2O)_3$-$(CF_3SO_3)_3$		1610 1638 (w)		1156 (w) 1223 (w) 1238 (vw) 1272 (s) 1309 (vw)
$Nd(TMSA)_2(H_2O)_3$-$(CF_3SO_3)_3$		1612 1657 (w)		1309 1272 1239 1225 1157 1033
$Eu(TMSA)_2(H_2O)_3$-$(CF_3SO_3)_3$		1612 1642 (w)		1156 (w) 1224 (w) 1238 (vw) 1272 (s) 1311 (vw)
$Yb(TMSA)_2(H_2O)_3$-$(CF_3SO_3)_3$		1615 1649 (w)		1156 (w) 1225 (w) 1240 (vw) 1272 (s) 1316 (vw)
$Lu(TMSA)_2(H_2O)_3$-$(CF_3SO_3)_3$		1614	1285 1255 (w) 1231 (w) 1165 1032 1042 (sh)	

Infrared Titration Experiments. The amount of water present in the as-received $Ln(SO_3CF_3)_3 \cdot xH_2O$, $La(ClO_4)_3 \cdot xH_2O$, and $Ce(ClO_4)_3 \cdot xH_2O$ reagents was accurately determined by TGA as described above immediately before the titration experiment. For each system, the addition of four TMSA ligands resulted in the complete disappearance of the 3200−3400 cm^{-1} band characteristic for metal-bound water.[26] Additionally, beyond this TMSA/Ln endpoint, the appearance of unbound TMSA was observed at 1645 cm^{-1}.

Discussion

Compounds possessing a 4:1 TMSA:Ln composition can be prepared from the lanthanide triflates as well as the early lanthanide perchlorates (Ln = La, Ce) by adding stoichiometric or greater quantities of TMSA to an alcohol solution of the lanthanide followed by solvent removal and crystallization of the residual solid. However, if this approach is used with the later lanthanide perchlorates, perhaps because the lanthanide source (40 wt % in water) introduces large amounts of water along with the lanthanide reagent, mixed TMSA−aquo species possessing a lower TMSA:Ln ratio are obtained. However, compounds with the 4:1 TMSA:Ln stoichiometry can be readily prepared with these later lanthanide perchlorates by adding an in situ dehydrating agent, triethyl orthoformate, an approach that has been reported previously for preparing *N*,*N*,*N*′,*N*′-tetramethylmalonamide−Ln compounds.[20]

Mixed aquo−TMSA compounds possessing a 2:1 TMSA:Ln stoichiometry can also be prepared by mixing the lanthanide salt with a stoichiometric amount of TMSA. However, the mixed aquo−TMSA compounds of a 3:1 TMSA:Ln stoichiometry could not be isolated by a simple stoichiometric reaction of TMSA with the lanthanide salt; $[Yb(TMSA)_3(H_2O)]^{3+}$ was found only by serendipity from the reaction of lanthanide triflates or perchlorates with excess TMSA.

For the TMSA complexes of lanthanide triflates, thermogravimetric analysis of these products is consistent in all cases with their proposed formulas. Two features of the TGA data indicate the absence of metal-coordinated water in all of the 4:1 TMSA:Ln adducts. First, since the loss of water coordinated to the metal typically occurs below 200 °C, the absence of any observed weight loss in this region itself supports an anhydrous formula composition. Second, as shown in Table 2, there is good agreement between the observed and calculated weight losses for a formula weight based solely on an anhydrous 4:1 TMSA:Ln stoichiometry. For the proposed 3:1 and 2:1 TMSA:Ln compounds, the amount of water present was assigned by comparing the weight losses from ambient temperature to 200 °C for the targeted stoichiometry; the number of TMSA ligands present in the molecule was obtained by fitting the observed weight losses from 200 to 700 °C from an anhydrous TMSA−Ln triflate salt to its corresponding LnF_3 or by fitting the observed weight losses from 200 to 1100 °C from an anhydrous TMSA−Ln triflate to its corresponding Ln oxide. Again there is good agreement between the observed and calculated weight losses for the proposed compound formulations.

Infrared analysis of these isolated compounds both as solids and upon dissolution in anhydrous acetonitrile also supports an anhydrous formula for the $Ln(TMSA)_4(SO_3CF_3)_3$ compounds; both the solid and solution IR spectra show an absence of any bands in the 3200−3400 cm^{-1} region characteristic for metal-coordinated water.[26] However, these bands are also not observed for $Yb(TMSA)_3(H_2O)(SO_3CF_3)_3$, where the presence of a water molecule was detected by the TGA. However, control experi-

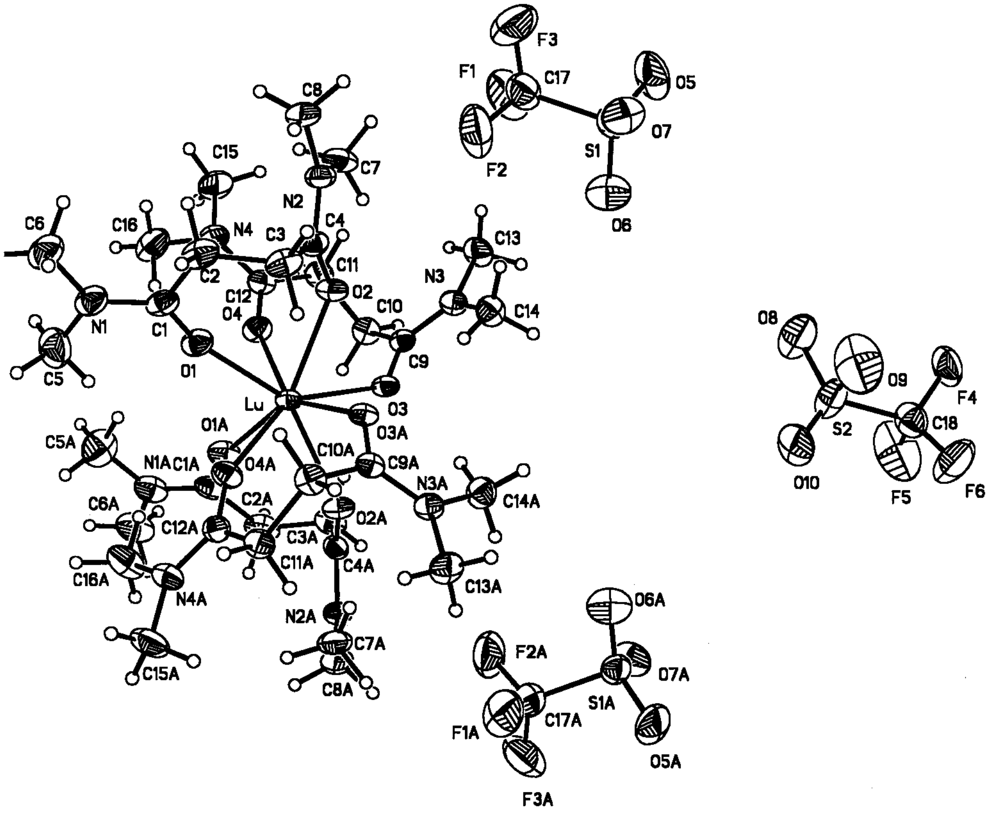

Figure 1. ORTEP illustration of Lu(TMSA)$_4$(CF$_3$SO$_3$)$_3$ (**5**).

ments suggest that under the concentrations used in these IR measurements 1 equiv of water would be difficult to detect. Perhaps because of the greater water-to-Ln ratio present in the Ln(TMSA)$_2$(H$_2$O)$_3$(SO$_3$CF$_3$)$_3$ compounds, metal-coordinated water is detected both in the solid-state IR and in the anhydrous acetonitrile solution spectra.

Although the thermal instability of the perchlorate salts prevented a full TGA analysis with these products, the agreement between proposed species and the number of water molecules as determined by TGA, together with the IR analysis of all of the isolated compounds and inferences based on the analogous reaction chemistry with the triflate salts, suggest the presence of analogous 4:0:1, 3:1:1, and 2:3:1 TMSA:H$_2$O:Ln compounds as perchlorate salts.

Structure determinations by single-crystal X-ray diffraction of the Ln(TMSA)$_4$(CF$_3$SO$_3$)$_3$ compounds (Ln = La (**1**), Nd (**2**), Eu (**3**), Lu (**5**), of Eu(TMSA)$_4$(ClO$_4$)$_3$ (**4**)), of Yb(TMSA)$_3$(H$_2$O)(CF$_3$SO$_3$)$_3$ (**6**), of Yb(TMSA)$_3$(H$_2$O)(ClO$_4$)$_3$ (**7**), and of Yb(TMSA)$_2$(H$_2$O)$_3$(CF$_3$SO$_3$)$_3$ (**8**) verify the conclusions based on the TGA and IR data. Compounds **1**–**5** are chemically, although not crystallographically, isostructural with respect to the metal's coordination sphere; an ORTEP plot of **5** is shown in Figure 1. Similarly, the structures of **6** and **7** are essentially isostructural with respect to the metal's primary coordination sphere; an ORTEP plot of **6** is shown in Figure 2, and an ORTEP plot of **7** is shown in Figure 3. An ORTEP plot of compound **8** is shown in Figure 4.

In the 4:1 TMSA:Ln compounds, each metal ion is surrounded by eight oxygen atoms derived from four bidentate succinamide ligands; the anions are absent from the inner coordination sphere. The eight oxygen atoms around the metal form an intermediate structure between a bicapped trigonal prism and a dodecahedron with one oxygen atom from each of the four succinamide ligands located in an A-type position and the other four oxygen atoms occupying the four B-type positions. Such an intermediate structure might be expected[27] for four bidentate ligands with the normalized bite (distance between the coordinating oxygen atoms on the bidentate succinamide/succinamide oxygen–lanthanide bond length) of ca. 1.2 present in these TMSA–lanthanide compounds (Table 6).

As shown in Table 6, one relatively short and one relatively long Ln–O bond characterize the binding of the succinamide ligand's oxygen atoms to the lanthanide. The difference between the Ln–O bond lengths in a chelating succinamide is typically around 0.06 Å. As expected, the metal–oxygen bond distances gradually shorten as the metal varies from the early lanthanides to the late lanthanides. Indeed, if the metal's contribution to the metal–oxygen bond distance is removed using Shannon's crystal radii[28] for the appropriate 8-coordinated metal, the bond distances become identical within experimental error. An exception lies with the smallest lanthanide ion, lutetium, which appears to have slightly longer M–O bonds, perhaps due to the onset of steric repulsions. As expected, the counteranions appear to exert no influence on succinamide coordination to the metal; the bond distances for the europium triflate versus europium perchlorate salts are identical within the experimental uncertainty.

The amide functionality itself undergoes some changes upon lanthanide coordination. The C(amide)–O(amide) bond distance lengthens to an average 1.252(5) Å from the 1.231(2) Å found in free TMSA, and the C(amide)–N(amide) bond distance shortens to an average 1.331(5) Å from the 1.349(2) Å found in free TMSA. However, the amide functionality remains planar, with an average sum of the bond angles around the amide carbonyl carbon atom of 360.0(0)°. Both the planarity of the

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(27) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.
(28) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

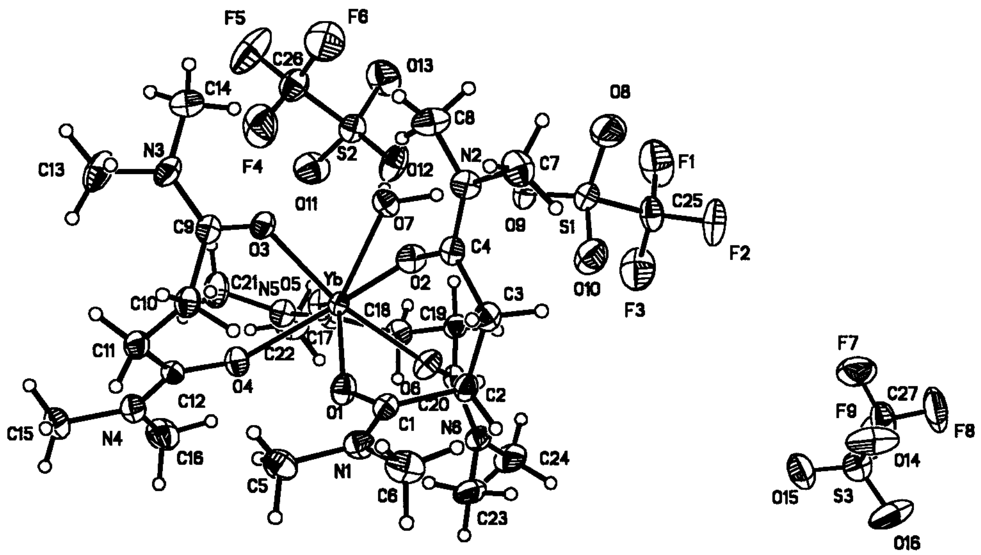

Figure 2. ORTEP illustration of Yb(TMSA)$_3$(H$_2$O)(CF$_3$SO$_3$)$_3$ (**6**).

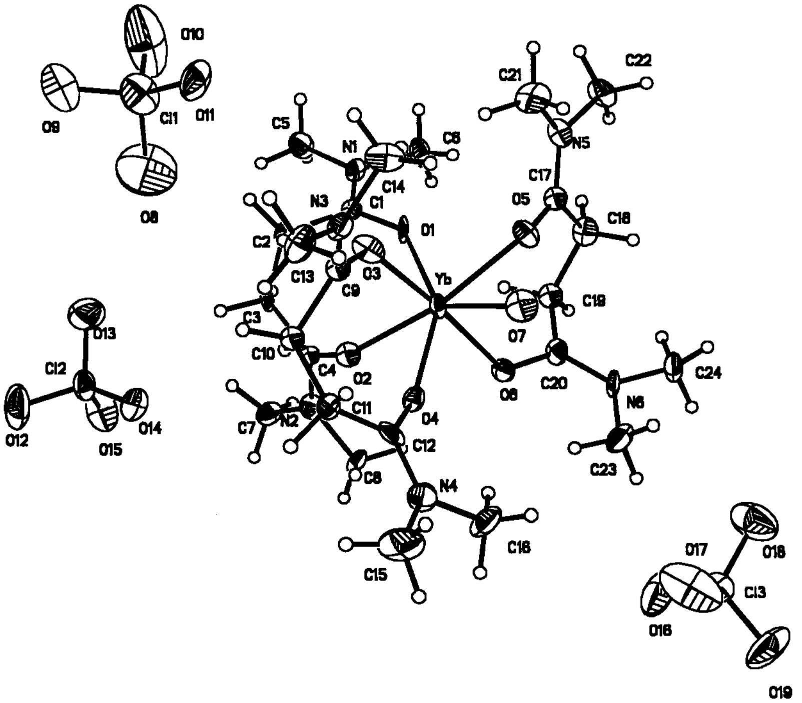

Figure 3. ORTEP illustration of Yb(TMSA)$_3$(H$_2$O)(ClO$_4$)$_3$ (**7**).

amide functionality and the changes in bond lengths are consistent with the changes observed previously with TMSA−lanthanide nitrate compounds as well as with the trends found upon coordination of *N*,*N*-dialkylacetamides to lanthanide metal ions.[13,17]

As with the lanthanide−TMSA bond lengths, the lanthanide−amide bond angles found in the two amides of a chelating succinamide also markedly differ, with a typical difference between the two Ln−O−C bond angles of about 28° (Table 6). The more acute angle is associated with the shorter M−O bond with all of these 4:1 TMSA:Ln compounds. The magnitude of this difference in lanthanide−amide bond angles appears independent of the specific lanthanide.

In Table 7, the average torsion angles present for the four chelating TMSA ligands in compounds **1**−**5** are compared. There is excellent agreement between the torsion angles found for all of the chelating TMSA ligands in all of the 4:1 TMSA:Ln compounds examined. This suggests a marked preference for the observed binding conformation, which is quite different from the all-anti conformation observed for the isolated TMSA ligand.[17] The transition from the free TMSA conformer to that found in the metal compounds can be derived through two rotations that convert the all-anti 180° torsion angles in free TMSA to one anti and two gauche orientations in the chelating conformation. One of these rotations occurs at the sp^3−sp^3 bond in the succinamide backbone, and the second rotation occurs at one of the sp^3−sp^2 carbons connecting one of the amide carbonyl carbons with the succinamide backbone. This leaves the other amide's orientation essentially unchanged from that observed in free TMSA. It is of interest to note that, despite an almost 0.1 Å change in the distance between the oxygen atoms in the succinamide chelate across the lanthanide series (Table 4), the succinamide ligand is able to accommodate these variations without any significant change in these torsion angles.

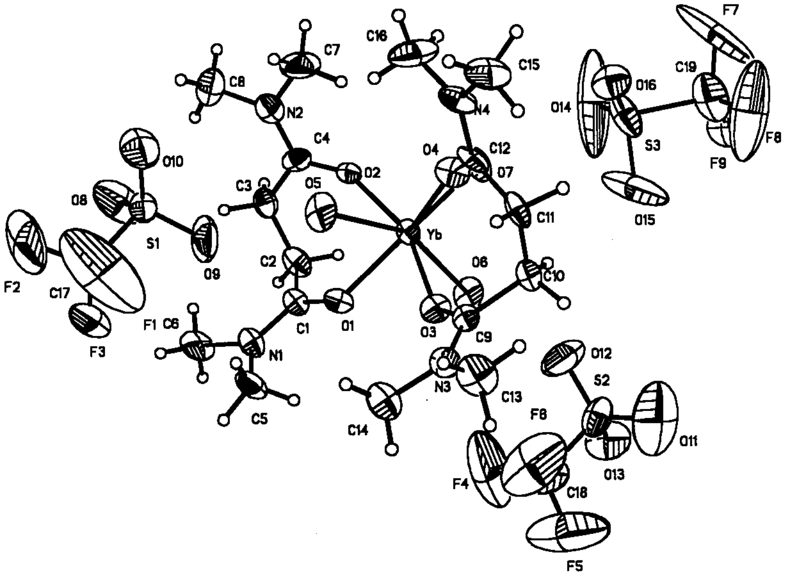

Figure 4. ORTEP illustration of $Yb(TMSA)_2(H_2O)_3(CF_3SO_3)_3$ (**8**).

Table 6. Lanthanide−Oxygen Bond Distances (Å), Oxygen−Oxygen Bond Distances in Chelating TMSA (Å), Normalized Bite Values, and M−O−C Bond Angles (deg) Found in 1−8

compd	av Ln−O_a[a]	av Ln−O_b[b]	av O···O	av bite[c]	av Ln−O−CR	av M−O_a−C_a[f]	av M−O_b−C_b[g]	diff
1	2.46(2)	2.51(1)	2.93(1)	1.181	1.18[d]	159(1)	130(1)	29
2	2.394(7)	2.458(10)	2.89(4)	1.191	1.18[d]	158(1)	130.4(8)	27.6
3	2.362(9)	2.420(20)	2.878(3)	1.204	1.19[d]	157.8(9)	130(1)	27.8
4	2.358(9)	2.418(20)	2.87(1)	1.201	1.18[d]	160(1)	132(3)	28
5	2.291(4)	2.345(38)	2.84(2)	1.224	1.20[d]	158(1)	131.3(4)	26.7
6	2.226(17)	2.256(30)	2.808(57)	1.253	1.18[e]	158(5)	136(2)	22
7	2.238(16)	2.270(36)	2.875(84)	1.276	1.19[e]	151(4)	132(6)	19
8	2.215(6)	2.263(25)	2.852(1)	1.274	1.17[e]	152(3)	140(1)	12

[a] Defined as the shorter metal−oxygen bond distance to any given succinamide. [b] Defined as the longer metal−oxygen bond distance to any given succinamide. [c] Defined as the oxygen−oxygen bond separation divided by the average metal−oxygen bond distance with a succinamide. [d] CR = Shannon's crystal radius for 8-coordinated compounds.[18] [e] CR = Shannon's crystal radius for 7-coordinated compounds.[18] [f] Defined as the larger metal−amide bond angle in any given succinamide. [g] Defined as the smaller metal−amide bond angle in any given succinamide.

Table 7. Summary of the Average Torsion Angles, $O_a-C_a-C_1-C_2-C_b-O_b$ (deg),[a] for the Succinamide Chelates Found in 1−8

compd	$O_a-C_a-C_1-C_2$	$C_a-C_1-C_2-C_b$	$C_1-C_2-C_b-O_b$
1	3(3)	−65(2)	107.4(0.9)
2	3.3(2.5)	−66.0(0.9)	106.5(0.6)
3	3.0(2.2)	−65.1(0.6)	106.0(0.3)
4	6(1)	−68(2)	103(3)
5	3.4(1.4)	−64.2(0.8)	103.6(0.2)
6	2.1(2.6)	−69.0(2.5)	94.1(4.2)
7	16(14)	−68(6)	109(2)
	14	67	−85
8	2(8)	−65.5(0.7)	96.5(0.3)

[a] The initial torsion angle O_a-$C_1-C_2-C_3$ is arbitrarily assigned a positive value. Standard deviations of the average torsion angle for the TMSA ligands in each compound are given in parentheses.

As noted above, single-crystal X-ray structure determinations of mixed aquo−TMSA compounds also confirm the conclusions reached by TGA and IR spectroscopy. All of the mixed aquo−TMSA compounds are 7-coordinate; in compound **8** the sites taken by the two amide oxygens from one of the three TMSA ligands present in **6** and **7** have been replaced by two additional water oxygens.

The coordination geometry formed by the ligating oxygen atoms in **6** and **7** forms an approximate pentagonal bipyramid, although distortions away from this ideal polyhedron are more severe in the triflate salt, compound **6**, than in the perchlorate salt, compound **7**. With both compounds, the unique water oxygen forms one vertex of the pentagon, with two oxygens from one TMSA ligand and one oxygen from each of the other two TMSA ligands forming the other pentagon vertexes. The other oxygen atoms, one from each of the two TMSA ligands, form the apexes of the pentagonal bipyramid. This type of coordination polyhedron has been described as stereochemistry C_3 in a study of the stereochemistry of 7-coordinate compounds.[29] Although the oxygen atoms form essentially identical coordination polyhedra in **6** and **7**, the compounds are geometrical isomers due to the manner in which the TMSA ligands are linked together in these polyhedra. Using the unique water oxygen atom as a starting point, the TMSA ligand in which both amide oxygen atoms occupy vertexes in the pentagon is located in a different position in **6** than in **7**. In **6**, one oxygen atom occupies a vertex in the pentagon adjacent to the water oxygen, with the other oxygen atom being two vertexes removed, whereas in **7**, each of the TMSA oxygen atoms are two vertexes removed from the water oxygen atom.

The coordinating geometry formed by the ligating oxygen atoms in $Yb(TMSA)_2(H_2O)_3(SO_3CF_3)_3$, compound **8**, is that of a capped trigonal prism. Two of the vertexes of each trigonal face are supplied by one oxygen from each succinamide ligand, with the third being supplied by a water ligand: e.g., oxygen atoms O2, O4, and O7 in Figure 4 form one trigonal face and oxygen atoms O1, O3, and O6 in Figure 4 form the other trigonal face. A square face formed by oxygen atoms O1, O2,

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(29) Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 42.

Table 8. Structural Parameters for Succinamide Chelates, $O_a-C_a-C_1-C_2-C_b-O_b$, in Selected Succinamide−Metal Compounds

	torsion angle (deg)			bond angle (deg)		bond length (Å)	
compd	$O_a-C_a-C_1-C_2$	$C_a-C_1-C_2-C_b$	$C_1-C_2-C_b-O_b$	$M-O-C_a$	$M-O-C_b$	$M-O_a$	$M-O_b$
$La(TMSA)_2(NO_3)_3$	28.0	−82.6	99.6	158.3	134.8	2.485	2.510
$Ce(TMSA)_2(NO_3)_3$	28.3	−82.8	98.7	157.9	135.0	2.459	2.479
$Ce_2(TMSA)_3(NO_3)_6$	1.5	−73.4	97.9	147.6	136.5	2.414	2.400
$Pr_2(TMSA)_3(NO_3)_6$	1.8	−73.7	98.6	147.9	136.3	2.403	2.380
$Nd_2(TMSA)_3(NO_3)_6$	2.3	−73.5	98.5	148.2	136.1	2.381	2.369
$Gd_2(TMSA)_3(NO_3)_6$	2.7	−72.9	98.2	148.7	135.7	2.334	2.315
$Yb_2(TMSA)_3(NO_3)_6$	3.0	−72.0	98.0	148.9	135.4	2.259	2.242
$UO_2(TBSA)(NO_3)_2$[a]	19	−79.9	28.6	136.0	134.9	2.392	2.323

[a] TBSA = *N,N,N′,N′*-tetrabutylsuccinamide.

O3, and O4 in Figure 4 is capped by the remaining water ligand, O5. This type of coordination geometry for a seven-coordinate geometry formed by two bidentate ligands and three monodentate ligands previously has been described as stereochemistry II and is the preferred observed stereochemistry for systems where the bidentate ligand has a normalized bite of greater than 1.2.[29] For the tetramethylsuccinamide ligands in compound **8** the normalized bite, reported in Table 6, is 1.27−1.28.

The average Yb−O(amide) bond distances, 2.241(27) Å for **6**, 2.254(30) Å for **7**, and 2.239(31) Å for **8**, compare well with the average Yb−O(amide) bond distance of 2.250(9) Å in $Yb_2(TMSA)_3(NO_3)_6$.[17] The marked difference in the Yb−O(amide) bond distances found in the 4:1 TMSA:Ln compounds is in general lacking in these mixed TMSA−aquo lanthanide compounds, where the differences are typically around 0.02 Å, much as was observed in$Yb_2(TMSA)_3(NO_3)_6$. However, it should be noted that the spread in these values is large, ranging from an essentially identical 0.003 Å to a 0.059 Å difference similar to that observed for the compounds with the 4:1 stoichiometry. The changes in the amide structure in the TMSA ligand are also similar to those found with the 4:1 stoichiometry. Compounds **6**−**8** possess an average C(amide)−O(amide) bond of 1.27(1) Å, an average C(amide)−O(amide) bond of 1.32(1) Å, and an average sum of angles around the amide nitrogen of 359.8(4)°. Unlike the compounds with the 4:1 TMSA:Ln stoichiometry, there are substantial differences in the observed Ln−O(amide)−C(amide) bond angles associated with any given diamide ligand, ranging from 9.7 to 26.7° for the eight diamides present in **6**−**8**. Also unlike the 4:1 complexes, there is no correlation of the relative magnitude of the bond angle with the relative magnitude in the Yb−O(amide) bond length.

The torsion angles that define the TMSA comformation in compounds **6**−**8** are presented in Table 7 and can be compared with previously reported metal−tetraalkylsuccinamide compounds in Table 8. In general, like the 4:1 compounds and like all of the previously reported metal−tetraalkylsuccinamide compounds, the TMSA ligand adopts a 0,−,+ conformation upon lanthanide complexation.

With compounds of the stoichiometry $[Ln(TMSA)_4]^{3+}$ no significant cation−anion interactions are apparent in either the triflate or perchlorate salts. This is not the case with the mixed TMSA−aquo compounds, where structural features indicative of substantial cation−anion hydrogen-bonding interactions are observed. The close (<3 Å) O(triflate)−O(water) distance suggests the presence of hydrogen bonding[30] of one metal-bound water to one oxygen from each of two anions for compounds **6**−**8**. The O(triflate)−O(water) distance in the triflate salt **6** is over 0.1 Å shorter (average 2.71 Å vs average 2.86 Å) than in the perchlorate salt **7**, suggesting the presence of stronger hydrogen bonding in the more basic triflate salts than in the perchlorate salts.

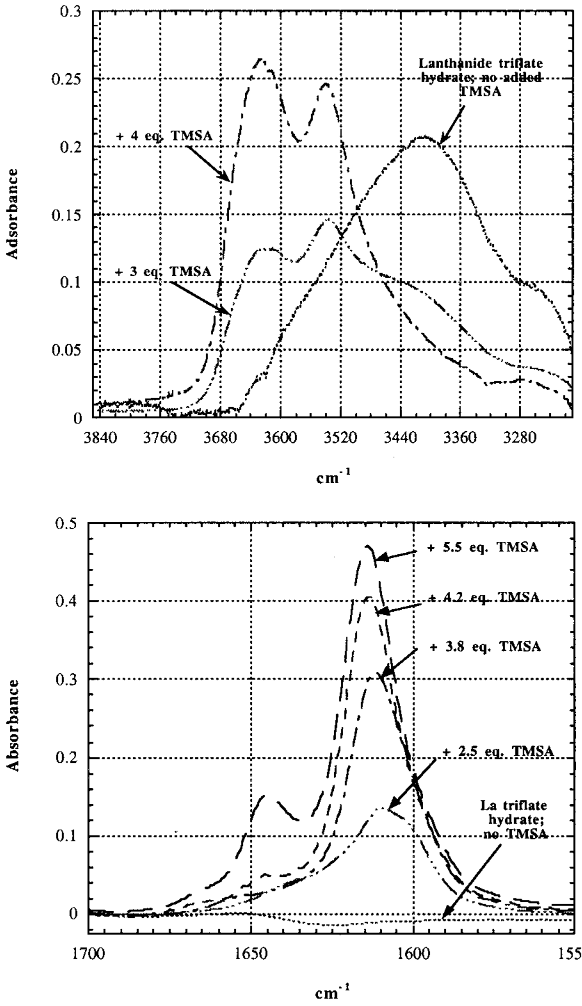

Figure 5. IR spectra from 3840 to 3150 cm^{-1} of TMSA mixed with lanthanum triflate (top) and from 1700 to 1550 cm^{-1} of TMSA mixed with praesodynium triflate (bottom) as a function of ligand-to-metal ratio in CH_3CN.

Solution IR studies were performed in anhydrous acetonitrile to ascertain the extent that the solid-state structure is maintained in solution. Figure 5 shows the progressive loss of metal-bound water from $La(CF_3SO_3)_3$ as a function of increasing amounts of TMSA. As was observed in previous studies of the lanthanide nitrates with TMSA,[17] at the point where the ligand-to-metal ratio present in solution corresponds to the ratio present in the isolated compounds, all metal-bound water was removed, consistent with the composition present in the solid-state structures. No further changes in this region are observed if additional ligand is added. Changes in the triflate band also

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(30) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997.

support the composition observed in the solid-state structures. With the simple hydrated lanthanide triflates, the bands assigned to the triflate are complex, presumably due to the extensive hydrogen bonding between the metal-bound water molecules and the triflate anion, as observed in their solid-state structures. Following reaction with TMSA, a much simpler spectrum is observed, consistent with an increase in local symmetry in the triflate anion.

Changes in the amide carbonyl region are more complex, but the presence of free TMSA is detected only when the ratio of TMSA to La exceeds 4:1. With the late lanthanides, the situation is less straightforward. Although 4:1 TMSA:Ln compounds can be isolated, the presence of free ligand is detected in the amide carbonyl region even when as little as 2 equiv of TMSA has been added. On the other hand, the region from 3400 to 3600 cm^{-1} suggest that dehydration of the metal is complete at a 3:1 TMSA:Ln ratio. The reason for these differing behaviors between the early and late lanthanides in solution with TMSA is unclear, but it may be that steric constraints inhibit the binding of the third and fourth TMSA ligands to the metal to a greater extent in the smaller lanthanides than the larger lanthanides. Some support for this hypothesis does come from the unexpectedly long M−O bonds observed in the 4:1 lutetium compound.

Conclusions

The coordination chemistry of TMSA with lanthanide triflates and perchlorates has been investigated with metals that span the entire lanthanide series. In all cases, in the presence of 4 equiv or greater of TMSA, compounds with a 4:1 TMSA:Ln stoichiometry can be prepared. A comparison of the solid- and solution-state IR spectra of these compounds indicates that the basic coordination features found in the solid state are maintained in solution.

All of the 4:1 compounds are 8-coordinate around the metal and are isostructural with respect to the lanthanide's coordination environment, with the solid-state structure characterized by four bidentate succinamide ligands in the metal's primary coordination sphere. The counteranions in these complexes show no evidence of interaction with the $[Ln(TMSA)_4]^{3+}$ moiety, on the basis of both IR spectroscopy and single-crystal X-ray structure analysis.

The binding of the TMSA ligand to the metal is asymmetric; the M−O(amide) bond lengths differ by approximately 0.06 Å, and the M−O(amide)−C(amide) bond angles differ by approximately 28°. The conformation formed by the bound TMSA differs from the all anti conformations found in the uncomplexed ligand by two C−C bond rotations: one around the sp^3-sp^3 bond and the second around one of the two sp^3-sp^2 bonds present in TMSA.

In the presence of substantial amounts of water, mixed aquo−TMSA compounds have been isolated. Seven-coordinate compounds of the composition $[Yb(TMSA)_3(H_2O)]^{3+}$ and $[Ln(TMSA)_2(H_2O)_3]^{3+}$ have been isolated. Like the 4:1 compounds, significantly asymmetric M−O(amide)−C(amide) bond angles are observed; unlike the 4:1 compounds, the M−O(amide) bond lengths in the bound TMSA ligands vary from essentially identical to markedly asymmetric. The TMSA conformation present in the aquo−TMSA compounds is the same as that observed in 4:1 compounds. Indeed, this conformation is also found in all reported examples of compounds with the $Ln_2(TMSA)_3(NO_3)_6$ stoichiometry and with the $Ln(TMSA)_2(NO_3)_3$ stoichiometry but differs substantially from the conformer found in the only other reported metal−*N*,*N*,*N*′,*N*′-tetraalkylsuccinamide compound, UO_2(*N*,*N*,*N*′,*N*′-tetrabutylsuccinamide)$(NO_3)_2$ (Table 8).[31] Still, of the 16 known examples of metal-succinamide compounds, 15 exhibit the succinamide conformer found with $[Ln(TMSA)_4]X_3$. This suggests that this conformer is the ligand's low-energy form for metal complexation. A more detailed examination of the interaction of TMSA binding to f-block metal ions is in progress and will be the subject of a future report.

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Supporting Information Available: Eight X-ray crystallographic files, in CIF format, a sample TGA scan for a 4:0:1 TMSA H_2O:Ln triflate, a 3:1:1 TMSA:H_2O:Ln triflate, and a 2:3:1 TMSA:H_2O:Ln triflate compound, IR data, including a plot of the amide region of the IR spectrum as a function of added TMSA to a solution of lanthanum triflate and plots of both a 4:0:1 TMSA:H_2O:Ln perchlorate compound and a 4:0:1 TMSA:H_2O:Ln triflate compound in CH_3CN solution and as a solid in a KBr matrix, and additional IR spectra showing both the CH_3CN and solid KBr spectrum of a 3:1:1 TMSA:H_2O:Ln triflate and a 2:3:1 TMSA:H_2O:Ln triflate compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Wang, H. Z.; Cui, L.; Cao, Z.-B.; Gu, J.-S.; Zhu, L.-M.; Yu, K.-B. *Chin. J. Chem.* **1993**, *51*, 880.