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Anhydrous Lanthanide Schiff Base Complexes and Their Preparation Using Lanthanide Triflate Derived Amides

Steven A. Schuetz,[†] Victor W. Day,[†]
Roger D. Sommer,[‡] Arnold L. Rheingold,[‡] and
John A. Belot*,[†]

Department of Chemistry, University of Delaware,
Newark, Delaware 19716, and Department of Chemistry
and Center for Materials Research,
University of Nebraska−Lincoln,
Lincoln, Nebraska 68588-0304

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Introduction

Anhydrous synthetic lanthanide chemistry is dominated by the use of bulky amides (e.g., $R_2Ln{-}N(TMS)_2$), alkyls (e.g., $R_2Ln{-}CH(TMS)_2$), and cyclopentadienides ($R_2Ln{-}Cp'$, $Cp' = C_5Me_5$) to ensure monomeric complexes.[1] Although the use of these materials as stoichiometric and catalytic reagents for organic transformations has dramatically increased,[1,2] ligand lability often results in deleterious side reactions or decomposition.[3] To address this issue, we recently began exploring alternative ligand frameworks based on anhydrous, saturated, tetradentate Schiff bases anticipating that hard O and N ligation should be more robust than the aforementioned systems. Herein we report the anhydrous synthesis of mononuclear and dinuclear lanthanide (i.e., not yttrium) Schiff-base complexes from homoleptic bis(trimethylsilyl)amido precursors.[4] The precursors were prepared from commercial $Ln(OTf)_3$ ($OTf = {}^{-}O_3SCF_3$), which is shown (vide infra) to be an effective alternative to $LnCl_3$ starting materials that usually require in-house thermal syntheses[5] using sesquioxides (Ln_2O_3).

Lanthanide triflates are widely employed in organic syntheses;[2,6] however, as anhydrous lanthanide sources their utility remains relatively unexplored. Previously, Edelmann,[7] Schumann,[8] and Tolman[9] exploited $Ln(OTf)_3$ during the syntheses of heteroleptic mono-Cp, COT (cyclooctatetraenyl), and polyamine compounds, whereas Karsch[10a] and Rabe[10b] isolated homoleptic "ate" phosphinomethanides and phosphides, respectively, using this method. We have expanded on these results and found commercial $Ln(OTf)_3$ to be a viable, inexpensive alternative in the direct preparation of $Ln[N(TMS)_2]_3$ (Ln = La^{3+}, Nd^{3+}, Sm^{3+}, and Er^{3+}) and $Ln[CH(TMS)_2]_3$[11] (Sm^{3+} and Er^{3+}).

Schiff-base ligands are among the most widely studied chelators in inorganic chemistry, and many lanthanide complexes have been isolated from aqueous solutions, characterized, and studied.[12] However, anhydrous or nonsolvated complexes are rare,[13] only recently receiving attention as potential Cp replacements while holding the metal in stable chiral environments.[14−17] Schiff bases offer opportunities for inducing substrate chirality, tuning metal-center electronic factors, and enhancing solubility and stability of either homogeneous or heterogeneous catalysts. Particularly noteworthy is the work of Anwander,[14] Roesky,[15] Liu,[16] and Evans,[17] all of whom are exploring model complexes using divalent, tetradentate ligands.

Experimental Section

Materials and Methods. Standard Schlenk techniques and a Vacuum Atmospheres N_2-filled glovebox were used throughout the isolation and handling of all metal complexes. The lanthanide triflates (Aldrich), 1,3-diaminopropane (Acros), absolute ethanol (EtOH, Pharmco), and diethyl ether (Et_2O, Fisher) were used as received whereas alkali earth bis(trimethylsilyl)amides (Gelest) were purified by sublimation at $\sim 10^{-5}$ Torr. 2,2-Dimethyl-3,5-hexanedione was synthesized using literature methods.[18] Tetrahydrofuran (THF) was dried and distilled from Na/benzophenone ketal, and heptane (C_7H_{16}) and pentane (C_5H_{12}) were dried and distilled from CaH_2. ^1H and ^{13}C NMR were recorded on a GE 300 MHz or Varian 200 MHz NMR and processed using NUTS software. The solid-state molecular structures of **2** and **3** were determined by single-crystal X-ray diffraction at the University of Illinois−Urbana-Champaign and the University of Delaware, respectively. Elemental analyses were performed at Midwest Microlabs (Indianapolis, IN).

Synthesis of Bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexen-3-one (1). Under ambient conditions, to a 250 mL 24/40 1-neck round-bottom flask charged with 50 mL of EtOH and 17.3 g (122 mmol) of 2,2-dimethyl-3,5-hexanedione was added 5.1 mL (61 mmol) of 1,3-diaminopropane in 35 mL of EtOH dropwise over 30 min via a 125 mL addition funnel. Following this, a condenser replaced the addition funnel and the reaction refluxed overnight, after which it was diluted with 100 mL of *d*-H_2O and extracted twice with 30 mL of Et_2O. The organics were washed with 4 × 20 mL of H_2O, dried over Na_2SO_4, filtered, and removed in vacuo, yielding a dull-yellow wax. This crude product recrystallized from C_7H_{16}, affording colorless crystals of **1** in

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[†] University of Nebraska−Lincoln.

[‡] University of Delaware.

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unoptimized yields between 50% and 71%. Mp: 65−68 °C. ^{1}H NMR (δ, $CDCl_3$): 1.1 (s, 18H), 1.9 (m, 2H), 2.0 (s, 6H), 3.4 (m, 4H), 5.2 (s, 2H), 11.1 (b, 2H). ^{13}C NMR (δ, $CDCl_3$): 19.9, 28.5, 30.7, 40.5, 41.8, 91.4, 164.5, 204.7. Anal. Calcd for $C_{19}H_{34}N_2O_2$: C, 70.76; H, 10.63; N, 8.69. Found: C, 70.68; H, 10.61; N, 8.64.

Synthesis of Tris(bis[trimethylsilyl]amido)lanthanide. In a representative procedure, a 500 mL 24/40 3-neck round-bottom flask was charged with 28.3 mmol of Na^+ $^-N(TMS)_2$ and fitted with a condenser, a rubber septum, and a Merlic solid addition funnel containing 9.47 mmol of $Ln(OTf)_3$. The flask was removed from the glovebox and interfaced to a Schlenk line, and 100 mL of heptane and 200 mL of THF were introduced via syringe. After the septum was replaced with a glass stopper, $Ln(OTf)_3$ was added and the reaction refluxed overnight, after which time the volatiles were removed in vacuo and the remaining solids returned to the glovebox. The crude products were purified by either sublimation (∼95 °C at 10^{-5} Torr) or recrystallization (C_5H_{12}) to repeatedly yield analytically pure products in yields of La 57%, Nd 63%, Sm 68%, and Er 54%.

Synthesis of Bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexen-3-onato Lanthanide Complexes. In a 100 mL Schlenk flask 0.794 mmol tris(bis[trimethylsilyl]amido)lanthanide was dissolved in 10 mL of C_7H_{16} and 0.791 mmol of **1**, in 30 mL of C_7H_{16}, added via a syringe. The solution was stirred overnight at 50−60 °C, the organics were removed in vacuo, and the crude product was recrystallized (5−8 days) from ∼5 mL of C_5H_{12} at −10 °C.

Bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexen-3-onato Samarium Bis(trimethylsilyl)amido (2). Yield: 64%. Mp: 135−140 °C. ^{1}H NMR (δ, C_7D_8): −1.8 (b, 4H), 1.0 (s, 18H), 1.8 (s, 6H), 1.9 (s, 18H), 7.5 (s, 2H). ^{13}C NMR (δ, C_7D_8): 6.5, 18.0 (br), 20.5, 28.9, 37.0, 45.3, 99.8, 176.6, 195.3. Anal. Calcd for $C_{25}H_{50}N_3O_2Si_2Sm$: C, 47.57; H, 7.98; N, 6.66. Found: C, 47.37; H, 7.95; N, 6.46.

Tris[bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexen-3-onato] Neodymium Dimer (3). Yield: 52%. ^{1}H NMR (δ, C_7D_8, all peaks paramagnetically broadened): −6.2, −4.6, −4.3, −3.4, −2.5, −1.1, −0.4, 0.2, 0.9, 1.2, 1.9, 3.9, 5.5, 6.2, 9.1, 11.4, 12.4. Anal. Calcd for $C_{57}H_{96}N_6O_6Nd_2$: C, 54.77; H, 7.74; N, 6.72. Found: C, 54.30; H, 7.54; N, 6.40.

Results and Discussion

$Ln(OTf)_3$, as a $LnCl_3$ replacement, proved invaluable as a starting material for homoleptic lanthanide complexes of bulky amides (eq 1). Advantages over chloride routes were mentioned above, and $Ln[N(TMS)_2]_3$ is repeatedly isolated in very good yields and analytical purity using commercial $Ln(OTf)_3$. Each amide was thoroughly analyzed, and their characterization conforms to those of products obtained through previous preparations, *never exhibiting residual OTf*. We attribute the former to $Ln(OTf)_3$ purity, devoid of oxychlorides and H_2O, which are avoided in the triflate preparation (presumably digestion[19] of Ln_2O_3 in HOTf), and the latter to favorable equilibrium for triflate dissociation[20] in moderately polar, aprotic solvent systems. Analogously, the triflates can also be directly converted to homoleptic bis(trimethylsilyl)methanides[11] which previously required multistep syntheses again using problematic $LnCl_3$.

$$Ln(OTf)_3 + 3\,M^+\,{}^-N(TMS)_2 \xrightarrow[C_7H_{16}]{THF} Ln[N(TMS)_2]_3 + 3\,M^+\,{}^-OTf \quad (1)$$

$$Ln = La, Nd, Sm, Er;\ M^+ = Li, Na, \text{ or } K$$

The acyclic Schiff-base ligand, **1**, is synthesized[21] by the reaction of 1,3-diaminopropane and 2,2-dimethyl-3,5-hexanedione; although the diketone is not commercially available, it can be readily isolated from a NaH-induced Claisen condensation of pinacolone with ethyl acetate.[18] Although three isomers are possible during the ketoiminate synthesis, **1** is the major product and evidence for scrambled amine−ketone condensation is not observed.

Scheme 1. General Synthetic Route to Anhydrous Schiff Base Lanthanides

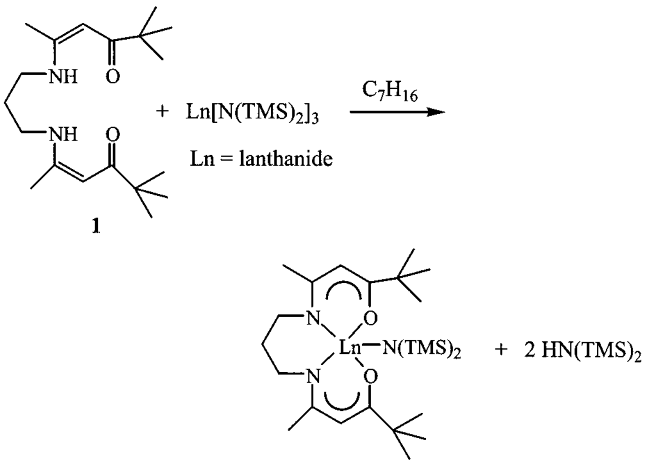

Table 1. Crystallographic Data for **2** and **3**[d]

	2	**3**
formula	$C_{25}H_{50}N_3O_2Si_2Sm$	$C_{62}H_{108}N_6Nd_2O_6$
fw	631.21	1322.02
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	10.640(2)	14.590(1)
b (Å)	25.826(4)	16.802(1)
c (Å)	12.042(2)	27.113(1)
α (deg)	90.000	90.000
β (deg)	106.338(2)	90.618(1)
γ (deg)	90.000	90.000
V (Å^3)	3175.4(8)	6646.3(6)
Z	4	4
ρ_{calcd} (g/cm^3)	1.320	1.321
μ(Mo Kα) (mm^{-1})	1.948	1.594
temp (K)	193(2)	173(2)
no. of rflns (collected/unique)	20423/7581	32324/13498
R^a ($I > 2\sigma(I)$)	0.0327 (5446)	0.0404 (9715)
$R_w{}^b$ (unique rflns)	0.0616 (7581)	0.0938 (13498)
goodness of fit indicator	0.939	0.994

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$. [c] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. [d] Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker-AXS: Madison, WI.

The Sm^{3+} and Nd^{3+} complexes were synthesized (Scheme 1) by direct reaction of $Ln[N(TMS)_2]_3$ with protio ketoiminate in C_7H_{16}, the silylamide route,[1c,14b] and recrystallized from C_5H_{12} to yield analytically pure, single crystals suitable for X-ray diffraction studies (Table 1). The solid-state structure of **2** consists of discrete mononuclear Sm(KI)[$N(TMS)_2$] (KI = ketoiminato) molecules (Figure 1) with the Sm^{3+} bonded to the tetradentate ketoiminate dianion and the amido ligand in a distorted square pyramidal arrangement. The molecule possesses no rigorous crystallographic symmetry but approximates C_s-*m* with the pseudo mirror plane passing through Sm, N(3), and the central CH_2 group of the propyl bridge. The four donor atoms[22] of the ligand define the vertexes of a severely (±0.19 Å) S_4-ruffled "square" base from which Sm^{3+} is displaced 0.98

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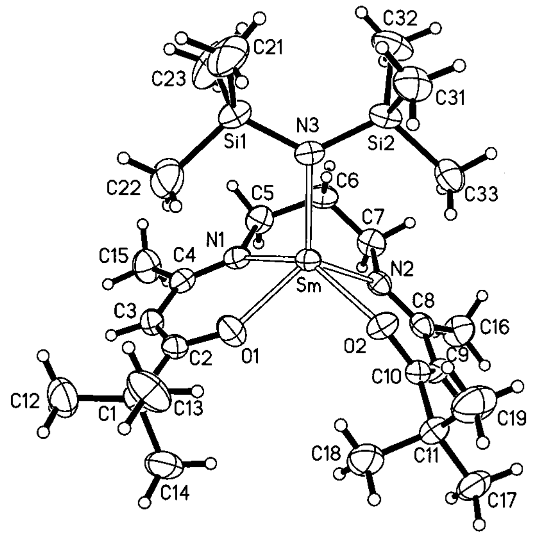

Figure 1. Diffraction-derived molecular structure of **2** with thermal ellipsiods at 50% probability. Selected bond lengths (Å): Sm−O(1) 2.202(2), Sm−O(2) 2.209(2), Sm−N(1) 2.459(2), Sm−N(2) 2.462(2), Sm−N(3) 2.314(2).

Å from the mean plane toward apical N(3). The Sm−O and Sm−N bonds to the ketoiminate average[23] 2.205 (2, 4, 4, 2) Å and 2.460 (2, 2, 2, 2) Å, respectively. The 2.314(2) Å amido Sm−N bond is within 4.1° of being parallel to the normal of this mean plane, and its slight elongation compared to lengths in less sterically demanding environments[24] suggests lability. Although the mechanism(s) are still under study, introduction of substoichiometric **2** to methyl methacrylate, ϵ-caprolactone, and cyclic lactide monomers yields polymers.[11]

The solid-state structure of **3** consists of discrete dinuclear $Nd_2(KI)_3$ complexes devoid of crystallographically-imposed symmetry (Figure 2). All ketoiminato nitrogen and oxygen atoms are coordinated to at least one metal ion. The first ligand is bound only to Nd(2), while the other two, associated with Nd(1), participate in μ-O bridging modes between Nd(1) and Nd(2). For these ligands, O(2) and O(6) contact both Nd(1) and Nd(2) whereas N(6) is uniquely bonded to Nd(2), Both Nd^{3+} ions are formally seven coordinate with average nonbridging Nd−O and Nd−N bond lengths of 2.302 (3, 8, 16, 4) Å and 2.567 (3, 15, 24, 6) Å, respectively. The bridging Nd−O bond lengths are 2.526 (3, 35, 69, 4) Å. Both Nd^{3+} stereochemistries are best described as equatorially monocapped trigonal prisms. This geometry (stereochemistry I[25]) is more distorted for Nd(2) where O(3) caps the "square" face of the eclipsed triangular faces defined by O(4), N(3), N(4) and N(6), O(2), O(6), respectively. For the more regular Nd(1) geometry, the triangular faces (N(1), O(1), N(5) and N(2), O(6), O(2)) have stereochemistry II[25] and O(5) is the "cap". Although this dinuclear species persists in solution, ^1H NMR indicates extensive intramolecular fluxional behavior at room temperature.

Since identical reaction conditions were used to synthesize **2** and **3**, the drastically different products are likely related to small differences in ionic radii, although it may be possible to produce mononuclear Ln(KI)[N(TMS)$_2$] species for larger rare earths by modifying the Schiff base.[11] Two features of the Sm(KI)[N(TMS)$_2$] structure are particularly noteworthy: the presence of bulky $-Si(CH_3)_3$ and $-C(CH_3)_3$ groups and the propyl link between the two "halves" of the ketoiminate. The former clearly serves to block potential available metal coordination sites and thereby stabilize low coordination numbers in smaller radii ions ($<Nd^{3+}$). The latter not only enlarges the coordination cavity by expanding the N···N separation compared with C_2H_4 bridges but, perhaps more importantly, also blocks potential coordination sites by folding into the cleft between adjacent $-Si(CH_3)_3$ groups of the TMS amido. In doing this, it produces a short 2.69 Å Sm···H interaction with a central methylene proton. Ironically, this same propyl link is probably *required* for the formation of dinuclear **3**. The slightly larger Nd^{3+} presumably permits incorporation of one-half of an additional ketoiminate ligand into each metal coordination sphere when there is a three-carbon link between the halves. Replacing the 5-methyl substituents with either isopropyl or CF_3 may prevent formation of dinuclear complexes like **3** since these groups would be well positioned for forcing the two metals apart.

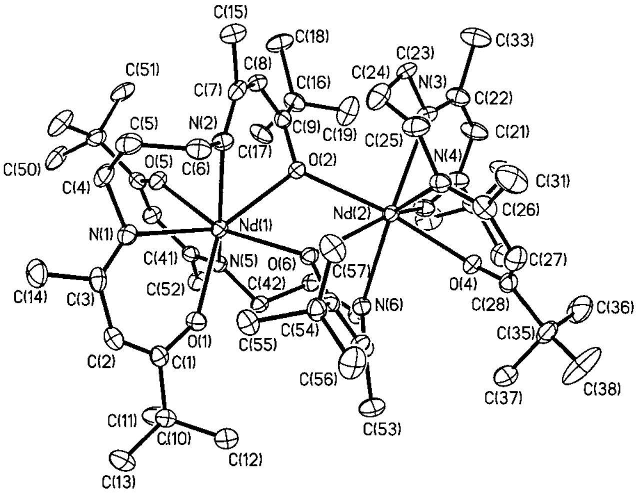

Figure 2. Diffraction-derived molecular structure of **3** with thermal ellipsiods at 30% probability. Selected bond lengths (Å): Nd(1)−O(1) 2.297(3), Nd(1)−O(2) 2.473(3), Nd(1)−O(5) 2.318(3), Nd(1)−O(6) 2.525(3), Nd(1)−N(1) 2.591(3), Nd(1)−N(2) 2.566(3), Nd(1)−N(5) 2.551(3), Nd(2)−O(2) 2.595(3), Nd(2)−O(3) 2.295(3), Nd(2)−O(4) 2.298(3), Nd(2)−O(6) 2.510(3), Nd(2)−N(3) 2.562(4), Nd(2)−N(4) 2.545(4), Nd(2)−N(6) 2.586(3).

Conclusions

In summary, this note presents a facile preparation of homoleptic lanthanide amides using commercially available Ln(OTf)$_3$. These compounds are ubiquitous solution (and vapor) phase reagents in synthetic lanthanide chemistry. The amides were subsequent starting materials for the isolated, anhydrous Schiff-base complexes derived from bis-5,5′-(1,3-propanediyldiimino)-2,2-dimethyl-4-hexen-3-one. The Sm^{3+} and Nd^{3+} ions display significant differences upon reaction with the tetradentate ketoiminate attributable to subtle radii changes. The former yields a monomeric complex which retains one bis(trimethylsilyl)amido group, and the latter forms a dimer incorporating three, divalent ketoiminato ligands and two Nd centers. Currently, studies are underway to decorate the ketoiminate periphery and develop chiral monomeric complexes for both small molecular transformations and polymerizations.

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(23) The first number in parentheses following an average value of a bond length is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements included in the average value.

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Supporting Information Available: Select ^{1}H and ^{19}F NMR spectra and elemental analyses of the triflate-derived homoleptic amides. Crystallographic files for **2** and **3** (including coordination polyhedra), in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic files may also be obtained at the Cambridge Crystallographic Data Center (12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk) under assigned CCDC numbers of 163596 (**2**) and 163595 (**3**).

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