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Articles

Synthesis and Structure of Lanthanide Complexes Derived from the O,N-Chelating, Bis(methylpyridine)-Substituted Alcohol $HOC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$

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Hydrolysis of the product formed by reacting 2 equiv of 2-(lithiomethylene)-6-methylpyridine with trimethylacetyl chloride gives the alcohol $HOC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$, **1** (HOR), in 44% yield. Three equivalents of **1** reacts with $Yb[N(SiMe_3)_2]_3$ to form $Yb(OR)_3$, **2a**. The analogous 2 equiv reaction generates $Yb(OR)_2[N(SiMe_3)_2]$, **3**. X-ray diffraction studies were successful on **3** and on **2b**, the Sm analog of **2a**. Two of the alkoxide ligands in $Sm(OR)_3$, **2b,** are bidentate such that each has an uncomplexed nitrogen donor atom oriented away from the metal. These chelates occupy basal positions in the distorted square pyramidal geometry around the metal center in **2b** such that the oxygen donors are trans. The axial position is occupied by the third alkoxide which is monodentate through its oxygen donor atom. This leaves a total of four unattached pyridine functionalities available for further coordination. The ligand arrangement in **3** is very similiar to that in **2b** except that the monodentate alkoxide in **2b** is replaced by a $N(SiMe_3)_2$ group. A ligand fragmentation product, $(R'O)_2Sm(\mu\text{-}OR)_2Na$, **4**, containing the chelating bidentate pyridine enolate ligand $[OC(CMe_3)(=2\text{-}CHNC_5H_3Me\text{-}6)]$ (OR′), formed by loss of a 2,6-dimethylpyridine group from OR, was also isolated in the course of these studies. Each OR ligand in **4** has its oxygen atom bridging Sm and Na, one pyridine nitrogen coordinated to Na, and one pyridine nitrogen which is not connected to any metal. The samarium center in **4** has a distorted octahedral geometry generated by two chelating R′O groups and the two bridging oxygens from the OR groups. The nitrogen donor atoms of the R′O groups have a cis orientation and are trans to the bridging ligands. The sodium atom has a distorted tetrahedral geometry. **2b** crystallizes from toluene in space group $P2_1$ with $a = 11.5464(7)$ Å, $b = 10.7865(5)$ Å, $c = 22.5041(9)$ Å, $\beta = 98.930(4)°$, $V = 2768.8(2)$ Å^3, and $Z = 2$. Least squares refinement of the model based on 5804 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final $R_F = 2.7\%$. **3** crystallizes from hexane in space group $P\bar{1}$ with $a = 11.109(2)$ Å, $b = 15.135(3)$ Å, $c = 16.197(3)$ Å, $\alpha = 96.482(12)°$, $\beta = 106.952(10)°$, $\gamma = 110.838(10)°$, $V = 2362.0(8)$ Å^3, and $Z = 2$. Least squares refinement of the model based on 5596 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 3.8\%$. **4** crystallizes from hexane in space group $P2_1/n$ with $a = 15.229(4)$ Å, $b = 24.826(4)$ Å, $c = 15.662(3)$ Å, $\beta = 97.70(2)°$, $V = 5868(2)$ Å^3, and $Z = 4$. Least squares refinement of the model based on 6124 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 5.5\%$.

Introduction

The chemistry of soluble lanthanide complexes is dominated by ligands which can provide electrostatic neutralization of the positive charge on the metal while sterically saturating the large metal center to prevent oligomerization to insoluble materials. Cyclopentadienyl ligands are excellent for this purpose since they are sterically bulky monoanions which occupy three coordination positions.[1] Alkoxide ligands are attractive monoanionic ligands for the lanthanides since they will have strong metal-ligand bonds and can be substituted to have large steric bulk. However, simple alkoxides are limited in that they have only one donor atom site. For this reason, exploration of the lanthanide chemistry of alkoxide ligands containing pendant donor functionalities has occurred.[2−8] Alkoxide and siloxide ligands containing additional donor groups have been designed and synthesized in efforts to tailor the solubility, volatility, and steric unsaturation to optimize utility in applications ranging

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from precursors for oxide-based ceramics to catalysis in organic transformations.

In this report, we introduce a new potentially tridentate alkoxide ligand to the lanthanide area which contains two substituted methylpyridine donor functionalities, $OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$ (OR). This ligand system is attractive because the more rigid nature of the methylpyridine group compared to aliphatic amino donor groups like $(CH_2)_nNMe_2$ should aid in crystallization. In the past, pyridine-based ligands of this general type have been used mainly in bioinorganic chemistry to model essential metalloenzymes.[9-11] We report here the facile synthesis of this ligand and some initial results on its complexation chemistry with lanthanide metals.

Experimental Section

General Procedure. The ligand synthesis was carried out under nitrogen using standard Schlenk line technique. The other reactions were carried out under nitrogen using standard glovebox techniques. Tetrahydrofuran and hexane were distilled from Na/benzophenone under nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker NR 300. Mass spectra were obtained on a Fisons AutoSpecE instrument. FT-IR spectra were recorded on a Mattson FTIR 5000 spectrometer using Nujol mulls. Elemental analyses were obtained either by complexometric analysis along with CH analysis on a Carlo Erba EA 1108 instrument or from the Analytische Laboratorien, Engelskirchen, Germany. The lanthanide amides $Ln[N(SiMe_3)_2]_3$[12] and $NaSm[N(SiMe_3)_2]_3$[13] were synthesized according to the literature. *n*-Butyllithium, 2-methylpyridine, and trimethylacetyl chloride were used as received from Aldrich.

$HOC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$, 1. In a 500 mL three-necked flask, equipped with a dropping funnel, reflux condenser, and thermometer, 2,6-dimethylpyridine (10 mL, 9.2 g, 0.86 mol) was dissolved under nitrogen in 150 mL of THF. The reaction apparatus was cooled to −78 °C, and *n*-butyllithium (64.4 mL of 1.6 M in hexane, 0.10 mol) was added. After the mixture was stirred for 3 h, trimethylacetyl chloride (5.18 g, 42.9 mmol) was added dropwise. The reaction mixture was then stirred at −78 °C for 5 h and allowed to warm to room temperature. A 100 mL portion of ice water was added, and the organic layer was separated from the mixture. The aqueous portion was extracted three times with 50 mL of diethyl ether. The combined organic layers were dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. This gave 12.9 g of a yellow oil. Recrystallization from hexane after 1 day yielded **1** as a white solid (5.25 g, 44%; mp 78 °C). ^1H NMR (benzene-d_6): δ 1.14 (s, 9H, CMe_3), 2.15 (s, 6H, Me), 3.20 (s, 4H, $-CH_2-$), 6.60 (m, 2H, py), 6.87 (m, 4H, py), 7.50 (s, 1H, −OH). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 22.10, 26.25, 39.84, 42.67, 78.86, 119.78, 122.58, 135.55, 156.24, 160.87. MS/CI (H^+): *m/z* 299 (100, M^+), 241 (36), 192 (55), 134 (7), 107 (14). High-resolution MS/CI (H^+): *m/z* 298.2045 calcd, 299.2126 found. IR: 3300 m, 1591 s, 1578 s, 1315 m, 1222 m, 1203 m, 1156 m, 1100 m, 1082 m, 1066 w, 1037 m, 1002 m, 992 w, 937 w, 862 w, 812 m, 793 m, 766 m, 685 w, 667 w, 614 w, 581 w, 504 w cm^{-1}. Anal. Calcd for $C_{19}H_{26}ON_2$: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.51; H, 8.77; N, 9.34.

$Yb[OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]_3$, 2a. In the glovebox, **1** (0.59 g, 1.98 mmol), dissolved in 5 mL of hexanes, was added dropwise to a stirred solution of $Yb[N(SiMe_3)_2]_3$ (0.43 g, 0.65 mmol) in 5 mL of hexanes which had been previously cooled to −35 °C. After 1 day of stirring at ambient temperature, a white precipitate formed. After 4 days of stirring, the mixture was filtered and the white solid was washed with hexane and dried under vacuum to give white solid **2a** (0.15 g, 18%). Upon standing at room temperature, the hexane solution yielded an additional 0.40 g (57% overall yield) of **2a** as colorless crystals. IR: 3054 m, 1602 m, 1591 s, 1575 s, 1317 m, 1270 m, 1221 w, 1200 w, 1184 w, 1163 w, 1153 w, 1110 s, 1090 s, 1045 m, 1013 m, 993 m, 942 w, 917 w, 804 w, 782 m, 755 m, 737 w, 660 m, 619 w, 585 m, 552 w, 517 w, 418 w, 339 w cm^{-1}. Anal. Calcd for $C_{57}H_{75}O_3N_6Yb$: C, 64.27; H, 7.10; N, 7.89; Yb, 16.2. Found: C, 65.04; H, 7.13; N, 7.78; Yb, 15.45.

$Sm[OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]_3$, 2b. In the glovebox, a solution of **1** (0.45 g, 1.52 mmol) was added to a hexane solution of $Sm[N(SiMe_3)_2]_3$ (0.32 g, 0.51 mmol) which had been previously cooled to −35 °C. After the reaction was stirred for 24 h at ambient temperature, the solvent was removed. The residue was again dissolved in hexane, and yellowish crystals of **2b** were deposited upon standing (0.24 g, 48%). ^1H NMR (benzene-d_6): −1.55, 1.15, 2.15, 2.46, 3.19, 5.43, 6.3, 6.72, 6.87, 8.68. IR: 3054 m, 1591 s, 1575 s, 1535 m, 1313 m, 1270 m, 1218 w, 1199 m, 1183 w, 1162 w, 1153 w, 1106 s, 1086 s, 1071 s, 1042 m, 1012 m, 992 m, 939 m, 910 m, 803 w, 781 m, 756 m, 736 w, 657 m, 619 w, 584 m, 575 m, 551 w, 499 w, 473 w, 406 m, 361 w, 308 w cm^{-1}. Anal. Calcd for $SmC_{57}H_{75}O_3N_6Sm$: C, 65.66; H, 7.25; Sm, 14.4. Found: C, 64.77; H, 8.84; Sm, 14.9.

$Yb[OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]_2[N(SiMe_3)_2]$, 3. In the glovebox, **1** (0.46 g, 1.53 mmol) dissolved in 5 mL of hexanes was added dropwise to a solution of $Yb[N(SiMe_3)_2]_3$ (0.50 g, 0.76 mmol) in 5 mL of hexanes previously cooled to −35 °C. The solution was stirred overnight, and the solvent was removed under vacuum to yield **3** (0.48 g, 68%) as a colorless solid. IR: 3058 m, 1577 s, 1531 m, 1358 m, 1315 m, 1278 m, 1247m, 1198 m, 1156 m, 1074 m, 974 m, 864 m, 832 m, 784 m, 756 m, 662 m, 612 m, 587 m, 556 m, 422 w, 373 m cm^{-1}. Anal. Calcd for $YbC_{44}H_{68}O_2N_5Si_2$: C, 56.93; H, 7.38; Yb, 18.6. Found: C, 55.71; H, 7.08; Yb, 18.3.

X-ray Data Collection, Structure Determination, and Refinement for $Sm[OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]_3$, 2b. A colorless crystal of approximate dimensions 0.16 × 0.33 × 0.42 mm was mounted in a glass capillary under nitrogen and transferred to a Siemens P4 rotating-anode diffractometer. The determinations of Laue symmetry, crystal class, unit cell parameters, and crystal orientation matrix were carried out according to standard procedures.[14] Intensity data were collected at 296 K using a $\theta-2\theta$ scan technique with Mo Kα radiation under the conditions described in Table 1. All 6996 data were corrected for absorption[15] and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$. The two possible monoclinic space groups are the noncentrosymmetric $P2_1$ or the centrosymmetric $P2_1/m$. It was later determined by successful refinement of the model that the noncentrosymmetric space group was correct.

All crystallographic calculations were carried out using either our UCI-modified version of the UCLA Crystallographic Computing Package[16] or the SHELXTL PLUS program set.[17] The analytical scattering factors for neutral atoms were used throughout the analysis;[18] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least squares analysis was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.002^2$.

The structure was solved by direct methods and refined by full-matrix least squares techniques. Hydrogen atoms were included using a riding model with d(C−H) = 0.96 Å and U(iso) = 0.08 Å^2.

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Table 1. Crystallographic Data for $Sm(OR)_3$, **2b**, $Yb(OR)_2[N(SiMe_3)_2]$, **3**, and $Sm(OR)_2(OR')_2Na$, **4**

	2b	**3**	**4**
formula	$C_{57}H_{75}N_6O_3Sm$	$C_{44}H_{68}N_5O_2Si_2Yb$	$C_{62}H_{82}N_6NaO_4Sm$
fw	1042.6	926.2	1144.6
space group	$P2_1$	$P\bar{1}$	$P2_1/n$
a, Å	11.5464(7)	11.109(2)	15.229(4)
b, Å	10.7865(5)	15.135(3)	24.826(4)
c, Å	22.5041(9)	16.197(3)	15.662(3)
α, deg		96.482(12)	
β, deg	98.930(4)	106.952(10)	97.70(2)
γ, deg		110.838(10)	
V, Å^3	2786.8(2)	2362.0(8)	5868(2)
Z	2	2	4
T, K	293	163	163
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
ϱ_{calcd}, g cm^{-3}	1.251	1.302	1.296
μ, mm^{-1}	1.106	2.069	1.058
no. of obsd rflcns	5804 ($F > 4.0\sigma(F)$)	5896 ($F > 3.0\sigma(F)$)	6124 ($F > 3.0\sigma(F)$)
$R(F_o)^a$	2.7	3.8	5.5
$R_w(F_o)^b$	3.0	4.8	5.5

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

Refinement of positional and thermal parameters led to convergence with $R_F = 2.7\%$, $R_{wF} = 3.0\%$, and GOF = 1.38 for 604 variables refined against those 5804 data with $F > 4.0\sigma(F)$. A final difference-Fourier synthesis yielded $\varrho(\max) = 0.53e$ Å^{-3}. The absolute structure was determined by refinement of the Rogers' η parameter.[19]

X-ray Data Collection, Structure Determination, and Refinement for $Yb[OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]_2[N(SiMe_3)_2]$, 3. A colorless crystal of approximate dimensions 0.25 × 0.30 × 0.34 mm was oil-mounted[20] on a glass fiber, transferred to the Siemens P4 diffractometer, and handled as described above for **2b**. Low-temperature (163 K) intensity data were collected as described in Table 1.

All 6471 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1 No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice.

All crystallographic calculations were carried out as described above with $\sum w(|F_o - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0008(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of the model led to convergence with $R_F = 3.8\%$, $R_{wF} = 4.8\%$, and GOF = 1.36 for 487 variables refined against those 5596 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\varrho(\max) = 1.84$ e Å^{-3}.

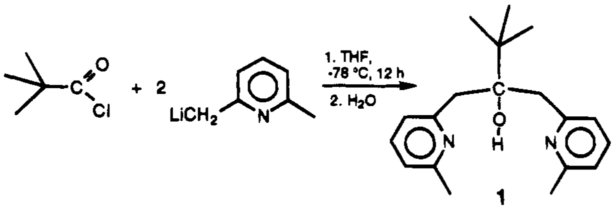
X-ray Data Collection, Structure Determination, and Refinement for $Sm[OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2]_2[OC(CMe_3)(=2\text{-}CHNC_5H_3\text{-}Me\text{-}6)]_2Na$, 4. A pale yellow crystal of approximate dimensions 0.30 × 0.33 × 0.36 mm isolated from a reaction of **1** with a mixture of $Sm[N(SiMe_3)_2]_2(THF)_2$ and $NaSm[N(SiMe_3)_2]_3$ was oil-mounted[20] on a glass fiber, transferred to the Siemens P3 diffractometer, and handled as described for **3**. Intensity data were collected at 163 K using an ω scan technique with Mo Kα radiation under the conditions described in Table 1. All 8282 data were corrected absorption[15] and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ [C_{2h}^5; No. 14] is therefore uniquely defined.

All crystallographic calculations were carried out as described above with $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0004^2$. The structure was solved by direct methods and refined by full-matrix least squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and thermal parameters led to convergence with $R_F = 5.5\%$, $R_{wF} = 5.5\%$, and GOF = 1.46 for 667 variables refined against those 6124 data with $F > 3.0\sigma(F)$. A final difference-Fourier synthesis yielded $\varrho(\max) = 0.73e$ Å^{-3}.

Results

Ligand Synthesis. The synthesis of $HOC(CMe_3)(2\text{-}CH_2\text{-}NC_5H_3Me\text{-}6)_2$, **1** (HOR), is similar to the procedures for preparing other ligands from 2,6-dimethylpyridine.[21] Typically, however, the pyridyl group is the central donor functionality in a tridentate ligand formed by lithiating each methyl group and attaching other donor ligand precursors to each side. In this case, two pyridyl units are used as pendant groups on a central alkoxide ligand.

Treatment of 2,6-dimethylpyridine with 1 equiv of n-BuLi forms the monolithium species $2\text{-}(LiCH_2)NC_5H_3Me\text{-}6$ cleanly in good yield. Nucleophilic attack of 2 equiv of this monolithiated compound on the commercially available trimethylacetyl chloride followed by hydrolysis provides the trifunctional *tert*-butyl-substituted alcohol **1** as the major product, eq 1. Pure **1** was obtained after repeated recrystallization from hexane as a white crystalline material in 44% yield. It is very soluble in both aromatic and aliphatic hydrocarbons.



(1)

Metal Complexes. $Ln(OR)_3$. Reaction of the amide complex $Yb[N(SiMe_3)_2]_3$[12] with 3 equiv of **1** in hexane resulted in the formation of $HN(SiMe_3)_2$ (identified by GC) and a white solid, **2a**, which precipitates from concentrated hexane solutions. Elemental analysis on crystalline **2a** was consistent with formation of the homoleptic alkoxide, $Ln(OR)_3$, according to eq 2. The IR spectrum of **2a** indicated that complete replacement of the silylamide ligands had occurred. A light yellow samarium analog, **2b**, was prepared similarly and characterized by X-ray diffraction (Figure 1) since NMR data on these paramagnetic complexes were not definitive.

$$Yb[N(SiMe_3)_2]_3 + \underset{\mathbf{1}}{3HOR} \xrightarrow{\text{hexane}} \underset{\mathbf{2a}}{Yb(OR)_3} + 3HN(SiMe_3)_2 \quad (2)$$

X-ray crystallography confirmed that a tris(alkoxide) complex had been formed and also revealed that the metal center in **2b** is five-coordinate. None of the OR ligands attach to the metal in a tridentate fashion. Instead, two are bidentate and have trans oxygen and nitrogen donor atoms in the basal positions of a distorted square pyramid. The other OR ligand is monodentate

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(20) The crystal was immersed in a lube-oil additive, which allowed for manipulation on the bench top and prevented decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acted as the adhesive) which was attached to an elongated brass mounting pin. Further details appear in: Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

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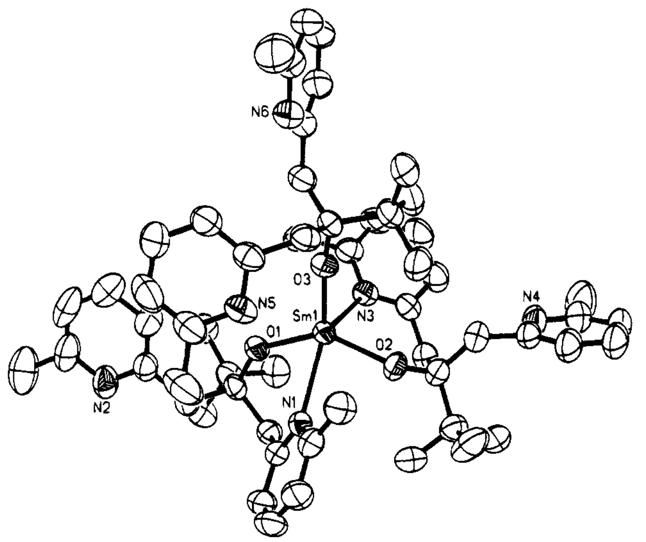

Figure 1. Molecular structure of Sm(OR)$_3$, **2b**. Thermal ellipsoids are drawn at the 50% probability level.

with its oxygen occupying the axial position and two uncomplexed nitrogen donor atoms oriented away from the metal with a Ln−N distances of >5 Å. A total of four unattached pyridine groups surround the molecule and define an elongated tetrahedron with N(4) being the vertex which is stretched away from the triangle defined by N(2), N(5), and N(6). As a result, the molecule has not only the usual inner coordination sphere but also an outer shell of radially distributed unattached donor groups. Bond distances and angles are given in Table 2.

Since the largest (donor atom)−Sm−(donor atom) angle is 137.3(1)°, the five-coordinate geometry around the metal is better described as square pyramidal rather than trigonal bipyramidal. Distortions occur due to the chelating nature of the ligands which form six-membered metallacyclic rings that adopt boat conformations. Hence, the O(1)−Sm−N(1) and O(2)−Sm−N(3) angles within the chelates are 75.6(1) and 75.2(1)°, whereas the O−Sm−N angles between the chelates are 81.2(1) and 94.9(1)°. The (basal donor atom)−Sm−O(3) angles are irregular ranging from 94.0(1) to 127.9(1)°. The 168.6(4)° Sm−O(3)−C(39) angle of the nonchelating alkoxide is significantly larger than the other Sm−O−C angles, and its Sm−O bond is the shortest of the three Sm−O distances.

The 2.116(2), 2.142(3), and 2.172(3) Å Sm−O bond lengths in **2b** are comparable to Ln−O distances in five-coordinate Nd[OC(CMe$_3$)$_3$]$_3$(NCCH$_3$)$_2$ (average 2.162(5) Å)[22] and Dy[OCH(CMe$_3$)$_2$]$_3$(NCCH$_3$)$_2$ (2.061(5) Å)[23] as well as in six-coordinate Ln[OC(CMe$_3$)CH$_2$PMe$_2$]$_3$ (Ln: Y, 2.090(4) Å; Nd, 2.174(2) Å).[24] The 2.604(4) and 2.654(4) Å Sm−N distances resemble the 2.656(3) Å Sm−N(pyridine) distance in ten-coordinate (C$_5$H$_5$)$_3$Sm(pyridine).[25] Ln−N distances have been shown to span a considerable range depending upon steric factors.[26]

Ln(OR)$_2$[N(SiMe$_3$)$_2$]. The reaction of 2 equiv of **1** with Yb[N(SiMe$_3$)$_2$]$_3$ yielded the colorless hexane-soluble compound **3**, which easily crystallizes from hexane at room temperature.

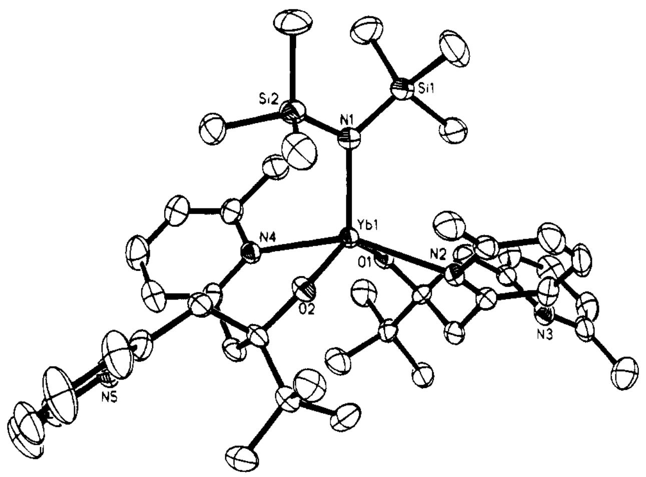

Figure 2. Molecular structure of Yb(OR)$_2$[N(SiMe$_3$)$_2$], **3**. Thermal ellipsoids are drawn at the 50% probability level.

3 was identified by X-ray crystallography as Yb(OR)$_2$[N(SiMe$_3$)$_2$], the first crystallographically characterized monomeric mixed-ligand lanthanide(III) complex[27] containing both alkoxide and amide ligands, eq 3 (Figure 2).

$$\text{Yb[N(SiMe}_3)_2]_3 + 2\underset{\mathbf{1}}{\text{HOR}} \xrightarrow{\text{hexane}} \underset{\mathbf{3}}{\text{Yb(OR)}_2\text{[N(SiMe}_3)_2]} + 2\text{HN(SiMe}_3)_2 \quad (3)$$

Like **2a**, complex **3** crystallizes as a five-coordinate complex in which neither of the OR ligands is tridentate. The overall structural features of **3** and **2a** are very similiar except that a monodentate OR ligand in **2a** has been replaced by a N(SiMe$_3$)$_2$ group in **3**. Each of the OR groups has a free pyridine functional group and generates a six-membered $\overline{\text{LnOCCCN}}$ ring that exists in a boat conformation.

The bond lengths and angles in **3** (Table 2) are equivalent to those in **2b** when the difference in the radial size of the metals is considered.[28] The 2.065 Å average Yb−O distance in **3** is comparable to the Yb−O(aryloxide) distances in three-coordinate Yb(OC$_6$H$_3$Ph$_2$-2,6)$_3$ (average 2.065(4) Å) and and five-coordinate Yb(OC$_6$H$_3$Ph$_2$-2,6)$_3$(THF)$_2$ (average 2.078 Å).[29] The 2.495(6) Å average Yb−N(pyridine) distance lies in the range found in the ytterbium complexes (C$_5$H$_5$)$_3$Yb(NCCH$_2$CH$_3$) (2.414(5) Å),[30] {tris(4-methyl-6-oxo-3-azahept-4-en-1-yl)amine}Yb (2.41(1)−2.46(1) Å)[31] and (C$_5$H$_5$)$_3$Yb(NC$_4$H$_4$N)Yb(C$_5$H$_5$)$_3$ (2.61(1) Å).[32] The 2.260(5) Å Yb−N[N(SiMe$_3$)$_2$] bond length is longer than the terminal Yb−N(silylamide) bonds in precursor Yb[N(SiMe$_3$)$_2$]$_3$ (2.158(13) Å)[33] and in five-coordinate {Yb[N(SiMe$_3$)$_2$]$_2$(μ-Cl)(THF)}$_2$ (2.174(5), 2.198(5) Å).[34]

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Table 2. Selected Bond Distances (Å) and Angles (deg) in $Sm(OR)_3$, **2b**, $Yb(OR)_2[N(SiMe_3)_2]$, **3**, and $Sm(OR)_2(OR')_2Na$, **4**

$Sm[OC(CMe_3)(2-CH_2NC_5H_3Me-6)_2]_3$, **2**			
Sm−O(1)	2.172(3)	Sm−O(2)	2.142(3)
Sm−O(3)	2.116(2)	Sm−N(1)	2.604(4)
Sm−N(4)	2.654(4)		
O(1)−Sm−O(2)	132.4(1)	O(1)−Sm−O(3)	115.2(2)
O(2)−Sm−O(3)	111.9(1)	O(1)−Sm−N(1)	75.6(1)
O(2)−Sm−N(1)	81.2(1)	O(3)−Sm−N(1)	127.9(1)
O(1)−Sm−N(3)	94.9(1)	O(2)−Sm−N(3)	75.2(1)
O(3)−Sm−N(3)	94.0(1)	N(1)−Sm−N(3)	137.3(1)
Sm−O(1)−C(1)	137.8(3)	Sm−O(2)−C(20)	147.8(3)
Sm−O(3)−C(39)	168.6(4)		
$Yb[OC(CMe_3)(2-CH_2NC_5H_3Me-6)_2]_2[N(SiMe_3)_2]$, **3**			
Yb−O(1)	2.072(3)	Yb−O(2)	2.057(4)
Yb−N(1)	2.260(5)	Yb−N(2)	2.511(5)
Yb−N(4)	2.479(6)		
O(1)−Yb−O(2)	133.5(2)	O(1)−Yb−N(1)	120.7(2)
O(2)−Yb−N(1)	105.8(2)	O(1)−Yb−N(2)	78.6(2)
O(2)−Yb−N(2)	94.3(2)	N(1)−Yb−N(2)	102.6(2)
O(1)−Yb−N(4)	87.0(2)	O(2)−Yb−N(4)	78.2(2)
N(1)−Yb−N(4)	105.6(2)	N(2)−Yb−N(4)	151.8(1)
Yb−O(1)−C(1)	143.0(4)	Yb−O(2)−C(20)	142.3(4)
$Sm[OC^tBu-(2-CH_2NC_5H_3Me-6)_2]_2[OC(^tBu)(2-CHNC_5H_3Me-6)]_2Na$, **4**			
Sm−O(1)	2.215(5)	Sm−O(2)	2.230(4)
Sm−O(3)	2.239(4)	Sm−O(4)	2.239(5)
Sm−N(5)	2.844(7)	Sm−N(6)	2.816(6)
Na−O(1)	2.328(5)	Na−O(2)	2.317(5)
Na−N(2)	2.389(7)	Na−N(3)	2.405(7)
C(39)−C(44)	1.361(11)	C(51)−C(56)	1.375(10)
O(1)−Sm−O(2)	88.0(2)	O(1)−Sm−O(3)	96.6(2)
O(2)−Sm−O(3)	92.8(2)	O(1)−Sm−O(4)	91.5(2)
O(2)−Sm−O(4)	95.0(2)	O(3)−Sm−O(4)	169.0(2)
O(1)−Sm−N(5)	166.4(2)	O(2)−Sm−N(5)	96.3(2)
O(3)−Sm−N(5)	70.5(2)	O(4)−Sm−N(5)	100.9(2)
O(1)−Sm−N(6)	98.5(2)	O(2)−Sm−N(6)	165.7(2)
O(3)−Sm−N(6)	99.0(2)	O(4)−Sm−N(6)	72.3(2)
N(5)−Sm−N(6)	80.3(2)	Sm−O(1)−C(1)	146.1(4)
Sm−O(2)−C(20)	146.4(4)	Sm−O(3)−C(39)	145.8(5)
Sm−O(4)−C(51)	143.3(4)		
Sm−O(1)−Na	94.3(2)	Sm−O(2)−Na	94.2(2)
O(1)−Na−O(2)	83.4(2)	O(1)−Na−N(2)	88.2(2)
O(2)−Na−N(2)	135.7(2)	O(1)−Na−N(3)	130.2(2)
O(2)−Na−N(3)	88.6(2)	N(2)−Na−N(3)	127.8(2)
Na−O(1)−C(1)	119.5(4)	Na−O(2)−C(20)	119.1(4)

In the course of examining the chemistry of **1**, fragmentation of the ligand was observed in one case, and this result is included here for completeness. In a reaction involving **1** and an inadvertent mixture of $Sm[N(SiMe_3)_2]_2(THF)_2$ and $NaSm[N(SiMe^3)_2]_3$,[13] a yellow trivalent samarium complex, $(R'O)_2Sm(\mu-OR)_2Na$, **4**, exhibiting a very complex ^1H NMR spectrum was isolated and identified by X-ray crystallographic analysis (Figure 3). The X-ray study revealed that two of the OR ligands in **4** had lost dimethylpyridine to form the bidentate pyridine enolate ligands $[OC(CMe_3)(2-CH-NC_5H_3-Me-6)]$, OR′. GC-MS analysis of the volatile products of this reaction confirmed the loss of 2,6-dimethylpyridine and $HN(SiMe_3)_2$.

The six-coordinate samarium center in **4** has a distorted octahedral geometry in which the bidentate OR′ ligands are oriented such that the pyridyl donors are cis to each other and the oxygen donors are trans. Incorporation of the double bond into the chelating six-membered rings causes them to be planar to within 0.05 Å as shown in Figure 4. These extended ring systems are nearly perpendicular as shown. The OR ligands in **4** again are not tridentate; each has one pendant pyridine group. The oxygen atoms of the OR groups bridge Sm and Na and the other pyridine nitrogen donor atoms are attached to Na to make six-membered rings. With the OR ligand bridging in this manner, no other coordination of solvent to Na is observed and a solvent-free distorted tetrahedral configuration results.

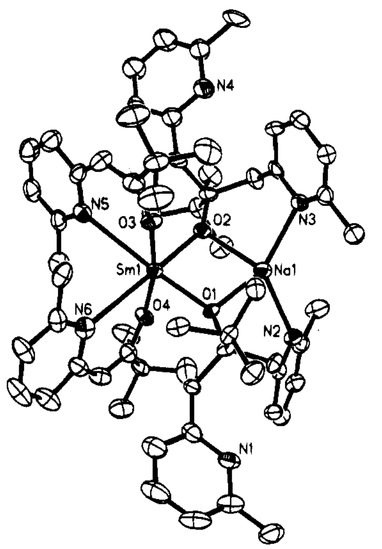

Figure 3. Molecular structure of $Sm(OR)_2(OR')_2Na$, **4**. Thermal ellipsoids are drawn at the 50% probability level.

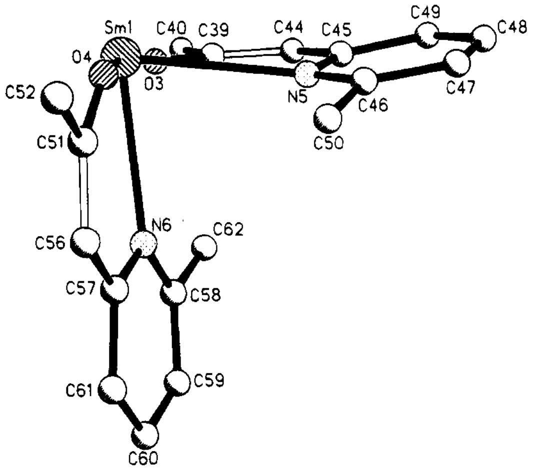

Figure 4. Partial view of **4** showing the planarity of two perpendicular metallacycles.

The Sm−O(enolate) distances of 2.239(4) and 2.239(5) Å are elongated by about 0.12 Å compared to the Sm−O(alkoxide) distances in **2b** (Table 1) and the eight-coordinate enolate complex $[(C_5Me_5)_2(Ph_3PO)Sm]_2(OCH{=}CHO)$ (2.107(7), 2.122(8) Å).[35] The 2.844(7) and 2.816(6) Å Sm−N(pyridine) distances are considerably longer than those found in **2b** and are even longer than the Sm−N(pyridine) bond in ten-coordinate $(C_5H_5)_3Sm(pyridine)$ (2.656(3) Å).[25] Given the similarity of distances in **2b** and **3**, the observed bond elongations in **4** are likely to be due to the presence of the C═C double bond in the metallacycle. Interestingly, the 2.215(5) and 2.230(4) Å bridging Sm−O(alkoxide) distances lie in the same range as the terminal Sm−O bonds in **2b** and are therefore are shorter than expected.[36] The bridging Na−O(alkoxide) and the Na−N(pyridine) distances are normal.[37,38]

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Discussion

The alcohol $HOC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$ is conveniently made in useful quantities, and the synthetic approach is quite powerful since it can be modified to include other donor functionalities including chiral components. This OR ligand system is suitable for displacing bis(trimethylsilyl)amide ligands in lanthanide complexes to make new classes of lanthanide alkoxide complexes. Importantly, this OR group is capable of forming *both* completely substituted $Ln(OR)_3$ complexes and the mixed-ligand system $Ln(OR)_2(NR_2)$. Complexes of the latter type are not common since displacement of amides by alcohols often forms exclusively the homoleptic product, $Ln(OR)_3$, and unreacted $Ln(NR_2)_3$. Isolation of the mixed-ligand $Ln(OR)_2(NR_2)$ complex provides other opportunities for formation of mixed-ligand systems since the $Ln-NR_2$ moiety can undergo further bond transformations. Hence, this OR ligand system offers some flexibility in generating lanthanide compounds with a variety of new ligand compositions. Recently mixed-ligand lanthanide alkoxide complexes have received attention as active catalysts for polymerization reactions.[39]

This OR group is apparently quite sterically bulky. Lanthanide alkoxide complexes are typically six-coordinate unless very large ligands are present. The fact that the five-coordinate complexes **2b** and **3** are formed in the presence of an extra donor group is best explained by steric crowding. The bond distances in **2b** and **3** are also consistent with the analysis of these complexes as sterically crowded. As a consequence, this tridentate OR ligand does not use all of its donor functionalities to bind to the lanthanide center. This presents the opportunity to make isolable lanthanide complexes which have a conventional inner donor sphere and an outer sphere containing additional donor atoms. This may be useful in the formation of mixed-metal complexes with specific Ln:M ratios and in electron transfer reactions which require external orientation of the substrate.

Elimination of 2,6-dimethylpyridine from OR in the formation of **4** shows another option in this chelating ligand system. In this case, a planar six-membered metallacyclic ring is generated. With the attached pyridine moiety, this provides quite an extended planar unit. The isolation of **4** also shows how the OR ligand can be used to incorporate a solvent-free heterometallic component by bridging with this ligand system.

Conclusion

The $OC(CMe_3)(2\text{-}CH_2NC_5H_3Me\text{-}6)_2$ ligand system provides routes to new $Ln(OR)_3$ and $Ln(OR)_2(NR_2)$ complexes which have pendant donor functionalities available for other purposes. This OR ligand also can form the planar bidentate $[OC(CMe_3)(2\text{-}CHNC_5H_3Me\text{-}6)]$ ligand.

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Supplementary Material Available: Molecular structure diagrams of **2b**, **3**, and **4** and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (41 pages). Ordering information is given on any current masthead page.

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