Table V. Curie-Weiss Parameters for the Compounds (4-15 K)

compd	g	Θ/K	TIP/emu mol^{-1}
$[Co(pz(COO)COOH)_2(H_2O)_2]$	4.60	−0.78	0.006
$[Co(pzCOO)_2(H_2O)_2]\cdot 2H_2O$	4.31	−1.00	0.008
$[Co(pzCOO)_2(H_2O)_2]$	4.17	−1.10	0.006

from 4 to 25 K. The data were analyzed in the low-temperature region (4–24 K) with the Curie–Weiss law plus a correction for temperature-independent paramagnetism (TIP). The equation used is

$$\chi = \frac{Ng^2\mu_\beta{}^2S(S+1)}{3k(T-\Theta)} + \text{TIP} \qquad (1)$$

Due to effects of spin–orbit coupling and distortion from octahedral symmetry, cobalt(II) has a low-lying anisotropic Kramers doublet. Its magnetic behavior may be approximated at low temperatures with an effective spin $S = {}^1/_2$ in eq 1. The lowest lying excited magnetic state is usually at least some 100 cm^{-1} above the doublet and is therefore appreciably depopulated at lower temperatures ($T < 25$ K).[34] However, the magnetic excited states necessitate the inclusion of a TIP term due to coupling with the ground state.[35]

The parameters obtained from the fits of the data to eq 1 are listed in Table V. The negative value for the Θ term may only be explained by antiferromagnetically coupled monomeric units since the Kramers doublet may not be further split.

Pyrazine has been shown to be an effective magnetic bridge in many magnetic systems. However, in this case, hydrogen bonding is required to propagate magnetic superexchange. These complexes are excellent candidates for investigating the magnetic properties of chemically similar materials with different magnetic-superexchange pathways. From the magnetic parameters, the critical region is expected to occur below 1 K in each of the complexes. Further measurements below 1 K will be required for information on the critical regions.

Acknowledgment. Support received under NSF Grant No. CHE77-01372 is gratefully acknowledged.

Registry No. $Co(pz(COO)COOH)_2(H_2O)_2$, 75658-52-5; $[Co(pzCOO)_2(H_2O)_2]\cdot 2H_2O$, 75600-06-5; $Co(pzCOO)_2(H_2O)_2$, 74184-89-7.

Supplementary Material Available: A listing of least-squares planes for $[Co(pz(COO)_2)_2]$ and tables of observed and calculated structure factors for $[Co(pz(COO)COOH)_2(H_2O)]$, $[Co(pzCOO)_2(H_2O)_2]\cdot 2H_2O$, and $[Co(pzCOO)_2(H_2O)_2]$ (19 pages). Ordering information is given on any current masthead page.

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Divalent Lanthanide Chemistry. Preparation of Some Four- and Six-Coordinate Bis[(trimethylsilyl)amido] Complexes of Europium(II). Crystal Structure of Bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane)europium(II)

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The yellow, hydrocarbon-soluble, divalent derivatives of europium(II) of the type $[(Me_3Si)_2N]_2Eu(L)_2$, where L is tetrahydrofuran or 1,2-dimethoxyethane, and $[(Me_3Si)_2N]_2Eu(bpy)$ have been prepared. The crystal structure of $[(Me_3Si)_2N]_2Eu[MeOCH_2CH_2OMe]_2$ has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic, $C2/c$, with cell dimensions $a = 13.398$ (4) Å, $b = 17.454$ (6) Å, $c = 15.013$ (5) Å, $\beta = 92.91$ (3)°, and $V = 3506$ Å^3. For $Z = 4$, the calculated density is 1.24 g/cm^3. The structure was refined to a conventional R factor of 0.039 by using 2259 data where $F^2 > \sigma(F^2)$. The Eu(II) atom is hexacoordinate and bonded to two nitrogen atoms of the two bis(trimethylsilyl)amido groups and to four oxygen atoms of the 1,2-dimethoxyethane ligands. The molecule has C_2 symmetry. The Eu(II)–N bond distance is 2.530 (4) Å and the Eu(II)–O distances are 2.634 (4) and 2.756 (4) Å. The ethane carbon atoms in the 1,2-dimethoxyethane ligand are disordered.

Introduction

Compounds of europium in its divalent oxidation state are rather less well characterized than are those of the more common trivalent oxidation state. Some simple halides, chalcogenides, and organometallic compounds have been prepared, and their physical properties have been studied.[1,2] These compounds are generally insoluble, and their solid-state structures are coordination polymers with high coordination number metal atoms. One way to prevent polymer formation is with use of sterically voluminous ligands, one such ligand being the bis(trimethylsilyl)amido ligand, $(Me_3Si)_2N$. This ligand has been used to prepare low coordination number complexes of most elements in the periodic table.[3,4] Even the trivalent uranium derivative, $[(Me_3Si)_2N]_3U$, is monomeric and three-coordinate, a most unusual constitution for this large actinide ion.[5]

In this paper we describe the synthesis of some coordination complexes of bis[bis(trimethylsilyl)amido]europium(II) and the crystal structure of one of them, viz., $[(Me_3Si)_2N]_2Eu(dme)_2$, where dme is the chelating ether 1,2-dimethoxyethane. This is the only monomeric, molecular compound of Eu(II)

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whose crystal structure has been determined.

Experimental Section

All analyses were by the microanalytical laboratory of this department. Magnetic susceptibility measurements were carried out as previously described.[6] All operations were performed under nitrogen.

Bis[bis(trimethylsilyl)amido]bis(tetrahydrofuran)europium(II) Complex. Tris[bis(trimethylsilyl)amido]europium[7] (2.2 g, 0.0034 mol) in tetrahydrofuran (75 mL) was added to europium trichloride (0.44 g, 0.0017 mol) suspended in tetrahydrofuran (25 mL). After 8 h of stirring, sodium naphthalene [prepared from sodium metal (0.12 g, 0.0052 mol) and naphthalene (0.65 g, 0.0051 mol) in tetrahydrofuran (75 mL)] was added to the homogeneous solution and the brown-red solutions was stirred for 12 h. Tetrahydrofuran was removed in vacuum, naphthalene was sublimed (40 °C, 10^{-2} torr), and the yellow residue was extracted with pentane (40 mL). The pentane extract was filtered, and the filtrate was concentrated in vacuum to ca. 10 mL and cooled (−10 °C). The orange-yellow crystals (0.45 g, 14%) were collected and dried under vacuum; mp 128–130 °C. Anal. Calcd for $C_{20}H_{52}EuN_2O_2Si_4$: C, 38.9; H, 8.50; N, 4.54. Found: C, 39.4; H, 7.73; N, 4.63.

Bis[bis(trimethylsilyl)amido]bis(bipyridine)europium(II) Complex. 2,2′-Bipyridine (0.064 g, 0.000 41 mol) in benzene (30 mL) was added to bis[bis(trimethylsilyl)amido]europium bis(tetrahydrofuran) (0.25 g, 0.000 41 mol) in benzene (20 mL). The dark brown solution was stirred for 1 h, and benzene was removed in vacuum. The residue was extracted with toluene (10 mL), and the extract was filtered. The filtrate was concentrated to ca. 5 mL and cooled (0 °C). The yellow needles (0.16 g, 62%) were collected and dried under vacuum; mp 85–87 °C dec. Anal. Calcd for $C_{22}H_{44}EuN_4Si_4$: C, 42.0; H, 7.05; N, 8.91. Found: C, 42.0; H, 6.66; N, 8.85.

Bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane)europium(II). Tris[bis(trimethylsilyl)amido]europium[6] (1.5 g, 0.0024 mol) in 1,2-dimethoxyethane (40 mL) was added to a suspension of europium trichloride (0.31 g, 0.0012 mol) in 1,2-dimethoxyethane (50 mL), and the orange solution was stirred for 8 h. A solution of sodium naphthalene [prepared from sodium (0.10 g, 0.0044 mol) and naphthalene (0.46 g, 0.0036 mol) in 1,2-dimethoxyethane (40 mL)] was added to the chlorosilylamide, and the brown-red solution was stirred for 12 h. 1,2-Dimethoxyethane was evaporated, and naphthalene was removed by sublimation at 40 °C (10^{-2} torr). Pentane (40 mL) was added to the residue, and the yellow solution was filtered. The filtrate was concentrated to ca. 25 mL and cooled (−10 °C, 3 weeks). The needles were collected and dried under vacuum: mp 83–86 °C; yield 0.25 g (11%). Anal. Calcd for $C_{20}H_{56}EuN_2O_4Si_4$: C, 36.8; H, 8.64; N, 4.29. Found: C, 35.7; H, 8.40; N, 4.28.

Some of the air-sensitive yellow crystals were inserted into thin-walled quartz capillaries in an argon-filled drybox. A crystal was subjected to Weissenberg photography to study the crystal symmetry and to evaluate its suitability for a structure determination. A second crystal was examined with a Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.14–0.18°. The space group is $C2/c$. The setting angles of 12 manually centered reflections ($40° < 2\theta < 45°$) were used to determine by least squares the following cell parameters: $a = 13.398$ (4) Å, $b = 17.454$ (6) Å, $c = 15.013$ (5) Å, $\beta = 92.91$ (3)°, and $V = 3506$ Å^3. For $Z = 4$ and a molecular weight of 652.98, the calculated density is 1.24 g/cm^3.

Intensity data were collected with the use of a θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each peak was scanned from 0.9° before the $K\alpha_1$ peak to 0.9° after the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range. The temperature during the data collection was 20 ± 1 °C. Three standard reflections were measured every 200th scan. A total of 6531 scans ($4° < 2\theta < 45°$) yielded 2308 unique data of which 2259 had $F^2 > 1\sigma$. An absorption correction ($\mu = 19.5$ cm^{-1}) was applied[8] which ranged from 1.21 to 1.32. The intensities of the three standard reflections decayed about 16% during the data collection period, and the data were corrected for this effect.

A three-dimensional Patterson calculation showed the Eu atom position, and a subsequent least-squares refinement and Fourier calculation revealed all the nonhydrogen atoms in the structure. After a few cycles of least-squares refinements of the structure in which only the Eu atom was assigned anisotropic thermal parameters, the R factor, $R = \sum||F_o| - |F_c||/\sum|F_o|$, was 0.062.

The methylene carbon atoms of the dimethoxyethane ligand were ill behaved in the refinements as indicated by large thermal parameters and chemically unsatisfactory bond distances to adjacent atoms. A difference Fourier map showed additional electron density in the region of the methylene carbon atoms, indicating disorder. The two methylene carbon atoms were subsequently described as four half-atoms. Additional refinements of the structure converged and gave reasonable thermal parameters on the disordered atoms but bond distances that were still chemically unacceptable. Restraints on the interatomic distances to the disordered atoms were included in a manner suggested by Waser[9] and described in a previous paper.[10] The distance restraints were applied as follows: C–C, 1.54 ± 0.01 Å; C–O, 1.43 ± 0.01 Å; C–C(methyl), 2.37 ± 0.08 Å; C–O (nearest nonbonded neighbor), 2.36 ± 0.05 Å.

Some of the hydrogen atoms were observed in regions where they were expected to be but were scattered among a larger number of "noise" peaks of comparable size. Isotropic hydrogen atoms at calculated positions, 0.95 Å from the atoms to which they are bonded, were included in the least-squares refinements but not refined; hydrogen atoms to the disordered atoms were not included. The least-squares procedure used minimizes the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$. The expressions used in processing the data and estimating weights are given in the supplementary material; the "ignorance factor" was set to 0.04. Scattering factors from Doyle and Turner[11] were used, and anomalous dispersion corrections[12] were applied. In the final least-squares refinement, all of the nonhydrogen atoms, with the exception of the disordered atoms, were refined with anisotropic thermal parameters.

The discrepancy indices for 2259 data where $F^2 > \sigma$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$$

R for all 2362 data is 0.042. The error in an observation of unit weight is 1.10. In the last cycle, no parameter changed more than 0.16σ. In the final difference Fourier, the two largest electron density peaks were ~0.8 e/Å^3 and were ~0.8 Å from the disordered carbon atoms.

Results and Discussion

The best synthesis of the tetrahydrofuran complex of the europium(II) silylamide, $Eu[N(SiMe_3)_2]_3(thf)_2$, is

$$2Eu[N(SiMe_3)_2]_3 + EuCl_3 \xrightarrow{thf} 3ClEu[N(SiMe_3)_2]_2$$

$$ClEu[N(SiMe_3)_2]_2 + Na(naph) \xrightarrow{thf} [(Me_3Si)_2N]_2Eu(thf)_2$$

Europium trichloride, which is only sparingly soluble in tetrahydrofuran, slowly dissolves in a tetrahydrofuran solution of the europium(III) silylamide, $Eu[N(SiMe_3)_2]_3$. All attempts to isolate the intermediate chloro amide have failed. However, addition of sodium naphthalene to the chloro amide, prepared in situ, yields a yellow solution from which yellow $Eu[N(SiMe_3)_2]_2(thf)_2$ may be isolated by crystallization from pentane. Though the yield is low (ca. 10%), the preparative method is the best that we have been able to develop. Further, we have been unable to prepare divalent silylamides of samarium or ytterbium, both of which have accessible divalent oxidation states.

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Table I. Positional Parameters[a]

atom	*x*	*y*	*z*
Eu	0.0	0.19015 (2)	$^1/_4$
N	0.1734 (3)	0.1341 (2)	0.2411 (3)
Si(1)	0.2594 (1)	0.1938 (1)	0.2010 (1)
Si(2)	0.2009 (2)	0.0436 (1)	0.2727 (2)
O(1)	0.0133 (3)	0.1674 (3)	0.4239 (3)
O(2)	0.0703 (3)	0.3065 (3)	0.3603 (3)
C(1)	0.1972 (5)	0.2815 (4)	0.1506 (5)
C(2)	0.3524 (6)	0.2350 (6)	0.2873 (6)
C(3)	0.3372 (5)	0.1520 (5)	0.1110 (5)
C(4)	0.326 (1)	0.0316 (6)	0.3334 (9)
C(5)	0.108 (1)	0.0042 (6)	0.3459 (9)
C(6)	0.2080 (8)	−0.0255 (5)	0.1775 (7)
C(7)	−0.0497 (6)	0.1275 (5)	0.4815 (5)
C(8)	0.0375 (6)	0.3821 (5)	0.3781 (7)
C(9)	0.067 (1)	0.2234 (7)	0.4809 (8)
C(9′)	0.1078 (9)[b]	0.1962 (8)	0.457 (1)
C(10)	0.1376 (8)	0.2657 (7)	0.4212 (8)
C(10′)	0.092 (1)[b]	0.2813 (8)	0.4533 (8)
H(1)	0.1623	0.3076	0.1950
H(2)	0.1517	0.2667	0.1033
H(3)	0.2466	0.3145	0.1284
H(4)	0.3885	0.1944	0.3162
H(5)	0.3179	0.2634	0.3300
H(6)	0.3976	0.2677	0.2588
H(7)	0.2944	0.1373	0.0613
H(8)	0.3726	0.1087	0.1336
H(9)	0.3830	0.1897	0.0923
H(10)	0.3288	0.0619	0.3859
H(11)	0.3773	0.0476	0.2957
H(12)	0.3359	−0.0208	0.3486
H(13)	0.0442	0.0040	0.3153
H(14)	0.1057	0.0348	0.3980
H(15)	0.1261	−0.0467	0.3621
H(16)	0.2588	−0.0092	0.1396
H(17)	0.1458	−0.0268	0.1448
H(18)	0.2239	−0.0750	0.2002
H(19)	−0.0941	0.1628	0.5074
H(20)	−0.0103	0.1029	0.5273
H(21)	−0.0877	0.0902	0.4483
H(22)	−0.0119	0.3887	0.4196
H(23)	0.0260	0.4155	0.3288
H(24)	0.1055	0.3756	0.4003

[a] In this and the following tables the number in parentheses is the estimated standard deviation in the least significant digit.
[b] The disordered atom pair has the same number, and the two positions are distinguished with a prime on one of them.

Table II. Interatomic Distances (Å)

Eu-2N	2.530 (4)	Si(2)-C(6)	1.88 (1)
Eu-2O(1)	2.638 (4)	O(1)-C(7)	1.42 (1)
Eu-2O(2)	2.756 (4)	O(1)-C(9)	1.47 (1)
N-Si(1)	1.686 (5)	O(1)-C(9′)	1.43 (1)
N-Si(2)	1.685 (5)	O(2)-C(8)	1.42 (1)
Si(1)-C(1)	1.88 (1)	O(2)-C(10)	1.44 (1)
Si(1)-C(2)	1.89 (1)	O(2)-C(10′)	1.48 (1)
Si(1)-C(3)	1.90 (1)	C(9)-C(10)	1.52 (1)
Si(2)-C(4)	1.88 (1)	C(9′)-C(10′)	1.50 (1)
Si(2)-C(5)	1.83 (1)		

Table III. Selected Angles (Deg)[a]

N-Eu-N′	134.5 (2)	N-Si(2)-C(6)	114.1 (4)
N-Eu-O(1)	88.7 (2)	C(1)-Si(1)-C(2)	103.2 (4)
N-Eu-O(1)′	84.6 (2)	C(1)-Si(1)-C(3)	105.9 (4)
N-Eu-O(2)	91.7 (2)	C(2)-Si(1)-C(3)	105.5 (4)
N-Eu-O(2)′	122.7 (2)	C(4)-Si(2)-C(5)	106.5 (6)
O(1)-Eu-O(1)′	162.7 (2)	C(4)-Si(2)-C(6)	102.6 (5)
O(1)-Eu-O(2)	60.8 (2)	C(5)-Si(2)-C(6)	106.1 (6)
O(1)-Eu-O(2)′	135.2 (2)	C(7)-O(1)-C(9)	105 (1)
O(2)-Eu-O(2)′	85.1 (2)	C(7)-O(1)-C(9′)	120 (1)
Eu-N-Si(1)	115.2 (2)	C(8)-O(2)-C(10)	122 (1)
Eu-N-Si(2)	122.4 (2)	C(8)-O(2)-C(10′)	98 (1)
N-Si(1)-C(1)	110.5 (3)	O(1)-C(9)-C(10)	106 (1)
N-Si(1)-C(2)	115.3 (3)	O(2)-C(10)-C(9)	103 (1)
N-Si(1)-C(3)	115.3 (3)	O(1)-C(9′)-C(10′)	116 (1)
N-Si(2)-C(4)	114.7 (4)	O(2)-C(10′)-C(9′)	124 (2)
N-Si(2)-C(5)	112.0 (4)		

[a] Prime labels inside the parentheses, e.g., C(9′), refer to a disordered pair. Primes outside the parentheses, e.g., O(1)′, refer to the symmetrically equivalent atom at $-x$, y, $^1/_2 - z$.

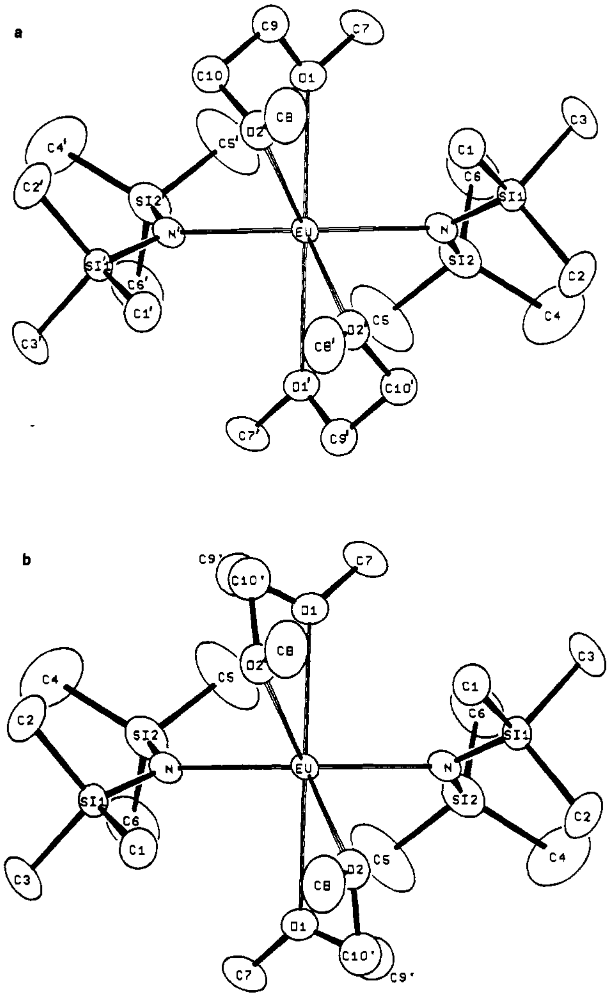

Figure 1. (a) ORTEP drawing as viewed down the twofold axis. The primed atoms are related to the unprimed atoms by the twofold axis perpendicular to the drawing on the Eu atom. (b) ORTEP drawing showing the molecule in the other configuration due to the disorder in C(9) and C(10).

The tetrahydrofuran in Eu[N(SiMe$_3$)$_2$]$_2$(thf)$_2$ can be displaced by 1,2-dimethoxyethane or bipyridine, yielding yellow [(Me$_3$Si)$_2$N]$_2$Eu(MeOCH$_2$CH$_2$OMe) or [(Me$_3$Si)$_2$N]$_2$-Eu(bpy), respectively. Both coordination complexes are soluble in hydrocarbon solvents from which they may be crystallized. The 1,2-dimethoxyethane complex follows Curie behavior, $\chi_M = C_M T^{-1}$, from 5 to 45 K with $C_M = 8.82$ and $\mu_{eff} = 8.43$ μ_B. The magnetic moment is similar to that found for the isoelectronic gadolinium(III) analogue (7.75 μ_B at 98 K)[7] which is consistent with a $^8S_{7/2}$ ground state. In contrast the base-free europium(III) silylamide, Eu[N(SiMe$_3$)$_2$]$_3$, is a temperature-independent paramagnet (TIP), the temperature-independent susceptibility being ca. 0.4 μ_B, consistent with a $^7F_0$ ground state. In addition, the ytterbium(III) derivative, Yb[N(SiMe$_3$)$_2$]$_3$, follows Curie behavior (5–45 K) with μ_{eff} = 3.10 μ_B.

Isolation of well-developed crystals of Eu[N(SiMe$_3$)$_2$]$_2$-(dme)$_2$ allowed us to carry out this first single-crystal X-ray analysis of a molecular complex of europium(II).

Positional parameters, distances, and angles are listed in Tables I–III. The list of thermal parameters and observed structure factors have been submitted as supplementary data.

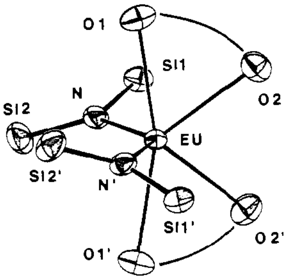

Figure 2. ORTEP view of the coordination sphere about Eu(II).

Figure 1a is an ORTEP view providing the atom-labeling scheme. The view is along a crystallographic twofold axis relating the two silylamide ligands and the two chelating ethers.

Figure 1 illustrates the two conformations of the 1,2-dimethoxyethane ligands that give rise to the disorder in the C(9) and C(10) atoms. It is not apparent whether this disorder is static or dynamic, but the two structures represent two different puckered conformations for the five-membered chelate rings. Disorder in the rest of the 1,2-dimethoxyethane ligand is probably present, but the effects are not as severe and are absorbed in the anisotropic thermal parameters; because of this disorder, bond distances involving this ligand are probably not as accurate as indicated (see Experimental Section).

Figure 2 is a stereochemical view of the coordination geometry about the six-coordinate europium(II) ion. The coordination polyhedron cannot be described by a simple regular geometric figure. The two bulky silylamide groups are surprisingly close to one another, resulting in a N–Eu–N angle of only 134.5°. Kepert has shown, from points-on-a-sphere repulsion energy calculations, that for six-coordinate complexes of the type M(bidentate)$_2$(unidentate)$_2$, the unidentate ligands are pulled together when the bidentate ligands have small normalized bites.[13] Kepert defines the normalized bite of a chelating ligand as the distance between donor atoms in the chelate group divided by the metal–donor atom distance. It is the bidentate nature of the 1,2-dimethoxyethane ligands that prevents the two silylamide groups from repelling each other to a greater extent. The normalized bite of the 1,2-dimethoxyethane ligands in this complex is among the smallest known, 0.98. Clearly, repulsive interactions between coordinated *atoms* are more important in defining this detail of the structure than the overall steric bulk of the ligands.

Bond angles and distances in the planar bis(trimethylsilyl)amido ligands are comparable to those found in other structures.[14-18] The Eu(II)–N bond distance is 2.53 Å, the first such bond length determined, whereas the Eu(III)–N bond length in Eu[N(SiMe$_3$)$_2$]$_3$ is 2.26 Å. The difference of 0.27 Å is due mostly to the change in bond length with oxidation state, estimated as 0.23 Å from the ionic radii listed by Shannon.[19] The Eu(II)–O bond lengths in this structure are 2.638 and 2.756 Å, and Kepert has shown that such a difference may accompany the bending distortion dicussed above. These Eu(II)–O distances are in good agreement with those reported in the EuCl$_2$·2H$_2$O[20] structure, which range from 2.69 to 2.74 Å.

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Registry No. [(Me$_3$Si)$_2$N]$_2$Eu(dme)$_2$, 75600-03-2; [(Me$_3$Si)$_2$N]$_2$Eu(bpy), 75600-04-3; [(Me$_3$Si)$_2$N]$_2$Eu(thf)$_2$, 75600-05-4; [(Me$_3$Si)$_2$N]$_3$Eu, 35789-02-7.

Supplementary Material Available: Data processing formulas, the table of anisotropic thermal parameters, and the listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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