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Divalent Lanthanide Chemistry. Preparation and Crystal Structures of Sodium Tris[bis(trimethylsilyl)amido]europate(II) and Sodium Tris[bis(trimethylsilyl)amido]ytterbate(II), $NaM[N(SiMe_3)_2]_3$

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A new synthetic method for high-yield preparations of the divalent silylamides $M[N(SiMe_3)_2]_2[MeOCH_2CH_2OMe]_2$, where M is Eu or Yb, has been developed that involves reaction of MI_2 and $NaN(SiMe_3)_2$ in $MeOCH_2CH_2OMe$. Reaction of EuI_2 and $NaN(SiMe_3)_2$ in Et_2O yields $NaEu[N(SiMe_3)_2]_3$. Reaction of YbI_2 with $NaN(SiMe_3)_2$ in Et_2O yields two products depending upon the crystallization conditions. If Et_2O is used, $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ is isolated. In contrast, if toluene is used, $NaYb[N(SiMe_3)_2]_3$ is isolated. The crystal structures of $NaEu[N(SiMe_3)_2]_3$ and $NaYb[N(SiMe_3)_2]_3$ were determined by X-ray diffraction methods. Crystals of $NaEu[N(SiMe_3)_2]_3$ are monoclinic, $P2_1/n$, with cell dimensions $a = 17.586$ (6) Å, $b = 19.170$ (6) Å, $c = 21.808$ (6) Å, and $\beta = 107.90$ (4)°; for $Z = 8$, the calculated density is 1.246 g/cm^3. Crystals of $NaYb[N(SiMe_3)_2]_3$ are orthorhombic, *Pbca*, with cell dimensions $a = 19.334$ (6) Å, $b = 18.534$ (6) Å, $c = 20.020$ (6) Å; for $Z = 8$, the calculated density is 1.254 g/cm^3. The structures were refined to conventional *R* factors of 0.031 (6757 data, $F^2 > \sigma(F^2)$) for the Eu complex and 0.056 (2546 data, $F^2 > 3\sigma(F^2)$) for the Yb complex. In the europium complex there are two crystallographically distinct, but chemically equivalent, molecules. The molecular structures of the Eu and Yb complexes are similar. The lanthanide atom bonds to one of the silylamide ligands exclusively and shares the two others with the sodium atom. The Eu–N and Yb–N (unshared) distances are 2.46 (1) and 2.38 (2) Å, respectively; the average Eu–N and Yb–N (shared) distances are 2.55 (2) and 2.46 (2) Å, respectively; the average Na–N distance is 2.46 (1) Å. Several noteworthy close contacts between the metal ions and methyl carbon atoms have been noted, i.e. Na–C = 2.71 Å, Eu–C = 2.97 Å, and Yb–C = 2.86 Å.

Our synthetic studies in f-metal chemistry have centered on the preparation of complexes with low coordination numbers so that the large, electropositive metal centers are accessible to external reagents.[1] In developing this theme we have studied the bis(trimethylsilyl)amido ligand, $(Me_3Si)_2N^-$, since its size prevents coordination numbers from exceeding 3 in binary compounds.[2] We have been particularly interested in the redox chemistry of monomeric divalent lanthanide complexes.[3]

We have described a synthetic method for $Eu[N(SiMe_3)_2]_2L_2$, where L is tetrahydrofuran or 1,2-dimethoxyethane, that involves sodium naphthalene reduction of $Eu[N(SiMe_3)_2]_2Cl$ in tetrahydrofuran.[4] This is a poor synthetic method since the yields are low (ca. 15%) and the method cannot be extended to ytterbium. Further, sodium naphthalene must be used in the relatively basic solvent, tetrahydrofuran. This latter deficiency is particularly troublesome since tetrahydrofuran tenaciously coordinates to the metal center. Accordingly, we wished to find a synthetic method that would allow us to prepare solvent-free, divalent silylamides or at the very least, diethyl ether complexes. Since diethyl ether is a weaker base than tetrahydrofuran, it can be displaced from $Yb(Me_5C_5)_2(OEt_2)$[5a] or $Yb[N(SiMe_3)_2]_2(OEt_2)_2$,[5b] whereas tetrahydrofuran cannot be displaced, by various phosphines. Thus, a synthetic method that yields diethyl ether complexes, rather than tetrahydrofuran ones, was derived.

Synthetic Studies

Europium diiodide reacts with sodium bis(trimethylsilyl)amide in 1,2-dimethoxyethane (dme) to give the six-coordinate, yellow complex $Eu[N(SiMe_3)_2]_2(dme)_2$, previously characterized by X-ray crystallography,[4] in 79% yield. The yield is significantly improved over that previously reported. If diethyl ether is used as a reaction solvent, the reaction takes a different course. Stirring sodium bis(trimethylsilyl)amide with europium diiodide in diethyl ether affords a yellow solution from which the anionic complex $NaEu[N(SiMe_3)_2]_3$ is isolated after crystallization from toluene, as shown by X-ray crystallography (see below).

Ytterbium diiodide and sodium bis(trimethylsilyl)amide in 1,2-dimethoxyethane give the blue, diamagnetic, six-coordinate complex $Yb[N(SiMe_3)_2]_2(dme)_2$, presumably isostructural with its europium analogue.[4] Thus, the new synthetic method is more general than the one previously described.[4] Curiously, the blue, 1:2 dimethoxyethane complex dissolves in pentane to give a red solution, and the red 1:1 complex, $Yb[N(SiMe_3)_2](dme)$, can be crystallized from the pentane solution. The ready loss of the ether from the ytterbium complex is presumably due to steric effects, Yb(II) being ca. 0.15 Å smaller than Eu(II).[6]

As observed for europium, use of diethyl ether as a solvent rather than dimethoxyethane changes the reaction product. Ytterbium diiodide and sodium bis(trimethylsilyl)amide yield an orange-red solution in diethyl ether from which orange $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ may be crystallized from pentane. In contrast, if the orange-red diethyl ether solution formed by reaction of ytterbium diiodide and sodium bis(trimethylsilyl)amide is taken to dryness and the residue extracted with toluene, the red $NaYb[N(SiMe_3)_2]_3$ is isolated, as shown by X-ray crystallography (see below). The behavior of these complexes as a function of the metal and solvent is summarized in Scheme I. The rather diverse behavior of the complexes with ethereal solvents can be described in terms of ligand-displacement reactions. 1,2-Dimethoxyethane and diethyl ether are better ligands toward ytterbium than $NaN(SiMe_3)_2$,

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[1] (a) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1507. (b) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Ibid.* **1980**, *19*, 2999. (c) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Ibid.* **1981**, *20*, 2991.

[2] (a) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1. (b) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood: Chichester, England, 1980.

[3] Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985; *J. Am. Chem. Soc.* **1982**, *104*, 1772.

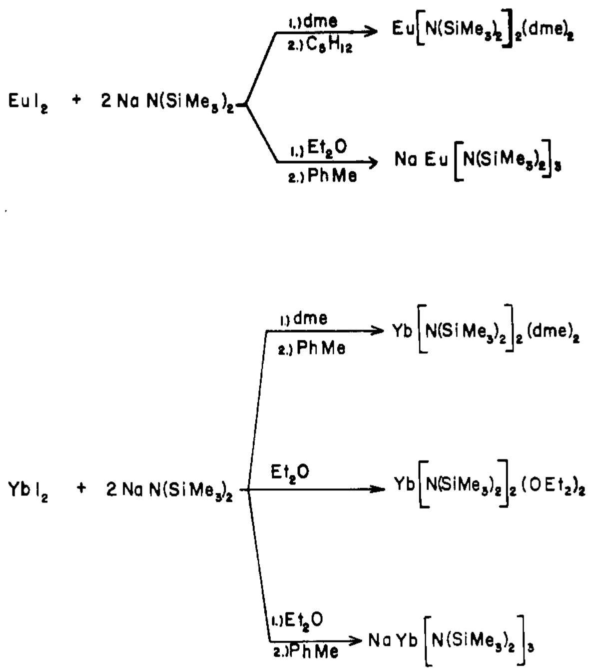
[4] Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551.

[5] (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 856. Watson, P. L.; Harlow, R. L.; Whitney, J. F.; Tilley, T. D.; Andersen, R. A. submitted for publication. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725.

[6] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

0020-1669/84/1323-2271$01.50/0

Scheme I



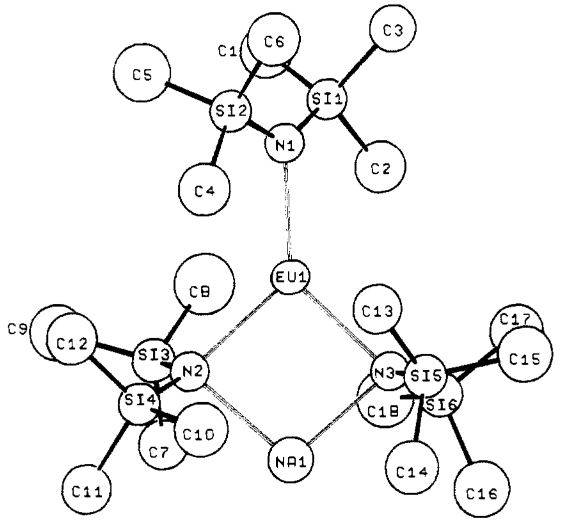


Figure 1. ORTEP drawing of $NaEu[(Me_3Si)_2N]_3$, molecule 1.

and the chelating ether is a better ligand toward europium than $[N(SiMe_3)_2]^-$, though diethyl ether is not.

Crystallographic Studies

ORTEP diagrams of the two complexes are shown in Figures 1 and 2. Table I gives the positional parameters, and Tables II and III list some selected bond lengths and angles.

The Eu and Yb complexes crystallize in different space groups. The europium complex crystallizes in a monoclinic space group and contains two crystallographically independent molecules that are chemically identical and geometrically very similar. The $NaYb[N(SiMe_3)_2]_3$ complex is in an orthorhombic space group, and its molecular geometry is very similar to those of the Eu complexes. In each case the NaN(2)MN(3)N(1) (M = Eu(1), Eu(2), Yb) atoms are coplanar. The coordination number of the lanthanide-metal atom is 3, and the metal atom is located in the center of an isosceles triangle. The coordination number of the alkali-metal atom is 2. In both cases the inter- and intramolecular $M\cdots CH_3Si$ interactions (see below) are ignored in counting the coordination numbers. The coordination number of N(1) and N(2) is 3, and the geometry is trigonal planar. The coordination number of N(2), N(3) and N(5), N(6) is 4, and the geometry is a distorted tetrahedron. These anionic complexes are further examples of the rather rare situation in which the nitrogen atom of a $N(SiMe_3)_2$ group bridges two metal atoms. The other examples are $Li_3[\mu\text{-}N(SiMe_3)_2]_3$,[7a] $[Na(\mu\text{-}N(SiMe_3)_2)]_x$ (x = large),[7b] $Cu_4[\mu\text{-}N(SiMe_3)_2]_4$,[7c] $Al_2Me_4(\mu\text{-}Me)[\mu\text{-}N(SiMe_3)_2]$,[7d] and $Mn[N(SiMe_3)_2]_2[\mu\text{-}N(SiMe_3)_2]_2$.[7e]

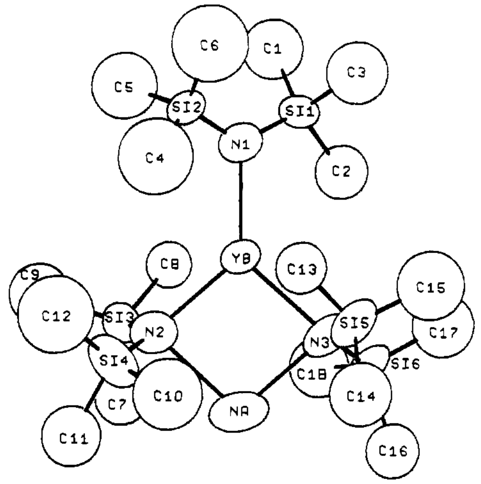


Figure 2. ORTEP drawing of $NaYb[(Me_3Si)_2N]_3$.

The averaged Eu–N(terminal) distance in the two independent molecules of 2.446 ± 0.003 Å is 0.07 Å longer than the Yb–N(terminal) distance of 2.38 (2) Å. The averaged Eu–N(bridging) distance of 2.55 ± 0.02 Å is 0.09 Å longer than the Yb–N(bridging) distance of 2.46 ± 0.02 Å. The difference in the Eu–N and Yb–N distances is slightly smaller than the difference in metal radii of 0.12 Å suggested by Shannon.[6] The averaged Eu–N(terminal) distance in the three-coordinate anionic complex is 0.08 Å shorter than that found in the six-coordinate europium(II) complex, $Eu[N(SiMe_3)_2]_2(dme)_2$, of 2.530 (4) Å.[4] The averaged Eu–N(terminal) distance in the anionic europium(II) complex is 0.019 Å longer than that found in the three-coordinate europium(III) complex, $Eu[N(SiMe_3)_2]_3$ (2.259 (9) Å.[8] The Yb–N(terminal) distance in the anionic ytterbium(II) complex is 0.23 Å longer than that found in the three-coordinate ytterbium(III) complex, $Yb[N(SiMe_3)_2]_3$, of 2.16 (2) Å.[8] These bond length changes are in accord with the change in metal radii as a function of oxidation state and coordination number, as suggested previously.[6,9]

The terminal europium and ytterbium to nitrogen bond lengths are shorter than the bridging europium and ytterbium to nitrogen bond lengths by 0.10 and 0.07 Å, respectively. A similar trend was found in $Mn_2[N(SiMe_3)_2]_2[\mu\text{-}N(SiMe_3)_2]_2$; the manganese to nitrogen (terminal) bond length is 0.19 Å shorter than the bridging bond length.[6e]

The average sodium to nitrogen bond lengths in the two europium complexes of 2.47 ± 0.02 Å are equal within experimental error to that found in the ytterbium complex of 2.46 ± 0.02 Å. The Na–N(bridging) bond lengths are ca. 0.1 Å longer than those found in polymeric $NaN(SiMe_3)_2$ of 2.355 (3) Å in which the coordination number of sodium is also 2.[7b]

In the europium structure the 36 Si–C bond lengths range from 1.87 to 1.92 Å, with an average value of 1.89 ± 0.02 Å. The 18 Si–C bond lengths in the ytterbium structure range

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[7] (a) Mootz, D.; Zinnius, A.; Bottcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. Rogers, R. D.; Atwood, J. L.; Gruning, R. *J. Organomet. Chem.* **1978**, *157*, 229. (b) Guning, R.; Atwood, J. L. *Ibid.* **1977**, *137*, 101. (c) Hursthouse, M. B., unpublished results as quoted in ref 2b. (d) Wiberg, N.; Baumeister, J. *J. Organomet. Chem.* **1972**, *36*, 277. (e) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Mosler, R. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 253.

[8] Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc.* **1973**, 669.

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Table I. Positional Parameters[a]

atom	x	y	z	atom	x	y	z
EuNa[N(SiMe$_3$)$_2$]$_3$–Molecule 1							
Eu(1)	0.20796 (2)	0.11221 (1)	0.20792 (1)	C(5)	0.0916 (5)	0.1992 (5)	−0.0010 (3)
Na(1)	0.21563 (13)	−0.02687 (11)	0.30288 (10)	C(6)	0.0799 (4)	0.3201 (4)	0.0857 (4)
N(1)	0.20451 (23)	0.20885 (21)	0.13375 (19)	C(7)	0.2724 (4)	−0.1255 (4)	0.1884 (3)
N(2)	0.15532 (22)	−0.01228 (21)	0.18463 (18)	C(8)	0.2904 (5)	0.0183 (4)	0.1354 (4)
N(3)	0.27129 (23)	0.09140 (21)	0.32780 (18)	C(9)	0.1596 (5)	−0.0800 (5)	0.0595 (3)
Si(1)	0.29184 (9)	0.24283 (7)	0.13387 (7)	C(10)	0.0225 (4)	−0.0037 (4)	0.2393 (4)
Si(2)	0.11119 (9)	0.22616 (8)	0.08607 (7)	C(11)	0.0502 (4)	−0.1380 (3)	0.1771 (3)
Si(3)	0.21324 (9)	−0.04876 (9)	0.14392 (7)	C(12)	−0.0146 (4)	−0.0147 (4)	0.0954 (4)
Si(4)	0.06005 (9)	−0.04056 (8)	0.17349 (7)	C(13)	0.1268 (4)	0.1771 (4)	0.3018 (3)
Si(5)	0.21198 (10)	0.13240 (9)	0.36498 (7)	C(14)	0.1636 (4)	0.0707 (4)	0.4086 (3)
Si(6)	0.36951 (9)	0.07664 (9)	0.36816 (8)	C(15)	0.2594 (5)	0.2035 (4)	0.4245 (4)
C(1)	0.3189 (4)	0.2274 (4)	0.0583 (4)	C(16)	0.3835 (5)	0.0309 (5)	0.4479 (4)
C(2)	0.3734 (4)	0.2040 (4)	0.2020 (3)	C(17)	0.4324 (4)	0.1574 (4)	0.3862 (4)
C(3)	0.2960 (4)	0.3402 (3)	0.1480 (3)	C(18)	0.4143 (4)	0.0187 (5)	0.3193 (4)
C(4)	0.0392 (4)	0.1745 (4)	0.1163 (4)				
EuNa[N(SiMe$_3$)$_2$]$_3$–Molecule 2							
Eu(2)	0.20448 (2)	0.74193 (1)	0.68633 (1)	C(23)	0.3214 (4)	0.8926 (4)	0.5574 (3)
Na(2)	0.19904 (14)	0.60261 (11)	0.77660 (11)	C(24)	0.3750 (3)	0.8333 (4)	0.6922 (4)
N(4)	0.20542 (22)	0.84978 (20)	0.62689 (19)	C(25)	0.2883 (4)	0.6477 (4)	0.6202 (4)
N(5)	0.14600 (25)	0.61854 (22)	0.65969 (20)	C(26)	0.1684 (7)	0.5466 (6)	0.5411 (4)
N(6)	0.25638 (23)	0.71961 (22)	0.80633 (18)	C(27)	0.2709 (5)	0.5068 (4)	0.6751 (4)
Si(7)	0.11418 (9)	0.87840 (8)	0.58579 (7)	C(28)	0.0413 (5)	0.4921 (4)	0.6472 (4)
Si(8)	0.29500 (8)	0.88553 (7)	0.63429 (7)	C(29)	0.0074 (5)	0.6261 (6)	0.7074 (7)
Si(9)	0.21064 (12)	0.58099 (10)	0.62483 (8)	C(30)	−0.0172 (6)	0.6149 (5)	0.5623 (6)
Si(10)	0.05047 (11)	0.58954 (10)	0.64369 (10)	C(31)	0.1146 (4)	0.8082 (4)	0.7757 (4)
Si(11)	0.19276 (10)	0.75788 (9)	0.84043 (8)	C(32)	0.1359 (5)	0.6916 (5)	0.8757 (4)
Si(12)	0.35288 (9)	0.70270 (9)	0.85125 (7)	C(33)	0.2358 (6)	0.8220 (4)	0.9067 (3)
C(19)	0.0425 (3)	0.8036 (4)	0.5800 (3)	C(34)	0.4056 (4)	0.6513 (5)	0.8027 (3)
C(20)	0.1015 (4)	0.9086 (5)	0.5015 (3)	C(35)	0.3559 (4)	0.6472 (4)	0.9238 (3)
C(21)	0.0779 (4)	0.9511 (4)	0.6265 (4)	C(36)	0.4169 (4)	0.7808 (5)	0.8817 (4)
C(22)	0.3048 (4)	0.9771 (3)	0.6678 (3)				
YbNa[N(SiMe$_3$)$_2$]$_3$							
Yb	0.20729 (3)	0.13042 (4)	0.17408 (3)	C(5)	0.4053 (14)	0.2704 (14)	0.1012 (13)
Na	0.0589 (4)	0.1038 (4)	0.2457 (4)	C(6)	0.3248 (16)	0.2128 (15)	−0.0100 (13)
Si(1)	0.36915 (26)	0.07293 (29)	0.12166 (25)	C(7)	0.1488 (11)	0.1552 (12)	0.3956 (11)
Si(2)	0.32313 (28)	0.22001 (29)	0.07941 (26)	C(8)	0.2527 (10)	0.1985 (10)	0.2947 (9)
Si(3)	0.21306 (28)	0.11706 (28)	0.33469 (23)	C(9)	0.2818 (13)	0.0762 (15)	0.3879 (13)
Si(4)	0.1588 (4)	−0.02371 (29)	0.2877 (3)	C(10)	0.1100 (14)	−0.0438 (15)	0.3641 (13)
Si(5)	0.04918 (26)	0.2447 (3)	0.1557 (4)	C(11)	0.0903 (18)	−0.0595 (19)	0.2260 (17)
Si(6)	0.0757 (3)	0.1119 (3)	0.0752 (3)	C(12)	0.2288 (23)	−0.0791 (23)	0.2973 (20)
N(1)	0.3154 (6)	0.1402 (7)	0.1175 (6)	C(13)	0.0534 (15)	0.3128 (15)	0.0868 (14)
N(2)	0.1762 (7)	0.0640 (7)	0.2750 (7)	C(14)	0.0836 (14)	0.2863 (14)	0.2331 (13)
N(3)	0.0089 (6)	0.1652 (8)	0.1405 (8)	C(15)	−0.0474 (12)	0.2323 (12)	0.1674 (10)
C(1)	0.4281 (17)	0.0851 (17)	0.1851 (15)	C(16)	−0.0027 (16)	0.0621 (16)	0.0797 (14)
C(2)	0.3283 (22)	−0.0048 (21)	0.1396 (20)	C(17)	0.0731 (18)	0.1593 (18)	−0.0048 (17)
C(3)	0.4129 (22)	0.0536 (23)	0.0485 (20)	C(18)	0.1475 (11)	0.0445 (11)	0.0670 (9)
C(4)	0.2522 (12)	0.2844 (12)	0.1009 (10)				

[a] Here and in the following tables the number in parentheses is the estimated standard deviation in the least significant digit.

Table II. Selected Interatomic Distances (Å)

Yb–N(1)	2.38 (2)	Eu(1)–N(1)	2.448 (4)	Eu(2)–N(4)	2.443 (4)
Yb–N(2)	2.45 (2)	Eu(1)–N(2)	2.554 (4)	Eu(2)–N(5)	2.573 (4)
Yb–N(3)	2.47 (2)	Eu(1)–N(3)	2.539 (4)	Eu(2)–N(6)	2.529 (4)
Na–N(2)	2.45 (2)	Na(1)–N(2)	2.484 (4)	Na(2)–N(5)	2.450 (5)
Na–N(3)	2.47 (2)	Na(1)–N(3)	2.463 (5)	Na(2)–N(6)	2.463 (5)
N(1)–Si(1)	1.63 (2)	N(1)–Si(1)	1.668 (4)	N(4)–Si(7)	1.672 (4)
N(1)–Si(2)	1.68 (2)	N(1)–Si(2)	1.684 (4)	N(4)–Si(8)	1.680 (4)
N(2)–Si(3)	1.69 (2)	N(2)–Si(3)	1.694 (4)	N(5)–Si(9)	1.709 (5)
N(2)–Si(4)	1.68 (2)	N(2)–Si(4)	1.706 (4)	N(5)–Si(10)	1.701 (5)
N(3)–Si(5)	1.68 (2)	N(3)–Si(5)	1.698 (4)	N(6)–Si(11)	1.690 (4)
N(3)–Si(6)	1.67 (2)	N(3)–Si(6)	1.704 (4)	N(6)–Si(12)	1.710 (4)
Yb–C(8)	2.86 (2)	Eu(1)–C(8)	3.042 (8)	Eu(2)–C(25)	2.971 (7)
Yb–C(18)	2.89 (2)	Eu(1)–C(13)	3.093 (1)	Eu(2)–C(31)	3.132 (7)
Yb–C(4)	3.33 (3)	Eu(1)–C(4)	3.253 (6)	Eu(2)–C(19)	3.291 (6)
Yb–C(2)	3.49 (4)	Eu(1)–C(2)	3.437 (7)	Eu(2)–C(24)	3.442 (6)
Na–C(1)[a]	2.91 (3)	Na(1)–C(3)[b]	2.796 (6)	Na(2)–C(22)[b]	2.705 (6)
Na–C(11)	3.11 (4)	Na(1)–C(10)	3.280 (8)	Na(2)–C(32)	3.207 (9)
Na–C(14)	3.43 (3)	Na(1)–C(14)	3.307 (8)	Na(2)–C(29)	3.273 (9)

[a] Atom in position $^1/_2 + x, y, ^1/_2 - z$. [b] Atom in position $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$.

from 1.68 to 1.92 Å, with an average value of 1.82 ± 0.07 Å; the shorter distance and larger deviation of the Yb–C distances are due to large thermal motions of the carbon atoms in the Yb structure. When the Si–C distances are corrected for

Table III. Selected Angles (deg)

N(1)-Yb-N(2)	130.3 (4)	N(1)-Eu(1)-N(2)	129.9 (2)	N(4)-Eu(2)-N(6)	129.3 (2)
N(1)-Yb-N(3)	131.7 (5)	N(1)-Eu(1)-N(3)	135.5 (2)	N(4)-Eu(2)-N(5)	136.5 (2)
N(2)-Yb-N(3)	97.4 (5)	N(2)-Eu(1)-N(3)	94.3 (2)	N(5)-Eu(2)-N(6)	94.0 (2)
N(2)-Na-N(3)	97.5 (5)	N(2)-Na(1)-N(3)	98.0 (2)	N(5)-Na(2)-N(6)	98.9 (2)
Yb-N(2)-Na	83.0 (5)	Eu(1)-N(2)-Na(1)	83.4 (2)	Eu(2)-N(5)-Na(2)	83.2 (2)
Yb-N(3)-Na	82.1 (5)	Eu(1)-N(3)-Na(1)	84.2 (2)	Eu(2)-N(6)-Na(2)	83.9 (2)
Yb-N(1)-Si(1)	118.8 (6)	Eu(1)-N(1)-Si(1)	117.3 (2)	Eu(2)-N(4)-Si(7)	113.6 (2)
Yb-N(1)-Si(2)	111.3 (6)	Eu(1)-N(1)-Si(2)	112.3 (2)	Eu(2)-N(4)-Si(8)	117.0 (2)
Yb-N(2)-Si(3)	100.4 (6)	Eu(1)-N(2)-Si(3)	104.5 (2)	Eu(2)-N(5)-Si(9)	102.3 (2)
Yb-N(2)-Si(4)	131.1 (7)	Eu(1)-N(2)-Si(4)	127.4 (3)	Eu(2)-N(5)-Si(10)	130.4 (3)
Yb-N(3)-Si(5)	127.4 (7)	Eu(1)-N(3)-Si(6)	127.8 (3)	Eu(2)-N(6)-Si(12)	127.2 (3)
Yb-N(3)-Si(6)	101.3 (6)	Eu(1)-N(3)-Si(5)	106.2 (2)	Eu(2)-N(6)-Si(11)	107.8 (2)
Si(1)-N(1)-Si(2)	129.9 (7)	Si(1)-N(1)-Si(2)	130.3 (3)	Si(7)-N(4)-Si(8)	129.4 (3)
Si(3)-N(2)-Si(4)	122.9 (8)	Si(3)-N(2)-Si(4)	121.1 (3)	Si(9)-N(5)-Si(10)	121.4 (4)
Si(5)-N(3)-Si(6)	126.2 (8)	Si(5)-N(3)-Si(6)	120.3 (3)	Si(11)-N(6)-Si(12)	120.3 (3)

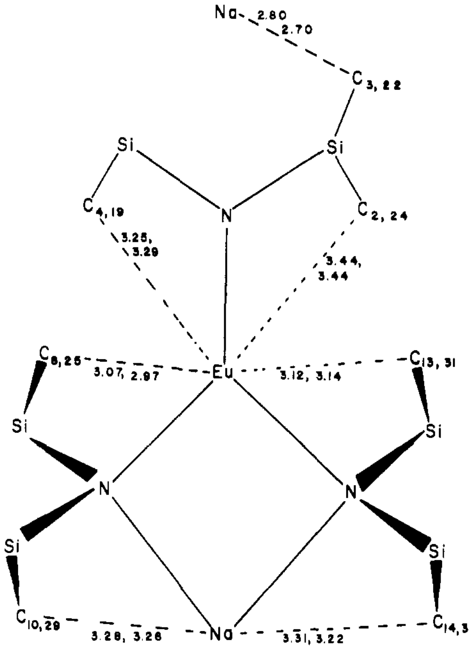

Figure 3. Line drawing of $NaEu[N(SiMe_3)_2]_3$ showing M···CH_3 interactions.

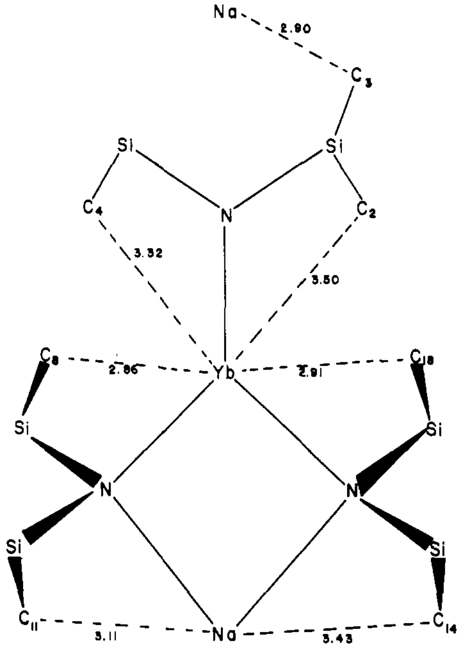

Figure 4. Line drawing of $NaYb[N(SiMe_3)_2]_3$ showing M···CH_3 interactions.

thermal motion by using a model in which the carbon atom rides on the silicon atom, the averages of the thermally corrected Si–C bond distances are 1.92 ± 0.02 Å (Eu) and 1.88 ± 0.05 Å (Yb), and the difference between these two values is not statistically significant. A complete listing of the Si–C bond lengths is in the supplementary material.

The anionic compounds are Lewis acid–base complexes; the lone pair of electrons on a nitrogen atom of two bis(trimethylsilyl)amido groups are acting as electron-pair donors toward either sodium or the lanthanide metal. The hydrocarbon solubility of the complexes is readily explained since the two electropositive atoms in each complex are effectively encapsulated by the very large $(Me_3Si)_2N$ groups, and the complexes appear, from the viewpoint of the solvent, to be saturated hydrocarbon molecules.

Close inspection of the interatomic distances (Table II) reveals some short methyl to sodium intermolecular distances and some short methyl to lanthanide intramolecular distances. The line drawings in Figures 3 and 4 illustrate the short contacts around the ytterbium and sodium ions. In the following discussion we shall describe these interactions in some detail for the ytterbium complex since the europium complex is similar, as shown in Figure 4.

The Yb···C(2,4,8,18) contacts yield an averaged value of 3.15 ± 0.33 Å, and the averaged intramolecular Na···C(11,14) contact is 3.27 ± 0.16 Å. The intermolecular Na···C(1) contact is 2.90 ± 0.03 Å. These distances are shorter than the sum of the van der Waals radius of a methyl group (2.0 Å)[10a] or a carbon atom (1.6 Å)[10b] and the metallic radius of Yb(II) (1.7 Å)[10c] or Na(I) (1.6 Å).[10c]

The Eu···C contacts in the two independent molecules of $NaEu[N(SiMe_3)_2]_3$ are also shorter than the sum of the van der Waals radii. The averaged Eu(1)···C(2,4,8,13) and Eu(2)···C(19,24,25,31) are 3.21 ± 0.18 and 3.21 ± 0.20 Å, respectively. The averaged intramolecular Na(1)···C(10,14) and Na(2)···C(29,32) distances are 3.30 ± 0.02 and 3.24 ± 0.04 Å, and the intermolecular Na(1)···C(3) and Na(2)···C(22) distances are 2.80 ± 0.01 and 2.71 ± 0.01 Å, respectively.

The short metal···carbon contacts also appear to distort the N–Si–C bond angles, though the differences in this angle, in which the carbon atom approaches the metal atoms, and those in which the carbon atom is further away are small. In the ytterbium complex the N(1)Si(1)C(2), N(1)Si(2)C(4), N(2)Si(3)C(8), N(3)Si(6)C(18), N(2)Si(4)C(11), N(3)Si(5)C(14), and N(1)Si(1)C(1) angles that are involved with the two metal atoms yield an averaged value of 111 ± 1°. The other N–Si–C angles average to 114 ± 2°. Similar values are observed in the europium complex, 110 ± 2° for those carbon atoms that closely approach the metal atoms relative to 114

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(10) (a) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1969; p 261. The van der Waals radius of a carbon atom is estimated from the tabulated radii of oxygen (1.4 Å) and nitrogen (1.5 Å): (b) *Ibid.* p 260. (c) *Ibid.* p 403.

± 2° for those that are further away.

The electropositive metal atoms in the anionic complexes clearly interact with some of the methyl groups of the ligand, causing them to become semibridging. This has been observed before[5b] and attributed to an electrostatic interaction of the type Yb(δ+)···C(δ−) or an interaction of the metal with the pair of electrons in the C–H bond. A more interesting question, though one that is more difficult to answer, is why this interaction occurs. The interaction might be a general one for large, electropositive metal atoms when they are placed in a coordinatively unsaturated environment. Under these circumstances the metal atom can relieve itself of coordinative unsaturation by interacting with a Lewis base or by forming associated molecules, or when these two alternatives are not sterically feasible, the metal may undergo secondary interactions with ligands in its immediate neighborhood. In the latter case the metal···carbon interaction might be viewed as a hydrocarbon activation. On the other hand, the interaction might be a manifestation of crystal-packing forces since we have observed this interaction only in the solid state by X-ray crystallography.[5b] That is, the molecule packs in the crystal so that it minimizes all H–H repulsions and maximizes attractions between atoms of different electronegativities. There are no low-energy absorptions in the C–H stretching frequency region of the infrared spectrum (solid state) for the anionic complex. This seems to indicate that the C–H bonds are not weakened appreciably by interaction with the metal atoms. No sign of the M···C interaction is observed in solution since the ^{1}H and ^{13}C{^{1}H} NMR spectra yield a singlet at room temperature and at −80 °C for NaYb[N(SiMe$_3$)$_2$]$_3$. Whatever the origin of the close contacts, the energy of the interaction is undoubtedly small.

Experimental Section

All operations were performed under nitrogen. The microanalyses were done by the microanalytical laboratory of this department. The nuclear magnetic resonance spectra were recorded on a JEOL-FX90Q instrument operating at 89.56 and 22.50 MHz for proton and carbon nuclei, respectively.

Eu[N(SiMe$_3$)$_2$]$_2$[MeOCH$_2$CH$_2$OMe]$_2$. Europium diiodide[11] (1.8 g, 0.0044 mol), sodium bis(trimethylsilyl)amide (1.6 g, 0.0088 mol), and 1,2-dimethoxyethane (75 mL) were stirred together for 10 h. The ether was removed under reduced pressure, and the residue was extracted with and crystallized from pentane (ca. 30 mL, −10 °C) in a yield of 79% (2.3 g). The infrared spectrum and melting point were identical with those previously reported.[4]

Yb[N(SiMe$_3$)$_2$]$_2$[MeOCH$_2$CH$_2$OMe]$_2$. Ytterbium diiodide[11] (3.9 g, 0.0092 mol), sodium bis(trimethylsilyl)amide (3.4 g, 0.018 mol), and 1,2-dimethoxyethane (75 mL) were stirred together for 10 h. The ether was removed under reduced pressure, and the residue was extracted into toluene (40 mL). The blue extract was filtered, and the filtrate was concentrated to ca. 10 mL and cooled (−10 °C). The resulting blue prisms (mp 162–165 °C) were collected and dried under reduced pressure. The yield was 3.9 g (63%). Anal. Calcd for $C_{20}H_{56}N_2O_4Si_4Yb$: C, 35.6; H, 8.37; N, 4.16. Found: C, 34.5; H, 8.07; N, 4.11. The mass spectrum contained a molecular ion at 674 amu. IR (Nujol): 1248 s, 1194 w, 1127 m, 1086 s, 1062 w sh, 968 s, 864 m, 832 s, 776 m, 757 m, 662 s, 601 m, 587 w, 387 m sh, 372 m cm^{-1}.

Yb[N(SiMe$_3$)$_2$]$_2$[MeOCH$_2$CH$_2$OMe]. The blue bis(dimethoxyethane) complex (1.8 g, 0.0026 mol) was dissolved in pentane (40 mL). The red solution was concentrated to ca. 10 mL. Cooling (−10 °C) yielded red prisms in quantitative yield, mp 118–120 °C. Anal. Calcd for $C_{16}H_{46}N_2O_2Si_4Yb$: C, 32.9; H, 7.94; N, 4.80. Found: C, 33.1; H, 7.95; N, 4.60. IR (Nujol): 1249 s, 1238 w sh, 1112 w sh, 1092 w sh, 1054 s, 1024 w sh, 962 s, 887 w sh, 862 m, 828 s, 749 w, 662 m, 604 w, 589 w, 373 w sh, 363 m cm^{-1}. A molecular ion was observed in the mass spectrum at 584 amu.

Yb[N(SiMe$_3$)$_2$]$_2$[OEt$_2$]$_2$. Diethyl ether (125 mL), cooled to 0 °C, was added to an intimate mixture of ytterbium diiodide (4.8 g, 0.011 mol) and sodium bis(trimethylsilyl)amide (4.1 g, 0.022 mol). The blue mixture was stirred at 0 °C for 1 h and then warmed to room temperature. The red solution was stirred for 10 h and filtered, and the filtrate was concentrated to ca. 20 mL and cooled (−70 °C). The yellow prisms that were isolated (−70 °C) became orange upon warming to room temperature. The orange prisms (mp 69–71 °C) were isolated in 56% (4.0 g) yield. The compound gives a red solution in either pentane or benzene. Anal. Calcd for $C_{20}H_{56}N_2O_2Si_4Yb$: C, 37.4; H, 8.79; N, 4.36. Found: C, 33.3; H, 8.06; N, 4.18. We cannot account for the discrepancy in the calculated and found analytical results. The spectroscopy, however, leaves no doubt as to the identity of the compound. The mass spectrum afforded a molecular ion at 570 amu. IR (Nujol): 1249 s, 1187 m, 1151 m, 1122 m, 1091 w, 1040 m, 968 s, 862 m sh, 830 s, 774 m, 753 w sh, 732 w sh, 663 w sh, 662 m, 609 m, 592 w, 503 w, 391 m, 372 m cm^{-1}. ^{1}H NMR (benzene-d_6, 26 °C): δ 0.41 (s, 36 H), 1.06 (t, J = 7 Hz, 12 H), 3.51 (q, J = 7 Hz, 8 H). ^{13}C{^{1}H} NMR: δ 5.57, 14.1, and 65.2 due to the Me$_3$Si, Me, and CH$_2$ resonances, respectively.

NaYb[N(SiMe$_3$)$_2$]$_3$. Ytterbium diiodide (4.4 g, 0.010 mol) and sodium bis(trimethylsilyl)amide (3.8 g, 0.021 mol) were stirred together for 1 h in diethyl ether (100 mL) at 0 °C. The mixture was warmed to room temperature and stirred for an additional 10 h. The diethyl ether was removed under reduced pressure, and the residue was extracted with toluene (60 mL). The red solution was evaporated to dryness, and the red residue was dissolved in pentane (40 mL) and filtered. The filtrate was concentrated to ca. 15 mL, and cooling (−10 °C) yielded red needles (mp 154–157 °C) in 46% (3.2 g) yield. IR (Nujol): 1241 s, 1203 w, 1046 s, 964 s, 857 s, 818 s, 752 s, 653 m, 602 w, 579 w, 392 m, 357 m cm^{-1}. ^{1}H NMR (benzene-d_6, 26 °C): 0.24 s. ^{13}C{^{1}H} NMR: δ 6.38. Anal. Calcd for $C_{18}H_{54}N_3Si_6NaYb$: C, 31.9; H, 8.04; N, 6.20. Found: C, 28.9; H, 7.29; N, 5.36.

NaEu[N(SiMe$_3$)$_2$]$_3$. Europium diiodide (5.4 g, 0.013 mol) and sodium bis(trimethylsilyl)amide (4.9 g, 0.027 mol) were stirred together for 14 h in diethyl ether (100 mL). The diethyl ether was removed under reduced pressure, and the residue was extracted with toluene (60 mL). The yellow solution was filtered, and the volume of the filtrate was reduced to ca. 15 mL. Cooling (−10 °C) afforded large, yellow prisms (mp 132–134 °C) in 41% (3.6 g) yield. A portion of the complex was dissolved in benzene-d_6, and the mixture was hydrolyzed with D$_2$O. Examination of the benzene solution by ^{1}H NMR spectroscopy showed the presence of DN(SiMe$_3$)$_2$. IR (Nujol): 1240 s, 1206 w, 1069 s, 982 s, 858 s, 811 s, 753 m, 739 w sh, 720 w sh, 652 s, 602 w, 577 m, 389 m, 359 m cm^{-1}. Anal. Calcd for $C_{18}H_{54}N_3Si_6NaEu$: C, 32.9; H, 8.30; N, 6.40. Found: C, 30.8; H, 8.11; N, 5.45. The elemental analyses for the europium and ytterbium anionic complexes are poor. The solution spectroscopy, however, is consistent with the X-ray crystallography results. We cannot account for the discrepancy, other than to suggest that the combustion gives rise to carbides and nitrides which do not burn completely, giving low C, H, and N data.

X-ray Diffraction

The crystals, because of their sensitivity to the atmosphere, were sealed inside thin-walled quartz capillaries and mounted on a CAD4 automatic diffractometer for a set of θ–2θ scan data. Details of the data collection are given in Table IV. Data were corrected for crystal decay, absorption,[12] and Lorentz and polarization effects. Transmission factors ranged from 1.30 to 1.52 (Eu) and 1.53 to 2.06 (Yb). Both space groups were unambiguously determined from the space group extinctions.

The lanthanide atomic positions were located with the use of three-dimensional Patterson maps, and subsequent least-squares refinement and electron density maps revealed the locations of all the non-hydrogen atoms. The structures were refined to convergence by using anisotropic thermal parameters on all but the carbon atoms in the Yb compound. Hydrogen atoms were not included. Atomic scattering factors of Doyle and Turner[13] were used, and anomalous scattering[14] corrections were applied. Extinction corrections were applied to the observed structure factors.[15] When the Yb structure

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(15) $(F_o)_{cor} = (1 + kI)F_o$, where $k = 1.15 \times 10^{-7}$ and 1.54×10^{-7} for the Eu and Yb complexes, respectively, and I is the uncorrected intensity.

Table IV. Data Collection Details for $NaEu(N(SiMe_3)_2)_3$ and $NaYb(N(SiMe_3)_2)_3$

Crystal Parameters[a]

	Eu	Yb
space group	$P2_1/n$	*Pbca*
a, Å	17.586 (6)	19.334 (6)
b, Å	19.170 (6)	18.534 (6)
c, Å	21.808 (6)	20.020 (6)
β, deg	107.90 (4)	
V, Å^3	6996	7174
Z	8	8
M_r	656.1	677.2
density (calcd), g/cm^3	1.246	1.254
μ(calcd, Mo Kα), cm^{-1}	20.2	28.2

Intensity Data Measurement

radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	highly oriented graphite, $2\theta_m = 12.2°$
scan type	θ(crystal)–2θ(counter)
reflcns measd	$3° < 2\theta < 45°$; $+h,+k,\pm l$ for Eu; $+h,+k,+l$ for Yb
scan speed	variable from 0.63 to 6.7° (θ)/min
scan width	$\Delta\theta = 0.5 + 0.347 \tan \theta$
bkgd	an additional $\Delta(2\theta)/4$ at each end of the scan
scans collected	for Eu 7643 (including standards), yielding 7397 unique reflcns; for Yb 3199 (including standards), yielding 2904 unique reflcns
std reflctns	3 measd after every 250 scans; 5% decay in intensity obsd for both complexes

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections.

was refined by using anisotropic thermal parameters on the carbon atoms, the R factor went from 0.056 to 0.048 but several of the carbon anisotropic thermal parameters were unacceptably large. A careful study of the electron difference maps of the Yb complex after the isotropic refinement had converged showed many peaks near the carbon atom positions, which suggests large thermal motions or disorder, but no clear pattern of disorder could be recognized. In comparison to the Eu structure the Yb structure is reasonable, if not accurate. Because of the large number of parameters in the Eu structure and the limited size of the available memory in our computer, the parameters of one molecule were refined by least-squares techniques while those for the other molecules were included but not refined; the parameters of each molecule were alternately refined. After the final refinements the largest shift/esd was less than 0.20 (Eu) and 0.09 (Yb). The standard deviations of a reflection of unit weight were 1.17 (Eu) and 1.99 (Yb). The final electron density difference maps showed maximum and minimum peaks of 0.5 and –0.7 e/Å^3 (Eu) and 0.9 and –0.8 e/Å^3 (Yb). In the final difference maps of the Eu complex some of the largest peaks are near carbon atoms at distances that could be interpreted as hydrogen atom peaks, but they were poorly resolved. The majority of the peaks represented "noise". The carbon atom C(8) in the Eu structure has large thermal parameters, but no indication of disorder was evident in the difference maps. The final R factors[16] are as follows: for the Eu complex $R_F = 0.031$ for 6751 data ($F^2 > \sigma(F^2)$) and $R_{wF} = 0.041$; for the Yb complex $R_F = 0.056$ for 2546 data ($F^2 > 3\sigma(F^2)$) and $R_{wF} = 0.080$.

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Supplementary Material Available: Listings of thermal parameters, Si–C distances, selected angles, and observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

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(16) $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

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Synthesis and Molecular Structure of Pentakis(triphenylphosphine)hexakis(4-chlorobenzenethiolato)hexasilver(I), Derived from a New $Ag_5(SR)_6$ Cage Structure

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The reaction of triphenylphosphine and (4-chlorobenzenethiolato)silver in toluene yields $Ag_6(SC_6H_4Cl)_6(PPh_3)_5(tol)_2$ (tol = toluene) as colorless crystals in which the toluene is lattice bound. The unprecedented $Ag_6(SR)_6(PPh_3)_5$ molecular aggregate, enclosed by 21 aryl substituents, contains an $Ag_5(SR)_6$ central cage, with phosphine ligands terminal at three of the silver atoms and an $Ag(PPh_3)_2$ appendage inserted between two bridging thiolates. The $Ag_5(SR)_6$ cage, when symmetrized, contains a basal unit comprised of an irregular hexagon of alternating silver and sulfur atoms ($Ag_{basal}^{peripheral}$ and S_{basal}), centered by a silver atom ($Ag_{basal}^{central}$) with trigonal-planar $(S_{bas})_3$ coordination. A trigonal-planar podal unit, $Ag_{pod}(S_{pod})_3$, is parallel to the basal plane and is attached to it by three S_{pod}–Ag_{bas}^{per} bonds. Tetrahedral coordination of each Ag_{bas}^{per} atom is completed by a terminal phosphine ligand. The additional $Ag(PPh_3)_2$ moiety (Ag_{bridge}) bridges two S_{pod} atoms. A structural relationship between the cage polyhedra of the $Ag_5(SR)_6$ core and the established $[M_5(S\text{-}t\text{-}Bu)_6]^-$ (M = Cu, Ag) molecular cage is proposed. The basal thiolate ligands are triply bridging, but with an unusual stereochemistry in which the sulfur atom lies outside the polyhedron of four atoms to which it is bonded. The distances between silver atoms (Ag_{bas}^{cen}–Ag_{bas}^{per}, mean 2.95 Å; Ag_{bas}^{cen}–Ag_{pod} = 3.05 Å; and Ag_{br}–Ag_{pod} = 3.19 Å) do not indicate metal–metal bonding, and the aggregate structure is maintained by doubly and triply bridging arenethiolate ligands. The complex undergoes phosphine-dissociative reactions in solution. Crystal data for $C_{140}H_{115}Ag_6S_6Cl_6P_5$: triclinic, $P\bar{1}$, a = 15.024 (5) Å, b = 18.488 (5) Å, c = 26.506 (10) Å, α = 82.14 (2)°, β = 86.19 (2)°, γ = 66.45 (3)°, Z = 2, 8093 observed (Mo Kα) reflections, R (R_w) 0.060 (0.074).

Introduction

There is very limited knowledge of the structures of the uncharged binary arenethiolates of copper and silver, $[MSAr]_n$, mainly due to difficulty in obtaining single crystals of diffraction quality. Copper compounds of this type, including CuSPh, are semiconducting,[1] while CuSPh electrochemically deposited on CdS electrodes in photoelectrochemical cells improves their stability and possibly performance.[2] It is generally assumed that these compounds are structurally

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