Journal of the Chinese Chemical Society, **1992**, *40*, 315-317

Communication

A Tri-Coordinate-Magnesium Silylamide Complex: $\{[(CH_3)_3Si]_2N\}_2MgO(CH_2CH_2)_2OMg\{N[Si(CH_3)_3]_2\}_2$

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The reaction of diethylmagnesium dioxane adduct solution with 1,1,1,3,3,3-hexamethyldisilazan ($(CH_3)_3SiNHSi(CH_3)_3$) gives $\{[(CH_3)_3Si]_2N\}_2MgO(CH_2CH_2)_2OMg\{N[Si(CH_3)_3]_2\}_2$ (**1**); this alkoxomagnesium silylamide in the solid state contains unprecedented three-coordinate magnesium and oxygen atoms.

Currently there is much interest in elucidating the various states of coordination possible for Mg in various compounds, particularly at the extreme limits of coordination-high and low coordination numbers-and in compounds with odd coordination numbers, as these compounds are uncommon.[1,2]

Reaction of alkylamines with alkylmagnesium compounds affords monomeric, oligomeric or polymeric magnesium amides and imides.[3,4,5,6] No X-ray diffraction measurements of single crystals of alkoxomagnesium silylamides which contain three-coordinate magnesium and oxygen atoms[2,10] have been reported. The possible influence of silyl groups on the geometry and coordinating ability of nitrogen, therefore the ability of silylamides to serve as ligands, is of fundamental interest.[7,8] The first example of a two-coordinate magnesium silyl complex in the solid state was reported.[9] Here, we report the crystal structure of $\{[(CH_3)_3Si]_2N\}_2MgO(CH_2CH_2)_2OMg\{N[Si(CH_3)_3]_2\}_2$ (**1**) the first example of alkoxomagnesium silylamide in the solid state, which contains atypical three-coordinate magnesium and oxygen atoms.[2,10] The distance between magnesium and nitrogen atoms indicates the existence of ionic character.[11,12,13]

Grinard reagent CH_3CH_2MgBr reacts with excess dioxane in diethyl ether to give diethylmagnesium solution. The solution reacts with 1,1,1,3,3,3-hexamethyldisilazan ($(CH_3)_3SiNHSi(CH_3)_3$) in molar ratio 1:1 to give compound (**1**) and $\{[(CH_3)_3Si]_2N\}_2MgO[CH_2CH_3]_2$ (**2**).[14]

The structure of compound **1**, determined by X-ray crystallography, is illustrated in Fig. 1. The molecule belongs to a C_i symmetry and consists of a pair of $[(CH_3)_3Si]_2N\}_2Mg$ subunits associated with a dioxane. The conformation of the dioxane fragment is a chair form with four carbon atoms in a plane, one oxygen atom above, and the other below the plane. The oxygen and magnesium atoms are three-coordinate in a triangular shape. O, Mg, C(1) and C(2) are roughly in a plane with C(1)-O-Mg 122.8(3)°, C(2)-O-Mg 125.2(3)° and C(1)-O-C(2)

Table 1. Bond Distances/Å and Bond Angles/deg

Bond Distances/Å			
Mg-O	2.053(4)	Si(3)-C(9)	1.844(9)
Mg-N(1)	1.957(5)	Si(3)-C(10)	1.89(1)
Mg-N(2)	1.934(5)	Si(3)-C(11)	1.86(1)
Si(1)-N(1)	1.704(5)	Si(4)-N(2)	1.707(6)
Si(1)-C(3)	1.854(8)	Si(4)-C(12)	1.869(9)
Si(1)-C(4)	1.860(8)	Si(4)-C(13)	1.876(9)
Si(1)-C(5)	1.863(9)	Si(4)-C(14)	1.863(9)
Si(2)-N(1)	1.694(5)	O-C(1)	1.433(7)
Si(2)-C(6)	1.874(8)	O-C(2)	1.433(7)
Si(2)-C(7)	1.877(9)	C(1)-C(2)	1.487(9)
Si(2)-C(8)	1.873(8)	C(2)-C(1)	1.487(9)
Si(3)-N(2)	1.700(6)		
Bond Angle/deg			
O-Mg-N(1)	107.3(2)	C(9)-Si(3)-C(11)	107.5(5)
O-Mg-N(2)	109.7(2)	C(10)-Si(3)-C(11)	107.7(6)
N(1)-Mg-N(2)	142.9(2)	N(2)-Si(4)-C(12)	109.7(3)
N(1)-Si(1)-C(3)	114.9(3)	N(2)-Si(4)-C(13)	112.7(4)
N(1)-Si(1)-C(4)	109.4(3)	N(2)-Si(4)-C(14)	114.4(4)
N(1)-Si(1)-C(5)	111.7(3)	C(12)-Si(4)-C(13)	106.7(4)
C(3)-Si(1)-C(4)	108.3(4)	C(12)-Si(4)-C(14)	106.3(4)
C(3)-Si(1)-C(5)	105.3(4)	C(13)-Si(4)-C(14)	106.6(5)
C(4)-Si(1)-C(5)	106.8(4)	Mg-O-C(1)	122.8(3)
N(1)-Si(2)-C(6)	110.4(3)	Mg-O-C(2)	125.2(3)
N(1)-Si(2)-C(7)	112.6(3)	C(1)-O-C(2)	109.8(4)
N(1)-Si(2)-C(8)	113.3(3)	Mg-N(1)-Si(1)	114.2(3)
C(6)-Si(2)-C(7)	106.9(4)	Mg-N(1)-Si(2)	120.8(3)
C(6)-Si(2)-C(8)	105.8(4)	Si(1)-N(1)-Si(2)	124.1(3)
C(7)-Si(2)-C(8)	107.4(4)	Mg-N(2)-Si(3)	115.2(3)
N(2)-Si(3)-C(9)	109.5(3)	Mg-N(2)-Si(4)	119.9(3)
N(2)-Si(3)-C(10)	113.4(4)	Si(3)-N(2)-Si(4)	124.4(3)
N(2)-Si(3)-C(11)	113.9(5)	O-C(1)-C(2)	110.1(5)
C(9)-Si(3)-C(10)	104.2(5)	O-C(2)-C(1)	110.2(5)

Table 2. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement

Formula,	C28 H80 N4 O2 Si8 Mg2
FW,	778.26
Diffractometer used,	Nonius
Space Group,	Monoclinic P $2_1/n$
a (angstron),	12.203(5)
b (angstron),	15.628(5)
c (angstron),	14.219(5)
beta (deg.),	108.32(4)
V(A**3),	2574(2)
Z,	2
Dcalc ($g \cdot cm^{-3}$),	1.004
lambda (Angstron),	0.71073
F(000),	856.
Unit cell detn: #; (2 theta range),	25; (18.80 - 22.24 deg.)
Scan type,	theta/2theta
Scan width (deg),	2(0.65 + 0.35 tan(theta))
Scan Speed (deg/min),	1.72-8.24
2 Theta (max),	45.0
h k l ranges,	(-13; 13)(0; 16)(0; 15)
mu (cm^{-1}),	2.519
Crystal size (mm),	0.35 x 0.45 x 0.55
Transmission,	0.965; 1.000
Temperature,	298.00
# of meas. reflns,	3358
# of obsed relfns (I > 2.0 sig(I)),	1698
# of unique reflns,	3358
RF; RW,	0.056; 0.059
GoF,	2.27
Refinement program,	NRCVAx
# of atoms,	62
# of refined params,	200 (1698 out of 3358 reflns.)
Minimize function,	SUM (w|Fo-Fc|**2)
Weights scheme,	(1/sigma**2)(Fo)
The weight modifier K in KFo**2 is,	0.000100
g (2nd. ext. coeff.) x 10e4,	2.03(20)
(delta/sigma)max,	0.0246
(D-map)max.min e/A**3,	-0.210; 0.250

NOTE:
RF = Sum(Fo-Fc)/Sum(Fo)
Rw = Sqrt[Sum(w(Fo-Fc)**2)/Sum(wFo**2)]
GoF = Sqrt[Sum(w(Fo-Fc)**2)/(No. of reflns - No. of params.)]

109.8(4)°. Mg, O, C(1) and C(2) are also in a plane with O-Mg-N(1) 107.3(2)°, O-Mg-N(2) 109.7(2)° and N(1)-Mg-N(2) 142.9(2)°. Therefore, N(1), N(2), Mg, O, C(1) and C(2) are almost in a plane. The distance of Mg-O (2.053(4)Å) is expected to be a σ bond from comparison with the published data.[15] The distances of Mg-N(1) and Mg-N(2) are 1.957(5)Å and 1.934(5)Å; as these are shorter than a true σ bond. Also within the 124.1(3)° angle of Si(1)-N(1)-Si(2) and the bond length 1.707(6)Å of Si(1)-N(1) may reflect the fact that the cation and anion interact in a somewhat ionic fashion.[11,12,13]

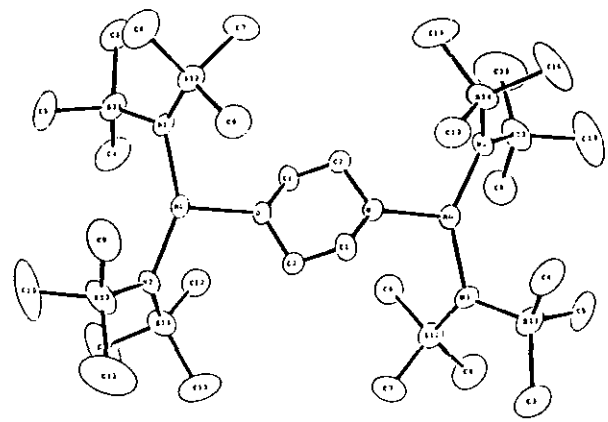

Fig. 1. Molecular structure of **1**.

ACKNOWLEDGMENT

We thank the National Science Council of the Republic of China for financial support.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of crystal data, distances and angles, final fractional coordinates, torsional angles, and thermal parameters (7 pages) and a list of the observed and calculated structure factors (12 pages) are available from chang.

Received February 1, 1993.

Key Words

Tri-coordinate; Magnesium; Silylamide.

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14. $((CH_3)_3SiNHSi(CH_3)_3)$ (15.6 mL, 75 mmol) was added dropwise to a stirred diethyl ether solution of $Mg(CH_2CH_3)_2$ (150 mL, 0.5 M, 75 mmol) containing dioxane at -60 °C under nitrogen. After 8 h a colorless solution was obtained, which after removal of diethyl ether under vacuum, gave a white solid. Sublimation at 100 °C under vacuum produced a solid and a colorless crystal. The colorless crystal is $\{[(CH_3)_3Si]_2N\}_2MgO(CH_2CH_2)_2OMg\{N[Si(CH_3)_3]_2\}_2$ (**1**): yield: 50%; mp 195-198 °C; Anal. Calcd for $C_xH_yO_zN_mMg_n$: C, 43.17; H, 10.36; N, 7.19. Found: C, 43.09; H, 10.37; N, 7.10. ^1H NMR (C_6D_6) δ 0.23 (*s*, 72H, CH_3), 3.90 (*s*, 8H, CH_2); ^{13}C NMR (C_6D_6) δ 5.90 (CH_3), 67.50 (CH_2). The solid is $\{[(CH_3)_3Si]_2N\}_2MgO[CH_2CH_3]_2$ (**2**): yield: 30%; mp 37 °C; ^1H NMR (C_6D_6) δ 0.27 (*s*, 36H, CH_3), 0.90 (*t*, 6H, CH_3), 3.41 (*q*, 4H, CH_2); ^{13}C NMR (C_6D_6) δ 5.92 ($SiCH_3$), 14.05 (CH_2CH_3), 66.33 (CH_2).
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