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Contribution from the Departments of Chemistry, Martin Chemical Laboratory, Davidson College, Davidson, North Carolina 28036, and Emory University, Atlanta, Georgia 30322

Synthesis and Characterization of *n*-Butyl- and Methyl((trimethylsilyl)amino)gallium Chloride

W. RODGER NUTT,*[1a] REBECCA E. STIMSON,[1a] MARY F. LEOPOLD,[1a] and BYRON H. RUBIN[1b]

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The reaction of $(Me_3Si)_2NH$ with either $MeGaCl_2$ or n-$BuGaCl_2$ has been found to yield $[Me(Cl)GaN(H)SiMe_3]_2$ and $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$, respectively. Both compounds are crystalline solids which exist as dimers in benzene. A crystallographic study of $[Me(Cl)GaN(H)SiMe_3]_2$ indicates a structure in which there is a planar four-membered Ga_2N_2 ring with equivalent substituents trans to each other. The compound $[Me(Cl)GaN(H)SiMe_3]_2$ crystallizes in the orthorhombic space group *Pbca* (No. 61) with $a = 18.712$ (10) Å, $b = 11.174$ (2) Å, $c = 9.355$ (2) Å, $V = 1956$ (2) Å^3, and d(calcd) = 1.416 g cm^{-3}, for $Z = 4$. The discrepancy indices were $R = 0.064$ and $R_w = 0.059$ for 1562 reflections. The Ga–Cl, Ga–C, Ga–N, and Si–N bond distances are 2.212 (3), 1.956 (11), 2.012 (8), and 1.744 (8) Å. The Ga–N–Ga bond angle is 91.0 (5)°. The IR and ^1H NMR spectra of both compounds are reported.

Introduction

Reactions involving the cleavage of Si–N bonds in bis(trimethylsilyl)amine and substituted trimethylsilylamines by trihalogenoboranes and substituted halogenoboranes have been studied extensively. Indeed, this type of cleavage reaction has proved to be a valuable synthetic route to substituted borazines,[2] diborylamines,[3] aminoboranes,[4] and bis(amino)boranes.[5,6] For example, 2,4,6-trialkylborazines have been prepared from the reactions of bis(trimethylsilyl)amine with alkyldichloroboranes[2] and 1,3,5-trimethyl-2,4,6-triphenylborazine has been obtained from the reaction of methylbis(trimethylsilyl)amine with dichlorophenylborane in a 1:1 mole ratio.[6] However, when $PhBCl_2$ was allowed to react with an excess of $(Me_3Si)_2NMe$, $PhB(N(Me)SiMe_3)_2$ and $MeN(B(Ph)N(Me)SiMe_3)_2$ were isolated.[6]

In contrast, analogous reactions involving gallium trihalides and substituted gallium halides have not been fully explored. A series of (trifluoroacetanilido)gallium dihalides have been prepared from reactions of gallium trichloride and gallium tribromide with the corresponding substituted trimethylsilylamine[7] and ((trimethylsilyl)amino)gallium dichloride has been isolated from the thermal decomposition of (bis(trimethylsilyl)amine)gallium trichloride.[8]

In view of this and the potential importance of substituted (silylamino)gallium chlorides as synthetic reagents, we undertook an investigation of the reactions of methylgallium dichloride and *n*-butylgallium dichloride with bis(trimethylsilyl)amine. To determine if $RGa(Cl)N(H)SiMe_3$ would react with a second mole of $(Me_3Si)_2NH$ in preference to dimerization and form $RGa(N(H)SiMe_3)_2$, we allowed $RGaCl_2$ to react with $(Me_3Si)_2NH$ in a 1:2 mole ratio.

Experimental Section

Materials and General Procedures. Gallium trichloride was prepared from gallium metal (Alcoa Co.) and chlorine (Air Products and Chemicals).[9] Bis(trimethylsilyl)amine (PCR Research Chemicals) was distilled at atmospheric pressure prior to use and *n*-butyllithium (Lithium Corp. of America) was used as received. Tetramethylsilane (Ventron Divison of Thiokol Corp.) was purified by trap-to-trap fractionation. Methylgallium dichloride was prepared according to the published procedure.[10] The method of Kovar, Loaris, Derr, and Callaway was used to prepare *n*-butylgallium dichloride.[9]

The ^1H NMR spectra were obtained from benzene solutions with a Varian EM-360L spectrometer. Methylene chloride (τ 5.67 in benzene) was used as an internal standard and all chemical shifts are reported with respect to Me_4Si (m, multiplet; s, singlet; t, triplet). Infrared spectra of Nujol mulls were recorded on the Perkin-Elmer Model 283 at high-resolution settings. The molecular weights were determined cryoscopically in benzene with an apparatus similar to that described by Dilts and Shriver.[11] All elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Standard inert-atmosphere techniques were used in all experiments.[12]

Synthesis of Methyl((trimethylsilyl)amino)gallium Chloride, $[Me(Cl)GaN(H)SiMe_3]_2$. To a stirred solution of freshly sublimed $MeGaCl_2$ (11.03 g, 70.86 mmol) in 50 mL of ether was added $(Me_3Si)_2NH$ (22.64 g, 140.3 mmol). After the solution was allowed to reflux for 12.5 h, the liquid portion was removed by vacuum distillation, leaving a white solid. From the liquid $(Me_3Si)_2NH$ (11.29 g, 49.8% recovered) was isolated by distillation and identified by a comparison of its IR spectrum with that of an authentic sample. Recrystallization of the solid from ether and then CH_2Cl_2 gave $[Me(Cl)GaN(H)SiMe_3]_2$ (5.43 g, 36.8% yield): mp 147–149 °C; ^1H NMR τ 9.93 (s, 3, CH_3Si) and 10.17 (s, 1, CH_3Ga). Anal. Calcd for $C_8H_{26}Cl_2Ga_2N_2Si_2$: C, 23.05; H, 6.29; Cl, 17.01; Ga, 33.45; N, 6.72; Si, 13.48. Found: C, 23.14; H, 6.42; Cl, 17.21; Ga, 33.90; N, 6.61; Si, 12.76. Molecular weight for $C_8H_{26}Cl_2Ga_2N_2Si_2$: calcd, 417; found, 417 (calcd molality based on 417: 0.0493 *m*).

Synthesis of *n*-Butyl((trimethylsilyl)amino)gallium Chloride, $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$. To a stirred solution of $(Me_2Si)_2NH$ (8.96 g, 55.7 mmol) in 25 mL of ether was added n-$BuGaCl_2$ (5.51 g, 27.8 mmol). After the solution was allowed to reflux for 9 h, the liquid portion was removed by vacuum distillation, leaving a white solid. From the liquid $(Me_3Si)_2NH$ (5.23 g, 58.4% recovered) was isolated by distillation and identified by a comparison of its IR spectrum with that of an authentic sample. The product $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$ (4.93 g, 70.7% yield, mp 104–106 °C) was purified by sublimation at 95 °C (0.001 torr): ^1H NMR τ 8.55 (m, 6.3, CH_2CH_2), 9.14 (t, 6.3, CH_3 and CH_2Ga), 9.86 (s, 9, CH_3Si). Anal. Calcd for $C_{14}H_{38}Cl_2Ga_2N_2Si_2$: C, 33.53; H, 7.59; Cl, 14.16; Ga, 27.83; N, 5.59; Si, 11.20. Found: C, 33.90; H, 7.58; Cl, 13.94; Ga, 28.09; N, 5.21; Si, 10.84. Molecular weight for $C_{14}H_{38}Cl_2Ga_2N_2Si_2$: calcd, 501; found, 491 (calcd molality based on 501: 0.0450).

Collection of Crystallographic Data, $[Me(Cl)GaN(H)SiMe_3]_2$. Colorless crystals were grown by slowly cooling a saturated methylene chloride solution. A suitable crystal was mounted in a capillary tube under an argon atmosphere. Determination of the unit cell parameters and the orientation matrix as well as the collection of intensity data were made on a Syntex $P2_1$ four circle diffractometer. The diffractometer was equipped with a graphite monochromator (Bragg 2θ angle = 12.2°) and used Mo Kα radiation at a takeoff angle of 3°. The final lattice parameters and orientation matrix were obtained from a least-squares refinement of 15 reflections ($12.5° \leq \theta \leq 37.4°$). The values found were $a = 18.712$ (10) Å, $b = 11.174$ (2) Å, $c = 9.355$ (2) Å, $\alpha = 89.97$ (2)°, $\beta = 89.97$ (3)°, $\gamma = 90.04$ (3)°, $V =$

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Table I. Final Positional Parameters

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ga	0.0350 (1)	0.0711 (1)	0.1068 (1)
Cl	0.0021 (2)	0.2612 (3)	0.1055 (4)
N	−0.0531 (4)	−0.0319 (7)	0.1000 (9)
Si	−0.1377 (2)	0.0058 (3)	0.1640 (4)
C(1)	0.1060 (7)	0.0359 (12)	0.2545 (14)
C(2)	−0.1948 (7)	−0.1298 (13)	0.1512 (18)
C(3)	−0.1311 (10)	0.0573 (15)	0.3523 (14)
C(4)	−0.1789 (9)	0.1256 (14)	0.0506 (17)

1956 (2) Å^3, and *d*(calcd) = 1.416 g cm^{-3} for $Z = 4$. The experimental density was found to lie between the densities of methylene chloride and carbon tetrachloride. The mosaic spread for the crystal was shown to be satisfactory from ω scans of several low 2θ angle reflections. These scans gave peak widths at half-height of less than 0.2°. The systematic absences $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, indicated the orthorhombic space group *Pbca* (No. 61[13]).

Intensity data were collected with θ–2θ scans with a variable scan rate of 2.02–23.9°/min and a scan width of 1°. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio, TR, of 1. The intensities of three standard reflections (10,0,0), (060) and (006) were monitored every 100 reflections and showed no significant fluctuations. Intensites were calculated from the total scan count (CT) and background counts by the relationship $I = \mathrm{CT} - (\mathrm{TR})(\mathrm{bgd1} + \mathrm{bgd2})$. The intensities were assigned standard deviations according to the formula $\sigma^2(I) = [\mathrm{CT} + (\mathrm{TR})^2(\mathrm{bgd1} + \mathrm{bgd2})]$. Lorentz and polarization corrections were made. A total of 1732 reflections were collected in a complete octant of data out to $2\theta = 50°$, and 1562 reflections were accepted as statistically above the background ($I \geq 1.5\sigma(I)$).

Structure Determination and Refinement. The positions of the gallium atoms were obtained from a Patterson map, and the positions of C, Cl, N, and Si atoms were taken from various Fourier maps. Several cycles of a full-matrix least-squares refinement with all nonhydrogen atoms anisotropic gave $R = 0.069$ ($R = \sum||F_o| - |F_c||/\sum|F_o|$). The methyl hydrogen atoms were generated at calculated positions (C–H = 1.08 Å; H–C–H = 109.5°) with rigid geometry pivoting around the C_3 axis. Three additional cycles of refinement led to $R = 0.064$ and $R_w = 0.059$ ($R_w = [\sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}]$). In the final cycle the shift/esd for the positional parameters was <1.

All calculations were performed on the Univac 90/80 computer using SHELX-76[14] and ORTEP.[15] Scattering factors for all atoms were taken from Cromer and Waber's tabulation and were corrected for the real and imaginary anomalous dispersion components.[16] In all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ and a weighting scheme based on counting statistics ($w = 1/\sigma^2(F_o)$) was employed for calculating R_w. The final positional parameters are found in Table I. The bond lengths and bond angles are given in Table II. Tables of observed and calculated structure factors and thermal parameters are available as supplementary material.

Results and Discussion

When $MeGaCl_2$ or *n*-$BuGaCl_2$ was allowed to react with $(Me_3Si)_2NH$ in a 1:2 mole ratio, $[R(Cl)GaN(H)SiMe_3]_2$ was obtained where R = Me or *n*-Bu (eq 1). These alkyl((trimethylsilyl)amino)gallium chlorides are colorless crystalline solids at room temperature. Cryoscopic molecular weight measurements in benzene indicate that both compounds are dimers.

$$RGaCl_2 + 2(Me_3Si)_2NH \rightarrow {}^1/_2[R(Cl)GaN(H)SiMe_3]_2 + Me_3SiCl + (Me_3Si)_2NH \quad (1)$$

Table II. Intramolecular Distances (Å), Bond Angles (Deg), and Dihedral Angles (Deg) for $[Me(Cl)GaN(H)SiMe_3]_2$

Ga· · ·Ga	2.870 (2)	Si–N	1.744 (8)
Ga–N	2.012 (8)	Si–C(2)	1.858 (13)
Ga–Cl	2.212 (3)	Si–C(3)	1.857 (13)
Ga–C(1)	1.956 (11)	Si–C(4)	1.874 (14)
N–Ga–Cl	108.7 (2)	C(3)–Si–N	109.9 (6)
C(1)–Ga–Cl	112.7 (4)	C(3)–Si–C(2)	110.6 (7)
N–Ga–C(1)	117.6 (5)	C(4)–Si–C(2)	108.0 (8)
Ga–N–Ga	91.0 (5)	C(4)–Si–N	110.6 (6)
Si–N–Ga	126.5 (4)	C(4)–Si–C(3)	110.1 (8)
C(2)–Si–N	107.6 (5)		
C(1)–Ga–N–Ga	125.4	Si–N–Ga–Cl	115.3
Cl–Ga–N–Ga	105.0	Si–N–Ga–C(1)	13.4
Si–N–Ga–N	135.6		

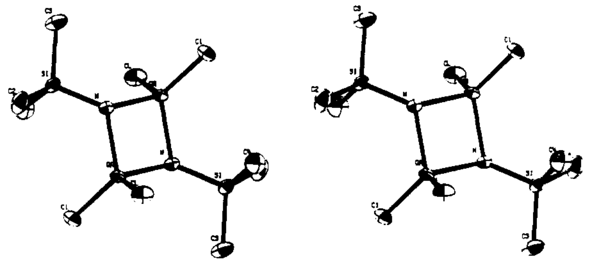

Figure 1. ORTEP diagram of $[Me(Cl)GaN(H)SiMe_3]_2$ (50% probability ellipsoids).

A recent study has shown that dimerization of aminogallium compounds probably proceeds by a series of gallium–nitrogen bond-forming reactions between monomers rather than by a concerted π-cycloaddition reaction.[17] Consequently, in our systems the excess $(Me_3Si)_2NH$ would compete with the Lewis base site of one monomer for the Lewis acid site of a second monomer. The recovery of nearly half of the initial $(Me_3Si)_2NH$ and the isolation of the dimer as the major product suggest that the dimer is considerably more stable than the potential adduct $(Me_3Si)_2NH{\cdot}RGa(N(H)SiMe_3)Cl$. If the adduct is formed, apparently the Si–N bond of the $(Me_3Si)_2NH$ is not sufficiently weakened to permit cleavage and the formation of $RGa(N(H)SiMe_3)_2$ under these reaction conditions.[18] Likewise, $[R(Cl)GaN(H)SiMe_3]_2$ is stable to elimination of Me_3SiCl at room temperature.

If the structure of the alkyl((trimethylsilyl)amino)gallium chloride dimer is assumed to contain a four-membered Ga_2N_2 ring, five geometrical isomers are possible. These are the trans–trans isomer in which the alkyl groups are trans to each other and the trimethylsilyl groups are trans to each other (C_i), the cis–trans (C_s), the trans–cis (C_s), the cis–cis (C_{2v}), and the all-cis isomer in which the alkyl and trimethylsilyl groups are on the same side of the Ga_2N_2 ring (C_{2v}). The same five geometrical isomers are also possible for the compound [*t*-BuN(H)Al(Br)Et]$_2$. Indeed, both the trans–trans and the cis–cis isomers of [*t*-BuN(H)Al(Br)Et]$_2$ were isolated by recrystallization and sublimation of a solid which was obtained by the thermal decomposition of *t*-$BuNH_2{\cdot}Et_2AlBr$.[19] This solid had a broad melting point range, but the elemental analysis and molecular weight determination were consistent with the molecular formula of the dimer.[19] In contrast, the products obtained from the cleavage reactions (eq 1) have narrow melting point ranges. This result suggests that only one isomer of $[R(Cl)GaN(H)SiMe_3]_2$ is present in the solid state. To determine which of the five isomers was isolated,

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we undertook a crystallographic study of a single crystal of $[Me(Cl)GaN(H)SiMe_3]_2$.

An ORTEP diagram of $[Me(Cl)GaN(H)SiMe_3]_2$ is shown in Figure 1. The dimer has a crystallographically imposed C_i symmetry. A least-squares plane calculation[20] $(-10.17X + 8.865Y - 2.570Z = 0)$ indicates that the four-membered Ga_2N_2 ring is very flat with a root-mean-square displacement from the ring of 1.2×10^{-7} Å for each ring atom. The N–Ga–N and Ga–N–Ga angles are 89.0 and 91.0°, respectively, and are significantly different from the values of 82.1 and 97.9° found in $[Me_2GaNCMe_2]_2$.[21] The Si–N bond makes an angle of 143.7° with the N···N diagonal of the ring while the angles of the Ga–C and Ga–Cl to the Ga···Ga diagonal are 133.7 and 113.6°. The dihedral angles along the Ga–N bond are listed in Table II.

The Ga–N bond length of 2.012 (8) Å compares favorably with the mean value of 1.989 Å in $[Me_2GaNCMe_2]_2$[21] and lies at the upper limit in the observed range of 1.930–2.009 Å for a tetrahedrally coordinated gallium atom.[22] Likewise, the Ga–C distance of 1.956 (11) Å is similar to the mean value of 1.966 Å in $[Me_2GaNCMe_2]_2$[21] and lies in the observed range of 1.943–2.004 Å for the series $(Me_2Ga)_2C_2O_{4-x}(NMe)_x$.[23] The Si–N bond distance of 1.738 (19) Å was found in a crystallographic study of $Tl[N(SiMe_3)_2]_3$[24] and is near our value of 1.744 (8) Å. However, the mean value of 1.863 Å for the Si–C distance is somewhat shorter than the corresponding mean value of 1.906 Å in $Tl[N(SiMe_3)_2]_3$.[24]

In addition to the major bands, the ^1H NMR spectra of both dimers contain several weak signals which may be due to the presence of impurities or different geometrical isomers of the dimer.[17] An examination of the spectra of both compounds at 10 and 60 °C revealed no significant differences in intensity or number of bands. In the spectrum of $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$, the triplet at 9.14 ppm has been assigned to the protons of both the methyl and α-methylene groups on the basis of the intensity and decoupling experiments. When the multiplet at 8.55 ppm was radiated, only one collapsed singlet was observed.

The IR spectra of the alkyl((trimethylsilyl)amino)gallium chlorides in Nujol mulls are reported in Table III. The bands which are associated with CH_3 deformation vibrations of the trimethylsilyl group ($\delta_s(CH_3)$, $\rho_{as}(CH_3)$, $\rho_s(CH_3)$) are easily identified. These bands are generally among the most intense and are usually found in very narrow regions of the spectrum.[25] Likewise, the Si–C_3 symmetric and asymmetric stretching frequencies are generally observed in the regions 610–660 and ~700 cm^{-1}.[25] The band at 589 cm^{-1} in the spectrum of $[Me(Cl)GaN(H)SiMe_3]_2$ has been assigned to the Ga–C stretching vibration on the basis of a comparison with the spectrum of $[MeGaCl_2]_2$.[26] The Ga–C stretching frequencies for $[n\text{-}BuGaI_2]_2$ have been reported at 544 and 624 cm^{-1}.[27] Clearly, the band at 557 cm^{-1} in the spectrum of $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$ is associated with the Ga–C stretching vibration. However, the nature of the bands at 638, 662, and 695 cm^{-1} is uncertain since bands of medium intensity at 563, 637, 667, and 694 cm^{-1} were observed in the spectrum of $[n\text{-}BuGaCl_2]_2$. On comparison with the IR spectra of $(Me_3Si)_2NH{\cdot}GaCl_3$[8] and $[MeGaCl_2]_2$,[26] the intense bands at 343 and 330 cm^{-1} have been assigned to the Ga–Cl stretching vibration.

Table III. Infrared Spectra in the Region 3250–3200 and 1300–200 cm^{-1} [a]

$[Me(Cl)GaN(H)SiMe_3]_2$	$[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$	assignts
3220 vs	3209 vs	$\nu(NH)$
	1295 m	
1271 s, sh		$\delta_s(CH_3)Si$
1260 vs, sh	1268 vs	
1252 vs	1255 vs	
1213 s	1200 m	
	1186 m	
1170 w, sh	1165 m, sh	
1134 vs	1135 vs	$\delta(NH)$
	1077 s	
	1053 m	
	1017 m	
	1004 m	
	963 m	
895 vs	898 vs	$\nu(SiN)$
	882 vs, sh	
839 vs	845 vs	$\rho_{as}(CH_3)Si$
770 vs, sh	765 vs, sh	$\rho_s(CH_3)Si$
750 vs	744 vs	
738 vs, sh		$\rho_s(CH_3)Si$
696 s		$\nu_{as}(SiC_3)$
	695 s	
	662 vs	
	638 s	
630 m	627 m, sh	$\nu_s(SiC_3)$
589 s	557 w	$\nu(GaC)$
515 vs	509 vs	$\nu(GaN)$
483 s	482 vs	$\nu(GaN)$
	417 w	
	396 w	
381 vw, sh		
343 s	330 vs	$\nu(GaCl)$
287 vw, sh		
	268 w	
231 vw	232 w	

[a] Abbreviations: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

The Ga–N stretching frequencies have been found between 375 and 559 cm^{-1}.[8,23,28] One major reason for this broad range is the coupling of the Ga–N stretching vibration. The band at 375 cm^{-1} in the IR spectrum of $Ga[N(SiMe_3)_2]_3$ is the result of extensive mixing of Ga–N_3 stretching, Si_2–N stretching, and Si–C_3 deformation motions;[28a] and while the band at 511 cm^{-1} in the IR spectrum of $H_3Ga{\cdot}NMe_3$ is primarily a Ga–N stretching vibration, the N–C_3 symmetric deformation and CH_3 rocking motions also make significant contributions.[28b] Thus, the intense bands between 482 and 515 cm^{-1} in the spectra of the alkyl((trimethylsilyl)amino)gallium chlorides have been assigned to the Ga–N stretching vibrations although these vibrations are probably coupled.

Coupling of the Si–N stretching vibrations is also observed in many substituted silylamines. For example, the band at 934 cm^{-1} in the IR spectrum of $(Me_3Si)_2NH$ results from the mixing of the asymmetric Si_2–N stretching and the N–H deformation vibrations, and the symmetric Si_2–N and Si–C_3 stretching motions are the major contributors to the band at 566 cm^{-1}.[25] On the other hand, the band at 828 cm^{-1} in the IR spectrum of Et_3SiNH_2 has been attributed to the uncoupled Si–N stretching vibration.[29] In view of these observations, the intense bands near 900 cm^{-1} have been assigned to the

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Si-N stretching vibration and those near 1135 cm^{-1} to the N-H deformation vibration. The strong intensity of the latter bands may be the result of mixing of the Si-N stretching motion with the N-H deformation vibration as has been found in the IR spectrum of $(Me_3Si)_2NH$.[25]

The IR spectrum of $[Me(Cl)GaN(H)SiMe_3]_2$ contains six intense bands which are primarily associated with the stretching vibrations of the skeletal structure $[C(Cl)GaN(H)Si]_2$. If the skeletal structure has a symmetry of C_i, then the selection rules predict 15 IR-active vibrations of which six are principally stretching motions. For the symmetries of C_s and C_{2v}, a significantly larger number of IR-active vibrations would be expected. Thus, the IR spectrum of $[Me(Cl)GaN(H)SiMe_3]_2$ supports the presence of the trans-trans structure as the predominate isomer in the solid state. Confirmation of this structure by Raman spectroscopy was prevented by the rather substantial fluorescence which the solid dimer exhibited.

In conclusion, the IR, melting point, and crystallographic data indicate that the trans-trans isomer of $[Me(Cl)GaN(H)SiMe_3]_2$ crystallized from a methylene chloride solution of the reaction mixture. The major signals in the ^1H NMR spectrum of a benzene solution of $[Me(Cl)GaN(H)SiMe_3]_2$ are consistent with the trans-trans isomer although other isomers may be present in low concentrations. The *trans*-$[Me_2GaN(Me)Ph]_2$ has also been found to be the predominate isomer in benzene and thermodynamically more stable than the cis isomer.[17] A comparison of the major features in the IR spectra of both alkyl((trimethylsilyl)amino)gallium chlorides suggests that $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$ probably has a trans-trans structure in the solid state.

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Registry No. $[Me(Cl)GaN(H)SiMe_3]_2$, 80765-15-7; $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$, 80765-16-8; $MeGaCl_2$, 6917-74-4; $n\text{-}BuGaCl_2$, 73873-08-2; $(Me_3Si)_2NH$, 999-97-3.

Supplementary Material Available: Tabulations of observed and calculated structure factors and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

Contribution from Departments of Chemistry, Texas A&M University, College Station, Texas 77840,
The Technion-Israel Institute of Technology, Haifa, Israel, and The Hebrew University, Jerusalem, Israel

Triangular Trinuclear Molybdenum(IV) Cluster Compounds with Two Capping Oxygen Atoms

MICHAEL ARDON,[1a] AVI BINO,*[1a] F. ALBERT COTTON,*[1b] ZVI DORI,*[1c] MENACHEM KAFTORY,[1c]
and GEORGE REISNER[1c]

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The preparation and structural characterization of two trinuclear molybdenum(IV) cluster compounds with capping oxygen atoms are reported. Reaction of $Mo(CO)_6$ with acetic acid under O_2 allows the isolation, after suitable workup by cation-exchange resin chromatography of **1**, $[Mo_3O_2(OAc)_6(H_2O)_3]Br_2{\cdot}H_2O$. This forms rhombohedral crystals in space group $R\bar{3}m$ with unit cell dimensions a = 11.784 (5) Å, α = 106.34 (5)°, V = 1386.6 (1) Å^3, and Z = 2. The structure consists of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ions having effectively D_{3h} symmetry residing on crystallographic positions of C_{3v} symmetry. The metal atoms form an equilateral triangle capped above and below by oxygen atoms. The edges of the triangle are each bridged by two acetate ions, and there is a water molecule coordinated to each metal atom with the $Mo\text{-}OH_2$ bond direction intersecting the center of the opposite Mo-Mo bond. The bromide ions and the additional H_2O are disordered over several positions in the rhombohedral cell. Reaction of $Mo_2(O_2CCH_3)_4$ with a mixture of propionic acid and propionic anhydride followed by cation column chromatography using CF_3SO_3H to elute gives $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3](CF_3SO_3)_2(CF_3SO_3H)(H_2O)_4$. This forms triclinic crystals in space group $P\bar{1}$ with a = 15.760 (5) Å, b = 14.848 (5) Å, c = 13.632 (4) Å, α = 70.4 (2)°, β = 118.5 (2)°, γ = 123.1 (2)°, V = 2336.6 (1) Å^3, and Z = 2. The trinuclear cation resides on a general position but is very similar to the one in the acetate and has essentially D_{3h} symmetry. The important dimensions within the $[Mo_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ ions are virtually identical in the two cases, with Mo-Mo = 2.766 (2) Å in the acetate and averaging 2.752 (3) Å in the propionate. This type of trinuclear cation can be formulated electronically as having six electrons for Mo-Mo bonding and bond orders of 1. They are very similar to the analogous $[W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ cations described earlier.

Introduction

The past five years have witnessed the discovery of a remarkable new area in the chemistry of molybdenum and tungsten.[2-14] that of compounds containing discrete triangular trinuclear clusters with the metal atoms in oxidation states of, or close to, +4. There are two, structurally different, principal types of compounds as represented by the general structures

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