Supporting Information

Unprecedented Gallium Nitrogen Anions: Synthesis and Characterization of

 $[(Cl_3Ga)_3N]^{3-}$ and $[(Cl_3Ga)_2NSnMe_3]^{2-}$

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Experimental

All manipulations were carried out under a pure dinitrogen atmosphere using standard Schlenk and glove-box techniques. Anhydrous tetrahydrofuran (THF), purchased from EMD, diethylether (Et₂O), purchased from EMD, and acetonitrile (MeCN), purchased from Burdick and Jackson were stored over activated 4 Å molecular sieves under a pure dinitrogen atmosphere. The compound GaCl₃ (Alfa Aesar, 99.999%) was used as received and stored under a pure dinitrogen atmosphere. The salt (Me₄N)Cl (Alfa Aesar, 97%) was dried *in vacuo* at 100 °C before being stored under a dinitrogen atmosphere. The compounds (Me₃Sn)₃N¹ and Cl₃Ga·N(SnMe₃)₃², were prepared *via* the published procedure, and compounds (Me₄N)[GaCl₄],³ and (Me₄N)[Me₃SnCl₂]⁴ were prepared via modifications of the literature procedures. Elemental analysis of (Me₄N)[GaCl₄] was performed at the Ecology Analytical Laboratory at San Diego State University. Elemental analysis of (Me₄N)₃**1** was performed at Columbia Analytics Laboratory in Tucson, AZ, and analysis of (Me₄N)₂**2**, was performed at the Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany.

 $(Me_4N)_3[(Cl_3Ga)_3N]$. $(Me_4N)_3(1)$. A solution of $(Me_4N)[GaCl_4]$ (1.57 g, 5.49 mmol) in 10 mL of THF was added to a solution of $Cl_3Ga \cdot N(SnMe_3)_3$ (1.25 g, 1.84 mmol) in 45 mL of THF. The resultant colorless solution was refluxed for 2 h under flowing N₂ yielding a white precipitate, which was collected by filtration, washed with THF (3 × 5 mL) and Et₂O (3 × 5 mL), and dried *in vacuo* to afford 0.79 g of a white solid. The white solid was dissolved in 250 mL of MeCN. The solution was filtered through celite. Vapor diffusion of THF into the filtrate afforded small triangular crystals which were collected by filtration, washed with successive aliquots of THF (5 × 3 mL) and Et₂O (4 × 3 mL), and dried *in vacuo* to afford 0.14 g, (10%) of $(Me_4N)_3[(Cl_3Ga)_3N]$,

 $(Me_4N)_3(1)$ as a white crystalline solid. Diffuse reflectance spectrum: λ_{max} 240 nm. Anal. calcd for $C_{12}H_{36}Cl_9Ga_3N_4$: C, 18.85; H, 4.75; N, 7.33. Found: C, 19.04; H, 4.39; N, 6.89. While the nitrogen value is slightly lower than the accepted 0.4% error from the calculated value, we attribute this difference to the extreme sensitivity of the product to air/hydrolysis.

(Me₄N)₂[(Cl₃Ga)₂NSnMe₃]. (Me₄N)₂(**2**). A solution of (Me₄N)[GaCl₄] (0.48 g, 1.7 mmol) in 13 mL of THF was added to a solution of (Me₃Sn)₃N (0.43 g, 0.84 mmol) in 5.0 mL of THF. Small white crystals began to form within one minute of mixing the reactants. The reaction mixture was allowed to stand for 24 h. After this time the crystals were collected by filtration, washed with successive aliquots of THF (5 × 3 mL) and Et₂O (4 × 3 mL), and dried *in vacuo* to afford 0.45 g (0.67 mmol, 79%) of (Me₄N)₂[(Cl₃Ga)₂NSnMe₃], (Me₄N)₂(**2**) as a white crystalline solid. ¹H NMR (CD₃CN): δ 0.28 ppm (s) [*J*_{(117/119)Sn-1H} 58 Hz] Diffuse reflectance spectrum: λ_{max} (nm) 248. Anal. calcd for C₁₁H₃₃Cl₆Ga₂N₃Sn: C, 19.48; H, 4.90; Cl, 31.36; Ga, 20.56; N, 6.20; Sn, 17.50. Found: C, 19.56; H, 4.91; Cl, 31.23; Ga, 20.84; N, 5.93; Sn, 17.53.

Diffuse Reflectance Spectroscopy

All measurements were taken on a JASCO V-670 UV-Vis spectrophotometer fitted with an integrating sphere. Pure samples were ground with a mortar and pestle and placed in the sample cell with a quartz window under an inert atmosphere. The sample cell was quickly transferred from the dry box to the instrument and measured immediately.



Figure S-1. Diffuse reflectance UV-Vis spectrum of $(Me_4N)_3[(Cl_3Ga)_3N]$ overlaid with spectra taken after successive exposures of the sample to air.



Figure S-2. Comparison of spectrum of $(Me_4N)_3[(Cl_3Ga)_3N]$ with that of the initial reaction precipitate. The transition at 420 nm is not as distinguishable in the intermediate (blue).



Figure S-3. Diffuse reflectance UV-Vis spectrum of $(Me_4N)_2[(Cl_3Ga)_2NSnMe_3]$ overlaid with spectra taken before and after exposure of the sample to air.

X-Ray Crystallography

Diffraction-quality crystals of (Me₄N)₃[(Cl₃Ga)₃N], (Me₄N)₃1, were obtained from diffusion of Et₂O in a MeCN solution. Crystals were coated in Paratone oil and mounted by mean of a glass capillary fiber on a Bruker APEX-II CCD area detector instrument operated by the APEX software package. A hemisphere of data was collected at 100 K in 40 s frames using scans of 0.5 deg/frame. Data reduction was performed by SAINT, absorption correction was applied using SADABS, and the space group was assigned using XPREP. The structure was solved by direct methods with SHELXTL⁵ and refined against all data by full-matrix least squares on F_2 . Hydrogen atoms were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. All atoms in the anion and cations were disordered equally over two positions and were refined accordingly. Disordered atom pairs in the cations were restrained to have equivalent anisotropic displacement parameters. All nitrogen–carbon bond lengths of the three disordered tetramethylammonium cations were restrained to be equivalent. The structure converged in the final stage of refinement, showing no movement in atom positions. Use of the checking program PLATON did not identify any missing or higher symmetry. Careful examination of the full hemisphere of diffraction revealed no weak reflections which would indicate a larger unit cell. Thus we could not resolve the disorder by using a larger unit cell.

Diffraction-quality crystals of $(Me_4N)_2[(Cl_3Ga)_2NSnMe_3]$ $(Me_4N)_22$ were obtained from THF. Crystals were coated in Paratone oil and mounted by mean of a glass capillary fiber on a Bruker APEX-II CCD area detector instrument operated by the APEX software package. A hemisphere of data was collected at 190 K using scans of 0.5 deg/frame. Data reduction was performed by SAINT, absorption correction was applied using SADABS, and the space group was assigned using XPREP. The structure was solved by direct methods with SHELXTL and refined against all data by full-matrix least squares on F_2 . Hydrogen atoms were attached at idealized positions on carbon atoms and were refined as riding atoms with uniform isotropic thermal parameters. The structure converged in the final stage of refinement, showing no movement in atom positions. Use of the checking program PLATON did not identify any missing or higher symmetry.

	$(Me_4N)_31$	$(Me_4N)_2$ 2
formula	$C_{12}H_{36}Cl_9Ga_3N_4$	$C_{11}H_{33}Cl_6Ga_2N_3Sn$
cryst. syst.	Rhombohedral	Orthorhombic
fw	764.66	678.23
space group	<i>R</i> 3	$P2_{1}2_{1}2_{1}$
<i>a</i> , Å	10.7081(18)	11.5910(4)
b, Å	10.7081(18)	14.2637(5)
<i>c</i> , Å	22.379(4)	15.6726(6)
α , deg	90.00	90
β , deg	90.00	90
γ, deg	120.00	90
$V, Å^{\bar{3}}$	2222.3(7)	2591.2(2)
Ζ	3	4
$\rho_{\rm calc}, {\rm g/cm}^3$	1.714	1.739
2θ range, deg	2.38 to 30.48	2.19 to 31.00
$\operatorname{GOF}(F^2)$	1.018	1.04
$R_1^{c}/wR_2^{D0/0}$	3.34/6.44	2.67/5.23

Crystallographic Data

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Figure S-4. [(Cl₃Ga)₃N]³⁻ (**1**) in (Me₄N)₃**1** disordered equally over two distinct orientations in the crystal lattice. The structure of both orientations of **1** viewed (a) down the three-fold axis (chlorine atoms in the second orientation are omitted for clarity) and (b) perpendicular to the three fold axis (all chlorine atoms omitted for clarity); thermal ellipsoids are drawn at the 50% probability level. Selected mean interatomic distances [Å] and angles [°] for one anion disordered over two positions: Ga–N 1.878(1), Ga–Cl 2.23(5), Ga–N–Ga 115.4(1), N–Ga–Cl 114(3), Cl–Ga–Cl 104.4(5). Distance between N1 and N2 0.72 Å

¹H NMR Spectroscopy of (Me₄N)₃1, (Me₄N)₂2, and Relevant Compounds

All ¹H NMR spectra were collected on a Varian Inova 400 Mhz instrument at 30°C. Chemical shifts were referenced to the signal of residual protons in the deuterated solvent. In Figure S-5, the ¹H NMR spectrum of $(Me_4N)_22$, taken 5 min after dissolution of the compound in CD₃CN, is shown. As compared to the ¹H-NMR spectra of the compounds $(Me_4N)[Me_3SnCl_2]$ (Fig. S-6), Me₃SnCl (Fig. S-7), and $(Me_3Sn)_3N$ (Fig. S-8) the product has a shift attributable to the dinuclear gallium compound. Over time, the peak shifts downfield, closer to that of Me₃SnCl. Thus, **2** is somewhat stable in solution. The ¹H NMR spectra in CD₃CN of Me₃SnCl, $(Me_4N)[Me_3SnCl_2]$, and $(Me_3Sn)_3N$ are included because they are not published.



Figure S-5. ¹H NMR spectrum of the intermediate in the synthesis of $(Me_4N)_3[(Cl_3Ga)_3N]$ in CD₃CN. The signal at 0.75 ppm is assigned to an uncharacterized minor product of the reaction. Some residual solvent was present in the sample as indicated in the spectrum.



Figure S-6. ¹H NMR spectrum of (Me₄N)₂[(Cl₃Ga)₂NSnMe₃] in CD₃CN.



Figure S-7. ¹H NMR spectrum of (Me₄N)[Me₃SnCl₂] in CD₃CN.



Figure S-8. ¹H NMR spectrum of Me₃SnCl (Alfa Aesar) in CD₃CN.



Figure S-9. ¹H NMR spectrum of (Me₃Sn)₃N in CD₃CN.

Decomposition of (Me₄N)₂2

¹**H NMR.** A small sample of $(Me_4N)_2[(Cl_3Ga)_2NSnMe_3]$, $(Me_4N)_2(2)$ was dissolved in anhydrous CD₃CN and analyzed by ¹H NMR. The spectrum was comparable to that previously shown (**Fig. S-6**). The sample was then stirred in air for 5 min during which time a white precipitate formed. The solution was again analyzed by ¹H NMR (**Figure S-10**) and the spectrum showed that the Me₃Sn moiety had been fully converted to the anion, $[Me_3SnCl_2]^{1-}$. This also implies the presence of an aprotic anion that is paired with the other Me₄N⁺ present in the original sample and observed in the NMR spectrum.

FT-IR Spectroscopy. A sample of $(Me_4N)_2(2)$ (130 mg) was dissolved in 1.7 mL of anhydrous MeCN under an inert atmosphere. The sample was then exposed to air and stirred for 30 min. A fine white precipitate formed and was collected on a fritted glass filter and washed with dry MeCN (3 × 2 mL) and dry Et₂O (4 × 5 mL) to afford 42 mg of white solid. Infrared spectroscopy was performed on a Perkin-Elmer RX I spectrometer equipped with an attenuated total reflectance accessory. IR (**Figure S-11**) (cm⁻¹) 3385 (m), 3140 (s), 3048 (s), 2840 (m), 1780 (w), 1650 (w), 1490 (m), 1445 (m), 1400 (s), 950 (m).

The broad IR band at 3385 cm⁻¹ may be assigned to the O-H stretching of water molecules in the precipitate. The bands at 3140 and 3048 cm⁻¹ may be from O-H stretching of hydroxyl groups bound to gallium. Similar, though not identical, features have been observed in the IR spectrum of GaO(OH) precipitated from aqueous gallium chloride.⁶ In that report broad IR bands at 3403 cm⁻¹, 3243 cm⁻¹, and a shoulder at 2990 cm⁻¹ were observed and assigned as above. However a band at 1015 cm⁻¹ that was assigned to O-H deformation vibrations in GaO(OH) was not

observed in our spectrum. The vibrations at 1490, 1400, and 950 cm⁻¹ may be assigned to the tetramethylammonium cation and the vibration at 2840 cm⁻¹ is likely C-H stretching of the cation methyl groups. Frequencies associated with vibration of MeCN or Et_2O were not apparent. A band at 917 cm⁻¹, characteristic of Sn-O-H deformation,¹ was not observed.



Figure S-10. ¹H-NMR spectrum of $(Me_4N)_2[(Cl_3Ga)_2NSnMe_3]$ in CD₃CN after 5 min of stirring in air.



Figure S-11. FT-IR spectrum of the decomposition product of $(Me_4N)_2[(Cl_3Ga)_2NSnMe_3]$ in CD₃CN after 30 min of stirring in air.

References

³ (Me₄N)[GaCl₄] was prepared by a modification of the literature preparation of $(NH_2Me_2)[GaCl_4]$ (*J. Phys. Chem. Solids* **1997**, *58*, 989-998). Briefly, a solution of GaCl₃ (3.36 g, 19.1 mmol) in 10 mL of conc. HCl was added to a solution of $(Me_4N)Cl$ (2.14 g, 19.0 mmol) in 20 mL of conc. HCl, producing a white precipitate which was collected by filtration and washed with successive aliquots of concentrated HCl (2 × 10 mL), cold ethanol (3 × 10 mL), and diethyl ether (3 × 10 mL) respectively. The white solid was dried *in vacuo* and recrystallized from acetonitrile/diethyl ether to yield 3.46 g (12.1 mmol, 64%) of (Me₄N)[GaCl₄]. Anal. calcd for C₄H₁₂NGaCl₄: C, 16.82; H, 4.23; N, 4.90. Found: C, 16.69; H, 3.99; N, 5.05.

⁴ (Me₄N)[Me₃SnCl₂] was prepared by a modification of the literature preparation of (Et₄N)[Me₃SnCl₂] (*Organomet.* 1992, *11*, 3684-3690). Briefly, a solution of Me₃SnCl (Alfa Aesar (0.11 g, 0.55 mmol) in 3 mL of acetonitrile was added to solid (Me₄N)Cl (0.06 g, 0.53 mmol) and stirred overnight. This solution was filtered through celite and cooled to -35°C to afford colorless crystals, which were then collected and washed with diethylether (3 × 2 mL) to yield 0.078 g (0.25 mmol, 48%) of (Me₄N)[Me₃SnCl₂]. ¹H NMR (CD₃CN): δ 0.635 (*J*_{(117)Sn-(1)H} 69.8 Hz, *J*_{(119)Sn-(1)H} 73.0 Hz).

⁵ Sheldrick, G. M. Acta Cryst. **2008**, A64, 112-122

⁶ Ristić, M.; Popović, S.; Musić, S. Mater. Lett. 2005, 59, 1227-1233

¹ Shishido, K.; Kojima, S. J. Org. Chem. **1964**, 29, 907-909.

² Cheng, Q. M.; Stark, O.; Merz, K.; Winter, M.; Fischer, R. A. J. Chem. Soc., Dalton Trans. **2002**, 2933-2936