

Dimeric Gallium Oxide and Sulfide Species Stabilized by a Sterically Encumbered β -Diketiminato Ligand

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Organo group 13 metal chalcogenides of formula $(RME)_n$ (R = alkyl, aryl, or related group; M = Al, Ga, or In; E = O, S, Se, or Te)^{1–22} can be synthesized by a variety of synthetic routes. For the organometalloxanes $(RMO)_n$, the most widely used method involves the controlled hydrolysis of metal trialkyls MR_3 .^{5,6} For the heavier chalcogenides, the direct reaction of organo $M(I)$ or $M(III)$ precursors with the elemental chalcogens usually affords the $(RME)_n$ (E = S, Se, or Te) congeners.^{1–4,7–13,18–20} A common feature of these products is that they are oligomeric, with n = 4–8 as the most common association numbers. In the lighter oxo derivatives, in particular those of aluminum, relatively high degrees of association are often found, even with fairly large organic groups such as *t*-Bu. Only in the case of the very large substituent $-C_6H_2-2,4,6-t-Bu_3$ (Mes*) was a lower degree of aggregation (4) observed in the compound $(Mes^*AlO)_4$,¹⁴ which has an unusual Al_4O_4 ring structure instead of a three-dimensional cubane arrangement.²¹ In contrast, structurally characterized $(RGaO)_n$ cages are limited to the silyl substituted species $\{(t-Bu)_3SiGaO\}_4$ which has an almost perfectly cubic Ga_4O_4 core and an average Ga–O distance near 1.92 Å.²² It is now shown that use of the sterically encumbering β -diketiminato ligand $[HC(MeCDippN)_2]^-$ (Dipp = $C_6H_3-2,6-i-Pr_2$)²³ stabilizes the first dimeric galloxane derivative $\{[HC(MeCDippN)_2]GaO\}_2$,

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- (21) Besides $(Mes^*AlO)_4$ (ref 14), the only other structurally characterized tetrameric group 13 metal $(RMO)_4$ species are $\{(Me_3Si)_2ClInO\}_4$ (ref 16) and $\{(t-Bu)_3SiGaO\}_4$ (ref 22) both of which have cubane structures.
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Table 1. Selected Bond Distances (Å) and Angles (deg) for $\{[HC(MeCDippN)_2]GaE\}_2$ (E = O (**1**), S (**2**))

	1	2
Ga–E(1)	1.8536(9)	2.2511(7)
Ga–E(1A)	1.8485(9)	2.2736(7)
Ga–N(1)	1.970(1)	1.986(2)
Ga–N(2)	1.978(1)	1.983(2)
Ga(1)⋯Ga(1A)	2.5989(3)	3.0127(6)
Ga–E–Ga	88.18(4)	83.49(2)
E–Ga–E	90.82(4)	96.51(2)
N–Ga–N	94.96(4)	94.01(2)

1, as well as its sulfur analogue $\{[HC(MeCDippN)_2]GaS\}_2$, **2**. In addition, compound **1** was obtained by a facile route involving the reaction of $\{[HC(MeCDippN)_2]Ga\}_2$ with N_2O .

Treatment of $\{[HC(MeCDippN)_2]Ga\}_2$ with N_2O or S_8 in toluene solution at room temperature produced compounds **1** or **2** as colorless crystals that possess low solubility in hydrocarbon solvents.²⁵ The compounds were characterized by C, H, N analysis, ¹H NMR spectroscopy, and X-ray crystallography.²⁶ The structures of **1** and **2** may be illustrated by the thermal ellipsoid plot of **1** in Figure 1. Selected bond lengths and angles are provided in Table 1. Both compounds are dimeric, which can be attributed to the large size and bidentate nature of the β -diketiminato ligands. There is a center of symmetry in the middle of the

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- (25) All manipulations were carried out under anaerobic and anhydrous conditions. A toluene solution (63 mL) of $\{[HC(MeCDippN)_2]Ga\}_2$ (0.805 g, 1.65 mmol) was added dropwise under slightly positive pressure to a septum-capped, 100 mL Schlenk tube that had been flushed with N_2O and vented with a needle. A white precipitate formed immediately. Upon completion of the addition, stirring was continued for 1 h, whereupon the mixture was heated to redissolve the precipitate. Cooling to room temperature afforded the product **1** as large colorless crystals. Yield: 0.52 g, 62%. Mp: 246–249 °C. Anal. Calcd for $C_{29}H_{41}GaN_2O$: C, 69.19; H, 8.21; N, 5.57. Found: C, 69.91; H, 8.34; N, 5.12. ¹H NMR (C_7D_8 , 400 MHz): δ 7.13, 7.10 (m, 6H, aromatic H of Ar group), 4.77 (s, 1H, methane CH), 3.18 (sept, ³J_{HH} = 7.2 Hz, 4H, CHMe₂), 1.32 (s, 6H, CMe), 1.24 (d, ³J_{HH} = 6.8 Hz, 12H, CHMe₂), 1.12 (d, ³J_{HH} = 7.2 Hz, 12H, CHMe₂). **2**: A toluene solution (50 mL) of $\{[HC(MeCDippN)_2]Ga\}_2$ (0.42 g, 0.803 mmol) was added to sulfur (0.04 g, 1.25 mmol) with rapid stirring and cooling in an ice bath. The solution was allowed to come to room temperature and stirred for a further 12 h. The resultant white precipitate was redissolved by heating. Cooling the solution to room temperature over a 2 h period produced **2** as colorless crystals. Yield: 0.15 g, 34%. Mp: decomposes slowly above 280 °C. Anal. Calcd for $C_{29}H_{41}GaN_2S$: C, 67.05; H, 7.96; N, 5.39. Found: C, 67.91; H, 7.76; N, 5.01. ¹H NMR (C_7D_8 , 300 MHz): δ 7.10 (br, s, 6H, aromatic H's of Ar group), 4.73 (s, 1H, methane CH), 3.25 (sept, ³J_{HH} = 6.9 Hz, 4H, CHMe₂), 1.61 (s, 6H, CMe), 1.28 (d, ³J_{HH} = 6.9 Hz, 12H, CHMe₂), 1.10 (d, ³J_{HH} = 6.9 Hz, 12H, CHMe₂).
- (26) Crystal data at 90 K with Mo $K\alpha$ (λ = 0.710 73 Å) radiation: **1**, $C_{29}H_{41}GaN_2O$, fw = 503.36, colorless parallelepipeds, a = 13.7132(7) Å, b = 13.7585(7) Å, c = 14.2230(7) Å, β = 107.278(1)°, monoclinic, space group $P2_1/n$, V = 2562.4(2) Å³, Z = 4, ρ_{calc} = 1.305 Mg m⁻³, μ = 1.098 mm⁻¹, R_1 = 0.0285 for 6739 ($I > 2\sigma(I)$) data; **2**, $C_{29}H_{41}GaN_2S$, fw = 519.42, colorless parallelepipeds, a = 22.4257(9) Å, b = 14.7953(6) Å, c = 16.3518(6) Å, β = 90.368(1)°, monoclinic, space group $C2/c$, Z = 8, ρ_{calc} = 1.272 Mg m⁻³, μ = 1.110 mm⁻¹, R_1 = 0.0503 for 5887 ($I > 2\sigma(I)$) data.

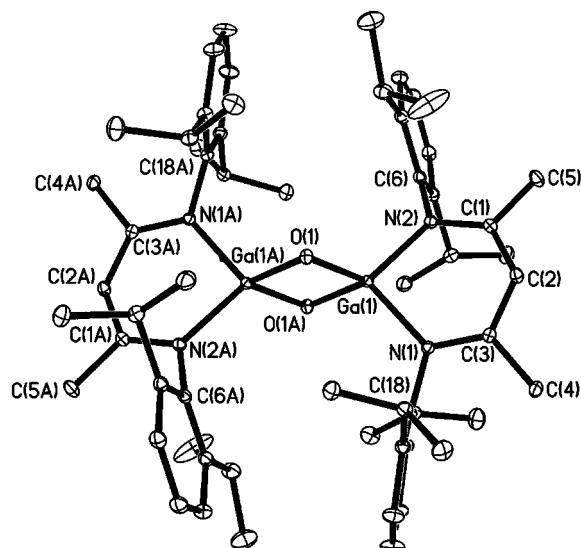


Figure 1. Thermal ellipsoid (30%) drawing of **1**. H atoms are not shown.

Ga_2O_2 or Ga_2S_2 cores. The Ga_2O_2 array is almost perfectly square with angles within ca. 0.8° of 90° and Ga–O distances that differ by only 0.005 \AA . The $\text{Ga}\cdots\text{Ga}$ separation is $2.5989(3) \text{ \AA}$, which is just slightly longer than double the covalent radius of gallium and shorter than $\text{Ga}\cdots\text{Ga}$ distances of $2.7052(9)$ – $2.7188(7) \text{ \AA}$ in $\{(t\text{-Bu})_3\text{SiGaO}\}_4$.²² However, owing to the electronegative nature of the nitrogen and oxygen ligand atoms, the gallium center has considerable ionic character which decreases its effective radius. Thus, significant $\text{Ga}\cdots\text{Ga}$ interaction is probably small. The Ga–N distances are both ca. 0.07 \AA shorter than the $2.054(2) \text{ \AA}$ average value seen in the Ga(I) precursor $\{\text{HC}(\text{MeCDippN})_2\}\text{Ga}$.²⁴ This is most probably a result of the change in oxidation state from Ga(I) in the precursor to Ga(III) in **1**.²⁷ The Ga–O distance, av $1.851(3) \text{ \AA}$, may be compared to the $1.821(3)$, $1.822(3)$, or $1.831(4) \text{ \AA}$ observed in the low-coordinate species $t\text{-Bu}_2\text{GaOC}_6\text{H}_2\text{-2,6-t-Bu}_2\text{-4-Me}$,²⁸ (2,2,6,6-tetramethylpiperidino) $_2\text{GaOPh}$,²⁹ or $t\text{-Bu}_2\text{GaOCPh}_3$ ³⁰ in addition to the $1.79(1) \text{ \AA}$ observed in the dimetalloxane $\text{O}\{\text{Ga}(\text{Mes}^*)\text{Mn}(\text{CO})_5\}_2$ ($\text{Mes}^* = \text{C}_6\text{H}_2\text{-2,4,6-t-Bu}_3$).³¹ All of these compounds feature

(27) In the compounds $\{\text{HC}(\text{MeCDippN})_2\}\text{GaX}_2$ ($X = \text{Cl}$ or I), the Ga(III)–N distances are in the range $1.906(3)$ – $1.948(1) \text{ \AA}$. See: Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.*, in press.

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three-coordinate gallium bound to two-coordinate oxygen. The slightly longer Ga–O bond in **1** can be attributed to the higher (4) coordination of the metal in this species.

The sulfur derivative **2** also has a bridged dimeric structure³² which is analogous to that of **1**. The Ga_2S_2 core is planar and has an average Ga–S bond length of $2.26(1) \text{ \AA}$. This distance is just within the currently known range (2.20 – 2.27 \AA) for low-coordinate Ga–S species.^{4,33–35} Unlike the almost square core geometry in **1**, the ring angle at sulfur $83.49(2)^\circ$ differs considerably from the $96.51(2)^\circ$ at gallium. Despite the narrower sulfur angle, the $\text{Ga}\cdots\text{Ga}$ separation is $3.0127(3) \text{ \AA}$, which is similar to the $\text{Ga}\cdots\text{Ga}$ separation of $3.099(6) \text{ \AA}$ in $(t\text{-BuGaS})_4$.² Although no dimeric gallium structures are available for comparison, the structure of the organoaluminum sulfide dimer $(\text{Mes}^*\text{AlS})_2$ ($\text{Mes}^* = \text{C}_6\text{H}_2\text{-2,4,6-t-Bu}_3$) was described recently.¹⁵ It is notable that this compound shows similar angular distortions in its core in that the angle at sulfur ($\text{Al–S–Al} = 78.09(3)^\circ$) is also narrower than the angle at the metal ($\text{S–Al–S} = 101.91(3)^\circ$). In contrast, the oxygen analogue $(\text{Mes}^*\text{AlO})_4$ is a tetramer with a unique, planar Al_4O_4 ring structure in which the Al–O–Al angle is a wide $151.32(13)^\circ$. It was argued that the reluctance of the sulfur atom to hybridize led to narrower angles which resulted in greater steric congestion and a lower degree of aggregation for that molecule. These findings suggest that there is considerable strain in the structure of **1** and that dissociation to monomeric species featuring formal GaO multiple bonding may be possible with suitable ligand modification.³⁶

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Supporting Information Available: Two X-ray files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. IC015506C

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