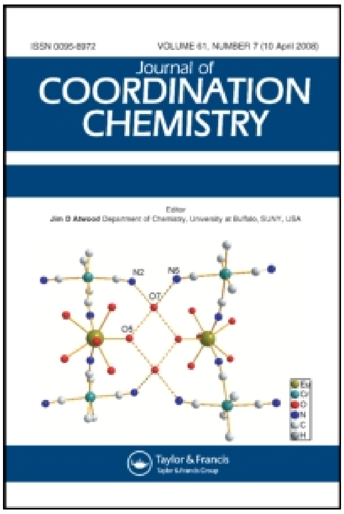

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Syntheses and Structures of [$NMe_2(\mu\text{-}NMe_2)GaCl]_2$ and [$TMP(\mu\text{-}OEt)GaCl]_2$ (TMP = 2,6-Tetramethylpiperidide)

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SYNTHESES AND STRUCTURES OF $[NMe_2(\mu\text{-}NMe_2)GaCl]_2$ AND $[TMP(\mu\text{-}OEt)GaCl]_2$ (TMP = 2,6-TETRAMETHYLPIPERIDIDE)

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The bis-dimethylamido gallium chloride, $[NMe_2(\mu\text{-}NMe_2)GaCl]_2$ (**1**) may be prepared by the reaction of two equivalents of lithium amide with $GaCl_3$. The amido ethoxide gallium chloride, $[TMP(\mu\text{-}OEt)GaCl]_2$ (**2**), (TMP = tetramethylpiperidide) is formed in the reaction of lithium amide with $GaCl_3$ in diethylether. The structures of **1** and **2** have been determined by X-ray methods. Crystals of **1** are orthorhombic, space group $P2_12_12_1$, with $a = 8.428(4)$, $b = 15.10(1)$, $c = 13.138(6)$ Å, $Z = 4$. Crystals of **2** are monoclinic, space group $P2_1/n$, with $a = 8.542(1)$, $b = 12.457(1)$, $c = 12.959(1)$ Å, $\beta = 95.483(9)$, $Z = 2$. The R values for **1** and **2** are 0.066 and 0.054, respectively. The solid state structure of **1** consists of a nitrogen-bridged dimer, while **2** consists of an oxygen-bridged dimer.

Keywords: Gallium(III), chloride, dimethylamido, piperidide, ethoxide, X-ray structure

INTRODUCTION

Amido gallium halides are useful as starting materials for the preparation of a wide range of alkyl amido gallium compounds, some of which have potential as precursors to compound semiconductors.[1] In the present paper we describe the synthesis of two such amido gallium halides, namely bis-dimethyl amido gallium chloride $[NMe_2(\mu\text{-}NMe_2(GaCl]_2$ (**1**) and $[TMP(\mu\text{-}OEt)GaCl]_2$ (**2**) which may be isolated from the reaction of piperidide with $GaCl_3$ in Et_2O. To our knowledge there are no other examples of structurally characterized neutral amido gallium chlorides. The synthesis of **1** has been previously reported.[2] Structurally characterized gallium ethoxide complexes are restricted to $[(\eta^1\text{-}C_5H_5)_2GaOEt]_2$[3] which is formed when Cp_2GaCl is prepared in Et_2O.[4]

EXPERIMENTAL

Both compounds were prepared under dry nitrogen with the use of standard vacuum-line and dry-box techniques. All solvents were dried over molecular sieves and distilled from sodium/benzophenone prior to use. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE300 instrument in C_6D_6 and THF-d_8 at

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ambient temperature and are referenced to Me_4Si. Mass spectra were recorded on Bell and Howell CEC 24-491 (EI) and Finnigan MAT 4023 (70 eV, CI) spectrometers.

Preparation of $[NMe_2(\mu\text{-}NMe_2)GaCl]_2$ (*1*)

Dimethylamine ($HNMe_2$) gas (excess) was condensed onto a solution of *t*-BuLi ($16.38\,cm^3$ of a 35.22 mmol, 2.15 M pentane solution) at −78°C. The reaction mixture was allowed to warm to 25°C over the course of 6 h and then stirred at that temperature an additional 12 h before being added dropwise to a stirred solution of $GaCl_3$(3.10 g, 17.61 mmol) at −78°C in Et_2O ($30\,cm^3$). The solution was allowed to warm to 25°C and then stirred 12 h before solvent removal and subsequent extraction into hexane ($100\,cm^3$). The solution was filtered, concentrated ($25\,cm^3$), and cooled (−20°C) for 5 days to afford 1.78 g of **1** as yellowish needles. Yield 64%, mp 78–79°C. Compound **1** does not sublime from 0–110°C at 10^{-3} torr. ^1H NMR (300.15 MHz, C_6D_6, 298K, TMS ext.): δ 1.85 (s, 12H, N-CH_3), 1.80 (s 12H, μ-N-CH_3); (there is rapid exchange between the *cis* and *trans* isomers in solution). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 295K, TMS ext.): δ 36.5 (s, N-CH_3). Anal: calcd; C (24.85), H (6.26), N (14.48%). Found: C (23.62), H (5.95), N (13.86%).

Preparation of $[TMP(\mu\text{-}OEt)GaCl]_2$ (*2*)

A solution of *n*-butyllithium ($39.3\,cm^3$ of a 1.8 M solution in hexane, 70 mmol) was added to a solution of TMPH (10.0 g, 70 mmol) in diethylether ($199\,cm^3$) at −78°C. Once the solution reached 25°C, stirring was continued for 3 h. A cloudy yellow suspension was obtained which was added dropwise to a solution of $GaCl_2$ (12.46 g, 70 mmol) in toluene ($50\,cm^3$). Once the addition was completed, the mixture was stirred (15 h) at 60°C. Volatile materials were then removed under vacuum, resulting in a light orange residue. The solid was extracted with toluene ($100\,cm^3$) and the solution filtered and concentrated. Cooling (−20°C) gave 8.5 g of orange crystals of (**2**) suitable for X-ray diffraction; Yield 42%, mp 180–185°C. ^1H NMR (300.15 MHz, C_6D_6, 298K, TMS ext.): δ 1.22 (t, 6H, CH_2-CH_3); 1.35 (m, 12H, -CH_2 (ring)); 1.47 (s, 24H, O-CH_2-CH_3); 4.12 (b, 4H, O-CH_2); MS (CI, CH_4): *m/z* 580 (M^+); 565 (M^+-CH_3); 545 (M^+-Cl); 440 (M^+-TMP). Anal: calcd: C (45.49), H (7.98), N (4.82%). Found: C (43.92), H (8.25), N (5.09%).

X-ray crystal structure analyses of $NMe_2(\mu.NMe_2)GaCl]_2$ (1) *and* $[TMP(\mu\text{-}OEt)GaCl]_2$ (2)

Crystals of **1** and **2** were sealed in Lindemann capillaries under an atmosphere of dry argon. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer at 25°C using the $\theta/2\theta$ technique. Reflections were measured in the range $2<2\theta<50$. Of 2622 (**1**) and 2785 (**2**) independent reflections collected, 1720 (**1**) and 2601 (**2**), having $I>3\sigma(I)$ were used for the structure analyses. The intensities were corrected for Lorentz and polarization effects. No empirical absorption correction was needed for either compound.

Crystal Data

Compound 1: $C_8H_{24}N_4Cl_2Ga_2$, $M=386.65$, orthorhombic, space group $P2_12_12_1$, $a=8.428(4)$, $b=15.10(1)$, $c=13138(6)$ Å, $Z=4$, $Dc=1.20\,g\,cm^{-3}$, $F(000)=1099.85$,

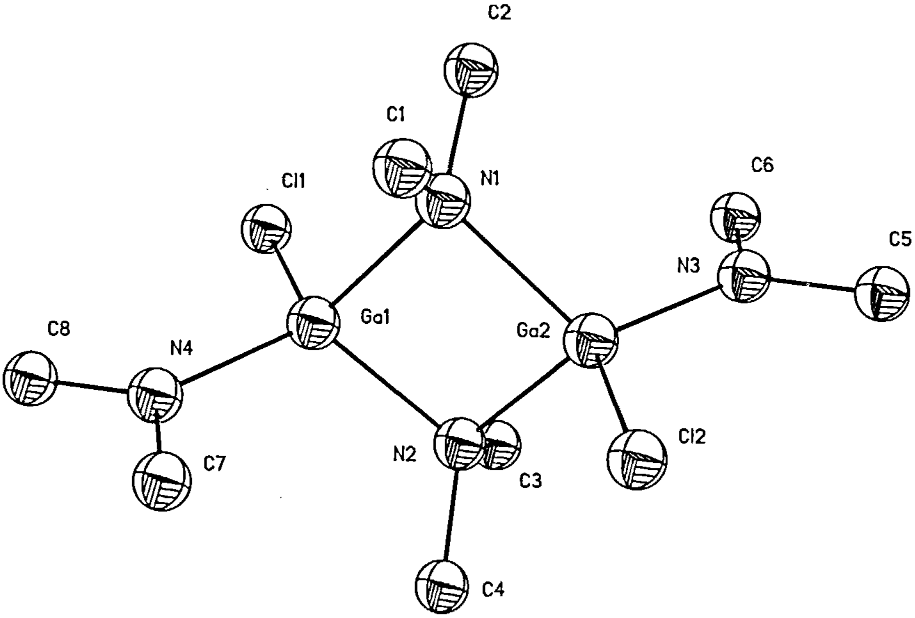

FIGURE 1 Structure of $[NMe_2(\mu\text{-}NMe_2)GaCl]_2$ (1) showing the atom numbering scheme.

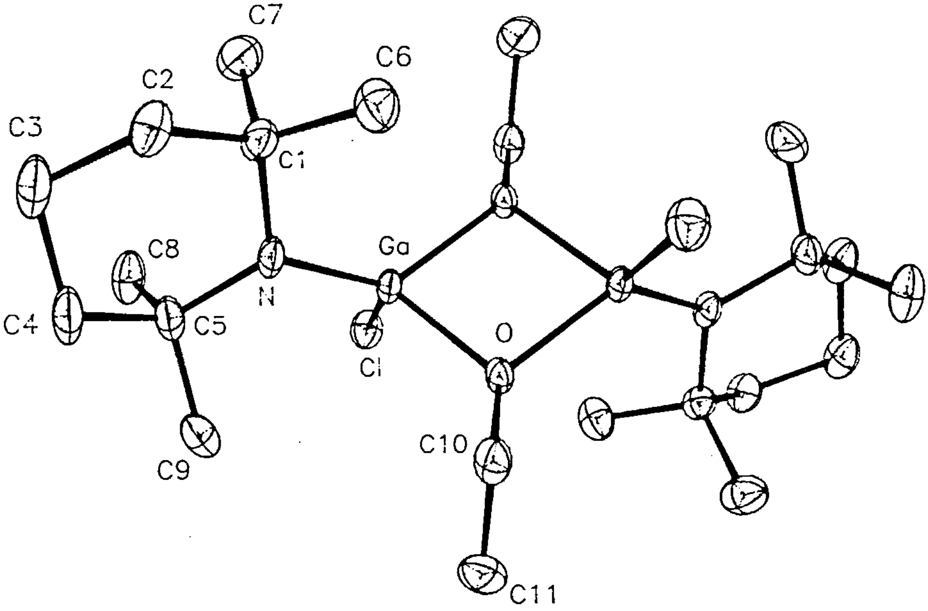

FIGURE 2 Structure of $[TMP(\mu\text{-}OEt)GaCl]_2$ (2) showing the atom numering scheme.

μ(MoKα) = 12.23 cm^{-1}; *compound* 2: $C_{22}H_{46}N_2O_2Cl_2Ga_2$, $M = 580$, monoclinic, space group $P2_1/n$, with $a = 8.542(1)$, $b = 12.457(1)$, $c = 12.959(1)$ Å, $\beta = 95.483(9)$, $Z = 2$, $Dc = 1.411$ g cm^{-3}, $F(000) = 608$, μ(MoKα) = 25.8 cm^{-1}.

All calculations were performed on a MICROVAX 3100 computer using the SHELX software package.[5] Both structures were solved by Patterson and Fourier methods. The hydrogen atoms were placed in their geometrically calculated positions

TABLE I
Atomic coordinates for $[NMe_2(\mu\text{-}NMe_2(GaCl]_2$ (1).

Atom	*x/a*	*y/b*	*z/c*
Ga(1)	0.9201	0.1193	0.9066
Ga(2)	0.8080	0.1434	0.7019
Cl(2)	0.9204	0.0523	0.5971
Cl(1)	0.8327	0.2016	1.0288
N(1)	0.9758	0.1964	0.7903
C(1)	1.1463	0.1806	0.7495
C(2)	0.9552	0.2931	0.8060
N(2)	0.7432	0.760	0.8236
C(3)	0.5753	0.1011	0.8628
C(4)	0.7343	−0.0232	0.8082
N(3)	0.6679	0.2200	0.6391
C(5)	0.6503	0.2194	0.5275
C(6)	0.5686	0.2838	0.6927
N(4)	1.0707	0.368	0.9533
C(7)	1.1436	−0.0234	0.8845
C(8)	1.1025	0.1319	1.0574

TABLE II
Atomic coordinates for $[TMP(\mu\text{-}OEt)GaCl]_2$ (2).

Atom	*x/a*	*y/b*	*z/c*
Ga	0.12847(9)	0.46361(6)	0.57607(5)
Cl	0.2661(2)	0.3434(2)	0.5025(2)
O	0.798(5)	0.5788(3)	0.4787(3)
N	0.1860(7)	0.5094(5)	0.7109(4)
C(1)	0.0674(9)	0.5010(6)	0.7878(5)
C(2)	0.118(1)	0.5690(7)	0.8839(6)
C(3)	0.285(1)	0.5485(7)	0.9275(6)
C(4)	0.392(1)	0.5711(7)	0.8431(6)
C(5)	0.3565(9)	0.5024(7)	0.7463(6)
C(6)	−0.086(1)	0.5493(7)	0.7404(6)
C(7)	0.35(1)	0.3846(7)	0.8193(6)
C(8)	0.417(1)	0.3873(7)	0.7709(7)
C(9)	0.4495(9)	0.5519(7)	0.6638(6)
C(10)	0.1325(9)	0.6872(6)	0.4918(6)
C(11)	0.264(1)	0.7115(7)	0.4275(7)

and included in the final structure factor calculations with fixed isotropic thermal parameters. The final *R* values for **1** and **2** are 0.066 and 0.054, respectively. Atomic coordinates for **1** and **2** are listed in Tables I and II, respectively. Full supplementary structural data are available from the authors on request.

RESULTS AND DISCUSSION

In the solid state, compounds **1** and **2** exist as nitrogen- and oxygen-bridged dimers, respectively, with the chlorides in both compounds in an *anti* configuration. Key bond distances and angles for **1** are given in Table III while those for **2** are in Table IV. The Ga_2E_2 (E = N,O) four-membered ring in **1** is close to square planar. In **1** the

TABLE III

Selected bond lengths (Å) and angles (degrees) for $[NMe_2(\mu\text{-}NMe_2)GaCl]_2$ (**1**).

Atoms	Distance (Å)	Atoms	Distance
Ga(1)-Ga(2)	2.873(3)	Ga(1)-Cl(1)	2.160(6)
Ga(1)-N(1)	1.98(2)	Ga(1)-N(2)	1.96(1)
Ga(1)-N(4)	1.88(2)	Ga(2)-Cl(2)	2.165(6)
Ga(2)-N(1)	2.00(1)	Ga(2)-N(2)	1.97(2)
Ga(2)-N(3)	1.85(2)	N(1)-C(1)	1.55(3)
N(1)-C(2)	1.49(3)	N(2)-C(3)	1.55(3)
N(2)-C(4)	1.51(2)	N(3)-C(5)	1.47(3)
N(3)-C(6)	1.46(3)	N(4)-C(7)	1.42(3)
N(4)-C(8)	1.40(3)		

Atoms	Angle (°)	Atoms	Angle
Ga(2)-Ga(1)-Cl(1)	120.7(3)	Ga(2)-Ga(1)-N(1)	44.0(4)
Cl(1)-Ga(1)-N(1)	108.5(5)	Ga(2)-Ga(1)-N(2)	43.3(4)
Cl(1)-Ga(1)-N(2)	110.3(5)	N(1)-Ga(1)-N(2)	87.0(6)
N(1)-Ga(1)-N(2)	87.0(2)	N(1)-Ga(1)-N(4)	127.7(7)
Cl(1)-Ga(1)-N(4)	111.6(7)	N(1)-Ga(1)-N(4)	118.8(8)
N(2)-Ga(1)-N(4)	118.3(7)	Ga(1)-Ga(2)-Cl(2)	111.8(2)
Ga(1)-Ga(2)-N(1)	43.4(5)	Cl(2)-Ga(2)-N(1)	108.3(5)
Ga(1)-Ga(2)-N(2)	42.9(4)	Cl(2)-Ga(2)-N(2)	108.0(5)
N(1)-Ga(2)-N(2)	86.1(6)	Ga(1)-Ga(2)-N(3)	135.1(6)
Cl(2)-Ga(2)-N(3)	113.2(6)	N(1)-Ga(2)-N(3)	117.5(7)
N(2)-Ga(2)-N(3)	120.6(7)	Ga(1)-N(1)-Ga(2)	92.6(6)
Ga(1)-N(1)-Ga(2)	92.6(2)	Ga(1)-N(1)-C(1)	113(1)
Ga(2)-N(1)-C(1)	113(1)	Ga(1)-N(1)-C(2)	116(2)
Ga(2)-N(1)-C(1)	113(1)	C(1)-N(1)-C(2)	108(2)
Ga(1)-N(2)-Ga(2)	93.9(6)	Ga(1)-N(2)-C(3)	115(1)
Ga(2)-N(2)-C(3)	113(1)	Ga(1)-N(2)-C(4)	116(1)
Ga(2)-N(2)-C(4)	115(1)	C(3)-N(2)-C(4)	104(2)
Ga(2)-N(3)-C(5)	120(2)	Ga(2)-N(3)-C(6)	124(2)
C(5)-N(3)-C(6)	115(2)	Ga(1)-N(4)-C(7)	120(2)
Ga(1)-N(4)-C(8)	119(2)	C(7)-N(4)-C(8)	120(3)

TABLE IV
Ga(2)-Ga(1)-Ga(1)Selected bond lengths (Å) and angles (degrees) for $[TMP(\mu\text{-}OEt)GaCl]_2$ (2).

Atoms	Distance (Å)	Atoms	Distance
Ga-Cl	2.178(2)	Ga-O	1.929(4)
Ga-O′	1.925(4)	Ga-N	1.859(5)
O-C(10)	1.429(8)	N-C(1)	1.491(9)
N-C(5)	1.488(9)	C(1)-C(2)	1.53(1)
C(1)-C(6)	1.52(1)	C(1)-C(7)	1.54(1)
C(2)-C(3)	1.51(1)	C(3)-C(4)	1.52(1)
C(4)-C(5)	1.53(1)	C(5)-C(8)	1.55(1)
C(5)-C(9)	1.52(1)	C(10)-C(11)	1.49(1)

Atoms	Angle (°)	Atoms	Angle
Cl-Ga-O	108.4(1)	Cl-Ga-O′	99.7(1)
O′-Ga-O	80.1(2)	Cl-Ga-N	121.1(2)
O-Ga-N	114.1(2)	O′-Ga-N	125.6(2)
Ga′-O-Ga	99.9(1)	Ga-O-C(10)	125.4(4)
Ga′-O-C(10)	124.9(4)	Ga-N-C(1)	118.1(5)
Ga-N-C(5)	115.8(5)	C(1)-N-C(5)	119.9(6)
N-C(1)-C(2)	110.2(6)	N-C(1)-C(6)	108.5(6)
C(2)-C(1)-C(6)	106.1(6)	N-C(1)-C(7)	113.1(6)
C(2)-C(1)-C(7)	110.5(6)	C(6)-C(1)-C(7)	108.2(7)
C(1)-C(2)-C(3)	113.4(7)	C(2)-C(3)-C(4)	108.2(6)
C(3)-C(4)-C(5)	113.6(7)	N-C(5)-C(4)	109.6(7)
N-C(5)-C(8)	114.5(7)	C(4)-C(5)-C(8)	108.3(7)
N-C(5)-C(9)	108.7(6)	C(4)-C(5)-C(9)	105.8(7)
C(8)-C(5)-C(9)	109.6(7)	O-C(10)-C(11)	111.7(6)

average Ga(1)-N-Ga(2) and N(1)-Ga-N(2) bond angles are 93.3(6) and 86.5(5)°, respectively. This compares to the same bond angles in the nitrogen-bridged dimer $[Me_2Ga(\mu\text{-}NH(t\text{-}Bu))]_2$[6] which are equivalent through symmetry (Ga-N-Ga′ 95.3(3)° and N-Ga-N′ 84.8(2)°). The average Ga-N bond distances in **1** are shorter (1.97(1) Å) than those found in other more sterically hindered dimers such as $[Me_2Ga(\mu\text{-}NH(t\text{-}Bu))]_2$ (Ga-N 2.011(1) Å) and $[t\text{-}Bu_2Ga(\mu\text{-}NHPh)]_2$[7] (Ga-N 2.065(3) Å).

Compound **2** possesses a crystallographic centre of symmetry which makes the Ga_2O_2 four-membered ring planar with Ga-O-Ga′ and O-Ga-O′ bond angles of 99.9(1) and 80.1(2), respectively. These values coincide closely with the same angles in $[\eta^1\text{-}C_5H_5)_2GaOEt]_2$ (100.5(2) and 79.5(2))[3] which also contains a crystallographically imposed centre of symmetry. The Ga-O bond distances follow this trend as well being nearly equivalent at 1.927(2) for **1** and 1.92(2) Å for the alkyl gallium ethoxide.

The slightly greater steric requirements of TMP compared to Me_2N can be seen in the Ga-Cl bond distances; for **1**, Ga-Cl(av) 2.163(2) Å; for **2**, Ga-Cl 2.178(2) Å. This effect is demonstrated most strongly in the N-Ga-Cl bond angles. In **1** this angle is 112.4(8)° (av) while in **2** the angle is 121.1(2)°. The terminal Ga-N bond distances are relatively unaffected, (Ga-N 1.87(2) Å for **1** and (Ga-N 1.859(5)) for **2**.

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REFERENCES

1. A.H. Cowley and R.A. Jones, *Angew. Chem. Int. Ed. Engl.*, **28**, 1208 (1989).
2. H. Noth and P. Konrad, *Z. Naturforsch.*, **30b**, 681 (1975).
3. A.H. Cowley, S.K. Mehrotra, J.L. Atwood and W.E. Hunter, *Organometallics*, 4, 1115 (1985).
4. For a discussion concerning the reactivity of gallium halides with diethylether, see O.T. Beachley, Jr., T.E. Getman, R.U. Kirss, R.B. Hallock, W.E. Hunter and J.L. Atwood, *Organometallics*, 4, 751 (1985).
5. G.M. Sheldrick, "SHELX—A System of Computer Programs for X-ray Structure Determination", (Cambridge, U.K., 1976).
6. D.A. Atwood, A.H. Cowley, R.A. Jones, S.G. Bott and J.L. Atwood, *J. Organomet. Chem.*, in press.
7. D.A. Atwood, R.A. jones, A.H. Cowley, S.G. Bott and J.L. Atwood, *Polyhedron*, **10**, 1897 (1991).