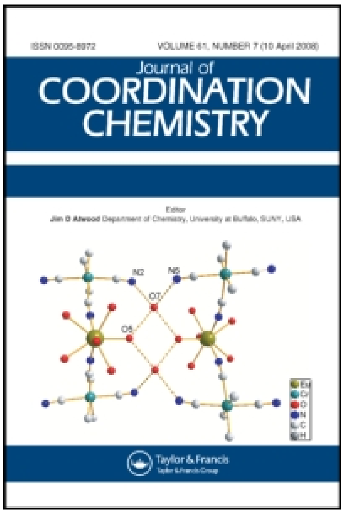

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF Me_3M (M = Al, Ga) OR Et_3In WITHBIS(DIMETHYLAMINO)-2-PROPANOL. X-RAY CRYSTAL STRUCTORE OF THE $[Me_2GaOCH(CH_2NMe2)2]2$ DIMER

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF Me_3M (M = Al, Ga) OR Et_3In WITH BIS(DIMETHYLAMINO)-2-PROPANOL. X-RAY CRYSTAL STRUCTURE OF THE $[Me_2GaOCH(CH_2NMe_2)_2]_2$ DIMER

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Reaction of R_3M with bis(dimethylamino)-2-propanol gave the dimeric compounds $[R_2MOCH(CH_2NMe_2)_2]_2$ (R = Me, M = Al, **1**; R = Me, M = Ga, **2**; R = Et, M = In, **3**). The resulting compounds have been characterized by elemental analyses, ^1H NMR and mass spectroscopy. The crystal structure of **2** has been determined by X-ray analysis. **2** contains a five-coordinate gallium center with a central four-membered Ga_2O_2 ring and a Ga–N dative bond. The geometry around the Ga atom can be described as a distorted trigonal bipyramid with a rather long Ga–N bond.

Keywords: Aluminum; gallium; indium; amino alkoxide; dimeric; X-ray analysis

INTRODUCTION

The MOCVD method has been employed for preparation of thin films of group III/V and II/VI semiconductors which are important in high-speed digital circuits, microwave devices and optoelectronics. Nevertheless, the conventional MOCVD method has great difficulty in maintaining the

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desired film stoichiometry when growing ternary and quaternary compounds.[1] It occurred to us that this problem might be overcome by use of single-source precursors of the heterometallic compounds which feature the desired stoichiometry of the group V and the two different group III elements. We endeavor to synthesize heteronuclear complexes by using amino alkoxide ligands with polyfunctional groups. The unusual structures and reactivity of alkylaluminum complexes containing dimethylamino-2-propanol have been reported recently.[2] The chemistry of organoaluminum complexes containing both amino and alcohol functionalities has received attention because the aluminum in these complexes has an uncommon five-coordinate geometry.[3–5] However, there have been few structurally characterized organogallium complexes in which the gallium center is five-coordinate. We report herein the structures and chemistry of group III alkyl complexes containing the bis(dimethylamino)-2-propanol ligand. The resulting compounds have been characterized by physical and spectroscopic techniques and compound **2** by X-ray crystallography. By comparison, the crystal structure of **2** has the general structure of other ligand systems possessing amino alkoxide groups. Moreover, **2** contains a second free amino group which might be further coordinated to another group III center such as aluminum or indium to afford heterobimetallic complexes.

EXPERIMENTAL

All experiments were performed using Schlenk techniques and a HE-493 Dry-Train Drybox under nitrogen. All solvents were carefully dried by distillation from sodium diphenyl ketone under nitrogen before use. ^{1}H NMR spectra were obtained with a Bruker AM500 spectrometer in C_6D_6 using $SiMe_4$ as an internal reference. Mass spectra were obtained using a ZAB-MS instrument. Microanalyses were performed on a 240C analyzer. Melting points (uncorrected) were obtained using a b-shaped tube with paraffin oil as the medium, and capillaries were flame-sealed under nitrogen. Trimethylaluminum, trimethylgallium and triethylindium were provided by the Special Gas Institute of Nanjing University. Bis(dimethylamino)-2-propanol was synthesized according to the literature method.[6]

Synthesis of $[Me_2AlOCH(CH_2NMe_2)_2]_2$ (1)

Me_3Al (1.94 mL, 20 mmol) in 5 mL THF was added slowly to a solution of bis(dimethylamino)-2-propanol (1.72 g, 20 mmol) in 10 mL THF accompanied by gas evolution. The reaction mixture was continuously stirred for 3 h at $T = 40°C$. The volume of the solution was slowly reduced *in vacuo* to leave a white crystalline solid. After recrystallization from toluene, colorless crystals were obtained. Yield: 90%. M.p. = 120–121°C. *Anal.* calcd. for $(C_9H_{23}N_2OAl)_2$ (%): C, 53.38; H, 11.36; N, 13.84. Found: C, 51.39; H, 9.04; N, 11.50. Mass spectra: $MeAlOCHCH_2NMe_2$ (128); $AlOCHCH_2NMe_2$ (114); Me_2Al (57); Me_2NCH_2CHO (88). ^1H NMR(C_6D_6): δ −0.87 (12H, s, $AlMe_2$); 2.41 (24H, s, NMe_2); 2.52 (8H, s, NCH_2).

Synthesis of $[Me_2GaOCH(CH_2NMe_2)_2]_2$ (2)

Compound **2** was synthesized in a similar manner to compound **1** using Me_3Ga (2.1 mL, 20 mmol) in 5 mL THF and a solution of bis(dimethylamino)-2-propanol (1.72 g, 20 mmol) in 10 mL THF. Compound **2** was obtained as a white crystalline solid. The solid was dissolved in THF and then cooled at −25°C for three days, whereupon colorless single crystals suitable for X-ray determination were obtained. Yield: 85%. M.p. = 90–91°C. *Anal.* calcd. for $(C_9H_{23}N_2OGa)_2$ (%): C, 44.07; H, 9.38; N, 11.42. Found: C, 42.39; H, 8.04; N, 10.50. Mass spectra: $Me_2GaOCHCH_2NMe_2$ (186), $GaOCHCH_2NMe_2$ (156), $GaMe_2$ (99), Me_2NCH_2CHO (88), GaMe (84). ^1H NMR(C_6D_6): δ −0.38 (12H, s, $GaMe_2$); 2.34 (24H, s, NMe_2); 2.46 (8H, s, NCH_2).

Synthesis of $[Et_2InOCH(CH_2NMe_2)_2]_2$ (3)

Compound **3** was synthesized in a similar manner to compound **1** using Et_3In (2.1 mL, 13.3 mmol) in 5 mL THF and a solution of bis(dimethylamino)-2-propanol (1.94 g, 13.3 mmol) in 10 mL THF. Compound **3** was obtained as a white crystalline solid. Yield: 78%. M.p. = 102–103°C. *Anal.* calcd. for $(C_{11}H_{27}N_2OIn)_2$ (%): C, 41.48; H, 8.48; N, 8.79. Found: C, 42.18; H, 7.97; N, 9.02. Mass spectra: Me_2NCH_2CHO (88); In (115). ^1H NMR(C_6D_6): δ 0.10 (8H, s, $InCH_2$); 1.12 (12H, m, $InCH_2CH_3$); 2.28 (24H, s, NMe_2); 2.52 (8H, s, NCH_2).

Determination of the Crystal Structure of 2

A single crystal of **2** was mounted in a Lindemann capillary and flame-sealed. The intensities were collected at 294 K on a Siemens P4 four-circle

TABLE I Crystal data and structure refinement for [Me_2Ga-$OCH(CH_2NMe_2)_2]_2$

Empirical formula	$C_{18}H_{46}Ga_2N_4O_2$
Fw	490.0
Temp, K	294
Radiation (wavelength, Å)	0.71073
Cryst system	Monoclinic
Space group	$P2_1/n$
a, Å	11.3740(15)
b, Å	9.4529(9)
c, Å	12.840(2)
α, deg	90.00
β, deg	108.457(10)
γ, deg	90.00
V, $Å^3$	1309.5(3)
D_{calcd}, g cm^{-3}	1.243
Z	2
Abs coeff, mm^{-1}	2.074
F(000)	520
Cryst dimens, mm	0.22 x 0.24 x 0.30
Cryst habit	Colorless prism
θ range for data coll, deg	2.03 to 25.0
No. of rflns coll	2563
Indepdt rflns	2149 ($R_{int} = 0.0543$)
Data/parameters	13.2 : 1
Goodness-of-fit on F^2	1.94
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0360 wR2 = 0.0468
R indices (all data)	R1 = 0.0498 wR2 = 0.0582
Extinction coefficient	0.0006(2)
D(*r*) and hole, $e/Å^{-3}$	0.51, −0.56

diffractometer with monochromated MoKα ($\lambda = 0.71073$ Å) radiation using $\omega/2\theta$ scan mode with a constant scan speed 5.00° min^{-1} in ω. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods. All the hydrogen atoms were assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms.

Crystal data, details of the intensity measurement and refinement data are given in Table I. All other data are included in the supplementary material.

RESULTS AND DISCUSSION

Synthesis of the Compounds

Reaction of R_3M with one equivalent of $Me_2NCH_2CH(OH)CH_2NMe_2$ in THF gave high yields of the compounds **1–3** (Scheme 1).

$$R_3M + Me_2NCH_2CH(OH)CH_2NMe_2 \xrightarrow{THF} [R_2MOCH(CH_2NMe_2)_2]_2$$

1 R = Me, M = Al; **2** R = Me, M = Ga; **3** R = Et, M = In

SCHEME 1

Compounds **1–3** have been isolated as colorless, transparent crystals. The complexes are both air- and moisture-sensitive, decomposing over a period of seconds in the solid state after exposure to air. They are very soluble in both aromatic hydrocarbons (i.e., benzene and toluene) and in donor solvents (i.e., tetrahydrofuran and diethyl ether). Compound **2** could be sublimed at 140°C/10^{-1} Torr. Compounds **1** and **3** were difficult to sublime.

X-ray Structure of 2

The structure of **2** has been determined by X-ray crystallography. The ORTEP diagram is shown in Figure 1. Selected bond lengths and angles are given in Table II.

The center of the Ga_2O_2 ring coincides with a crystallographic inversion center, so that only half of the atoms of the crystal are independent, the other half being symmetry related. The central Ga_2O_2 four-membered ring is planar with the ligands adopting a *trans* orientation. The geometry around the gallium center can be described as distorted trigonal bipyramidal, where both gallium methyl C atoms and the covalently bound O(1) atom of the ligand lie in the equatorial plane. The apical Ga(1)–O(1) distance [2.107(3) Å] is significantly longer than the equatorial Ga(1)–O(1a) distance [1.901(3) Å]. The Ga(1)–N(1a) bond distance is rather long and consequently weak as a result of the steric interactions. The Ga–O and Ga–N distances are similar to those found in analogous structures of five-coordinate gallium atoms.[2] The dihedral angle between the plane of the Ga_2O_2 ring and the mean plane of the five-membered GaOCCN chelate ring is 138°.

Although five-coordinate gallium coordination is not common for organogallium complexes, it has been reported previously. The first unusual trigonal–bipyramidal coordination was observed for $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$ which was prepared from reaction of $Ga(CH_3)_3$ with diaza-18-crown-6, $C_{12}H_{26}N_2O_4$.[7] In the complex $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$, the dimethylgallium unit resides within the cavity of the aza crown with the gallium atom bonding to two oxygen atoms and a nitrogen atom in addition to the two methyl carbon atoms. As the gallium atom, the

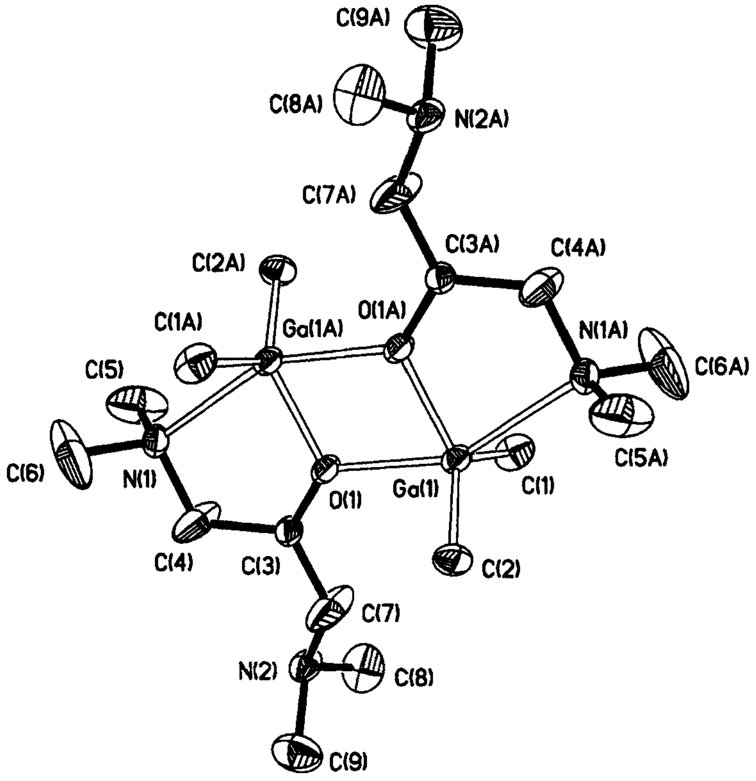

FIGURE 1 Molecular structure of $[Me_2GaOCH(CH_2NMe_2)_2]_2$ showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

TABLE II Selected bond lengths (Å) and angles (°) for $[Me_2GaOCH(CH_2NMe_2)_2]_2$ with estimated standard deviations in parentheses

Ga(1)-O(1)	2.107(3)	Ga(1)-C(1)	1.972(4)
Ga(1)-C(2)	1.962(3)	Ga(1)-O(1a)	1.901(3)
O(1)-Ga(1a)*	1.901(3)	Ga(1)-N(1a)	2.485(3)
O(1)-Ga(1)-C(1)	98.2(1)	O(1)-Ga(1)-C(2)	98.2(1)
C(1)-Ga(1)-C(2)	130.1(1)	O(1)-Ga(1)-O(1a)	75.3(1)
C(1)-Ga(1)-O(1a)	113.8(1)	C(2)-Ga(1)-O(1a)	115.9(1)
Ga(1)-O(1)-C(3)	131.4(2)	Ga(1)-O(1)-Ga(1a)	104.7(1)
C(3)-O(1)-Ga(1a)	123.6(2)	N(1a)-Ga(1)-O(1)	77.0(1)
N(1a)-Ga(1)-C(1)	94.1(1)	N(1a)-Ga(1)-C(2)	92.3(1)

*Symmetry transformation: a (1−*x*, −*y*, 1−*z*).

two carbon atoms, and the nitrogen atom constitute a basal plane while the two oxygen atoms of the crown are found to reside above and below the plane (O–Ga–O bond angle 157.2(2)°), the coordination of the core gallium atom may be described as distorted trigonal bipyramidal. The Ga–O bond distances in $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$ are 2.450(5) and 2.278(5) Å for Ga(3)–O(1) and Ga(3)–O(4), respectively, which can be considered among the longest reported in organogallium–oxygen compounds.[8] By comparison, the Ga(1)–O(1) distance [2.107(3) Å] and Ga(1)–O(1a) distance [1.901(3) Å] in compound **2** are exceeding short compared to those in $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$, whereas the Ga(1)–N(1a) bond distance [2.485(3) Å] in **2** is considerably longer than the Ga(3)–N(1) bond distance [2.024(5) Å] in the latter.

^{1}H NMR Spectra

In the ^{1}H NMR spectra of **1–3** the absence of the OH resonance of bifunctional amino alcohols, and the presence of a sharp upfield resonance for the MMe_2 moiety of Me_2MOR provide good evidence for O–M coordination in the compounds. The Me_2N signals of **2** (2.5 ppm) are shifted to lower field in comparison with the signal of the corresponding aminoalcohol (2.1 ppm), which indicates a dative Ga–N interaction.

Mass Spectra

The fragments $[R_2MOCHCH_2NMe_2]^+$ (M = Al, Ga, In), $[R_2M]^+$ were found in compounds **1–3**. None of these complexes showed a parent molecular ion.

Acknowledgements

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