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Synthesis of phenols and naphthol with *n*-morpholinomethyl pendants and their dimethylgallium complexes: crystal structure of dimethylgallium-[4-nitro-2-(*n*-morpholinomethyl)-1-phenoxide]

Jing-zhi Tian [a], Jin-qi Zhang [a,*], Xi Shen [a], Hui-xian Zou [b]

[a] *Department of Chemistry, Nanjing University, Nanjing 210093, PR China*
[b] *Department of Environmental Science and Engineering, State Key Laboratory of Pollution and Resource Reuse, Nanjing University, Nanjing 210093, PR China*

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Abstract

The one-pot Mannich reaction was used to synthesize 2-(*n*-morpholinomethyl)-1-phenol (**1a**), 4-methyl-2-(*n*-morpholinomethyl)-1-phenol (**1b**), 4-chloro-2-(*n*-morpholinomethyl)-1-phenol (**1c**), 4-nitro-2-(*n*-morpholinomethyl)-1-phenol (**1d**), and 1-(*n*-morpholinomethyl)-naphthol (**1e**). The dimethylgallium complexes of these compounds have been prepared, and compound **2d** has been determined by X-ray crystallography. The complex **2d** crystallized with one unit having two identical molecules which have intermolecular contacts between the two phenyls caused by face to face π–π stacking. The Ga–O bond distances are noticeably shorter than in the other dimethylgallium phenoxides reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: One-pot Mannich reaction; Phenol; Naphthol; Dimethylgallium complexes; Crystal structure

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1. Introduction

Aminomethyl phenols or aminomethyl naphthols have been known for their uses as pigments [1], insecticides [2], and as intermediates in the pharmaceutical industry [3]. In recent years, great attention has been paid to aminomethyl phenols owing to their uses as excellent mimics for the active site of enzymes. For example, mononuclear iron complexes with monoaminomethylated phenols as ligands have proven to be remarkable mimics for the active site of iron–tyrosinate proteins [4]. However, these studies are largely limited to mononuclear or binuclear transition metal complexes [5]. Their complexes with trialkyl Group III metal derivatives have not been reported. It is also noted that organometallic compounds of aluminum, gallium and indium have been drawing increasing interest because of a wide rang of possible uses: Group III/V semi-conductor materials as precursor compounds for MOCVD, Group III/VI compounds as precursors for ceramic materials [6], and gallium compounds have found utility in the diagnosis of diseases [7]. In view of their potential applications in the diagnosis of diseases, we have initiated a study of trimethylgallium complexes with *n*-morpholinomethylphenols or *n*-morpholinomethylnaphthols.

In the synthesis of the ligands, we used the one-pot Mannich reaction. Ki-Wan Chi and coworkers reported a one-pot method using Mannich reaction to synthesis double-armed ionizable crown ethers [8]; we applied it to morpholine and it has proven to be a convenient and efficient method, with high yields.

Several studies concerning compounds containing two or more nitrogen atoms [9], nitrogen and oxygen atoms [10], nitrogen and sulfur atoms [11] have been reported. In the molecules of *n*-morpholinomethyl phenols, there are not only two donor atoms—nitrogen

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* Corresponding author.
E-mail address: zhangjq@nju.edu.cn (J. Zhang)

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Table 1
Crystal data and structure refinement for compound **2d**

Empirical formula	$C_{13}H_{19}N_2O_4Ga$
Formula weight	337.02
Crystal color, habit	Yellow, prismatic
Crystal system	Monoclinic
Lattice parameters	
a (Å)	8.796(4)
b (Å)	11.045(5)
c (Å)	30.814(7)
β (°)	90.71(3)
V (Å^3)	2993.5601
Space group	$P2_1/c$ (no. 14)
Z	8
$D_{calc.}$ (g cm^{-3})	1.495
$F(000)$	1392.00
μ(Mo–K$_\alpha$) (cm^{-1})	18.52
Radiation (Å)	Mo–K$_\alpha$ ($\lambda = 0.71070$)
$2\theta_{max}$ (°)	55.1
Total reflections measured	4448
Reflections observed [$I > 3\sigma(I)$]	2731
No. of variables	362
Reflection/parameter ratio	7.54
Residuals R, R_w	0.069, 0.100
Goodness-of-fit	1.25
Maximum peak in final difference map	0.66 e Å^{-3}
Minimum peak in final difference map	−0.64 e Å^{-3}

and oxygen, but also an ionizable OH functional group. In fact, when trimethylgallium reacts with *n*-morpholinomethyl phenols at a ratio of 1:1 in our experiment, only the hydroxyl group takes part in the reaction to give elimination products with a four-coordinate gallium atom. One of these novel complexes, dimethylgallium-[4-nitro-2-(*n*-morpholinomethyl)-1-phenoxide] (**2d**), has been subjected to single-crystal X-ray studies. All complexes have been characterized by ^{1}H-NMR, MS, IR and elemental analyses.

Table 2
Selected bond lengths (Å) and bond angles (°) for compound **2d**

Ga_1–O_3	1.903(6)	Ga_1–N_1	2.092(7)
Ga_1–C_1	1.99(1)	Ga_1–C_2	1.95(1)
Ga_2–O_7	1.895(6)	Ga_2–N_3	2.112(7)
Ga_2–C_{14}	1.96(1)	Ga_2–C_{15}	1.96(1)
O_1–N_2	1.22(1)	O_2–N_2	1.25(1)
O_3–C_{13}	1.31(1)	O_4–C_4	1.40(1)
O_4–C_5	1.43(1)	O_7–C_{26}	1.32(1)
O_8–C_{17}	1.42(1)	O_8–C_{18}	1.43(1)
N_1–C_3	1.49(1)	N_1–C_6	1.50(1)
N_1–C_7	1.49(1)	N_2–C_{10}	1.45(1)
C_7–C_8	1.50(1)	C_8–C_9	1.37(1)
C_8–C_{13}	1.43(1)	C_9–C_{10}	1.38(1)
O_3–Ga_1–N_1	95.6(3)	O_3–Ga_1–C_1	111.0(4)
O_3–Ga_1–C_2	103.7(4)	N_1–Ga_1–C_1	104.9(4)
N_1–Ga_1–C_2	114.5(5)	C_1–Ga_1–C_2	123.8(6)
O_7–Ga_2–N_3	96.1(3)	O_7–Ga_2–C_{14}	110.5(4)
O_7–Ga_2–C_{15}	105.8(4)	N_3–Ga_2–C_{14}	105.3(4)
N_3–Ga_2–C_{15}	113.8(5)	C_{14}–Ga_2–C_{15}	122.3(6)
Ga_1–O_3–C_{13}	127.5(6)	Ga_2–O_7–C_{26}	126.6(6)
Ga_1–N_1–C_7	103.6(5)	Ga_2–N_3–C_{20}	104.2(5)
O_5–N_4–O_6	123.0(9)	O_1–N_2–O_2	124.0(9)
N_1–C_7–C_8	115.0(7)	C_7–C_8–C_{13}	118.9(8)
O_3–C_{13}–C_8	122.1(8)	C_8–C_{13}–C_{12}	117.9(8)

2. Experimental

2.1. General procedures

All manipulations of trimethylgallium were carried out under a nitrogen atmosphere in a glove box. Solvents were carefully dried by distillation from sodium and benzophenone under nitrogen prior to use. ^{1}H-NMR spectra were recorded on a Jeol PMX-60SI spectrometer in $CDCl_3$ using $SiMe_4$ as an internal reference. Mass spectra were obtained on a VG ZAB MS instrument. Microanalyses (C, H, N) were performed on a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded on a Shimadzu IR 408 instrument in KBr pellets. Melting points of dimethylgallium complexes were determined in a glass tube. Melting points of ligands were determined on a Yanaco microscopic melting point apparatus and were uncorrected. Trimethylgallium was provided by the National 863 Programme Advanced Material MO Precursors R&D Center of China.

2.2. Synthesis of ligands

2.2.1. General

To a solution of morpholine (3.5 ml, 40 mmol) and paraformaldehyde (1.8 g, 60 mmol) in dry benzene (80 ml) under a N_2 atmosphere was added the corresponding substituted phenol or naphthol (40 mmol) at room temperature (r.t.). The mixture was then heated and kept at reflux for 6 h. The solvent was removed in vacuum, and the crude product was recrystallized in petroleum ether:ethyl acetate to give aci form or lamellar crystals.

2.2.2. 2-(n-Morpholinomethyl)-1-phenol (1a)

Yield: 7.2 g (93%), m.p. (dec.) 82–84°C. MS (% intensity, *m*/*z*): 192.9 (82.10), 161.9 (15.06), 145.9 (29.85), 133.9 (17.12), 106.9 (100.00), 100.00 (7.59), 87.0 (18.79), 85.9 (61.96), 76.9 (30.38), 57.5 (30.69).

2.2.3. 4-Methyl-2-(n-morpholinomethyl)-1-phenol (1b)

Yield: 7.9 g (95%), m.p. (dec.) 48–51°C. MS (% intensity, *m*/*z*): 206.9 (90.85), 159.9 (28.37), 120.9 (73.99), 100.0 (7.31), 91.0 (34.33), 87.0 (30.82), 85.9 (100.00), 57.5 (42.21), 56.6 (31.40).

2.2.4. 4-Chloro-2-(n-morpholinomethyl)-1-phenol (1c)

Yield: 8.5 g (93%), m.p. (dec.) 66–68°C. MS (% intensity, *m*/*z*): 228.8 (32.71), 227.9 (15.16), 226.9

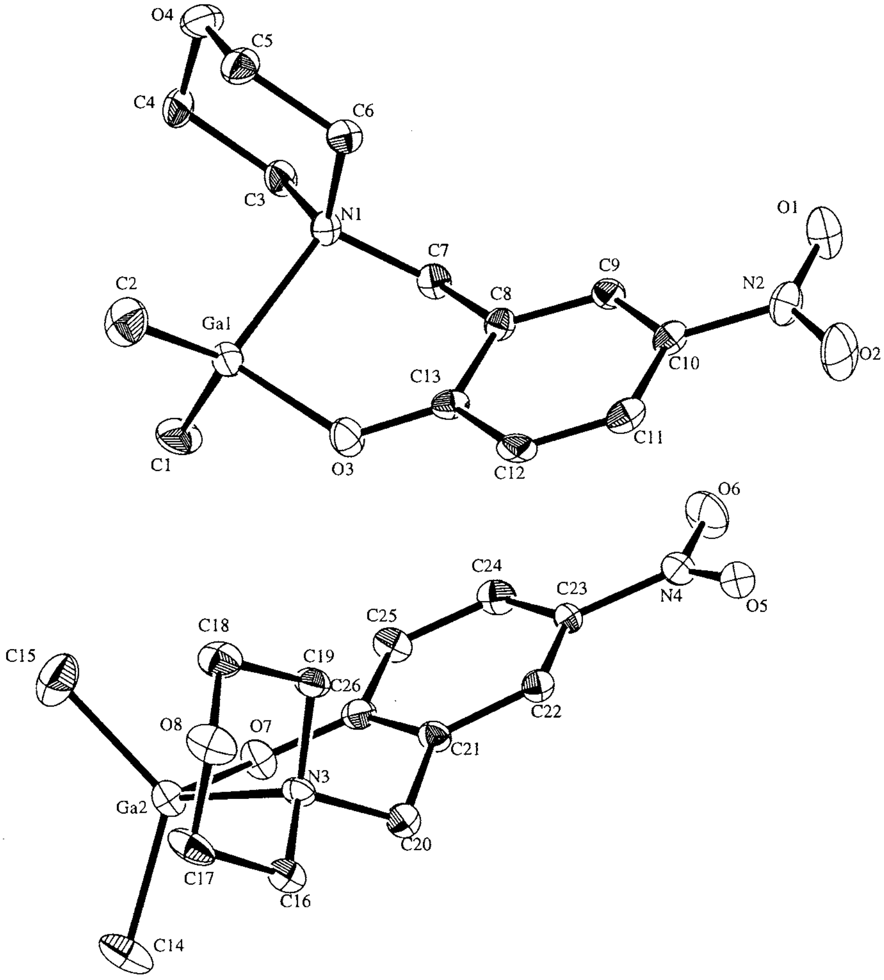

Fig. 1. Molecular structure of compound **2d** showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

(99.75), 179.9 (38.50), 167.9 (23.62), 142.9 (23.45), 140.9 (72.24), 139.9 (20.85), 100.0 (21.78), 87.0 (86.45), 86.0 (100.00), 76.9 (53.92), 57.5 (60.50).

2.2.5. *4-Nitro-2-(n-morpholinomethyl)-1-phenol (**1d**)*

Yield: 8.4 g (88%), m.p. (dec.) 96–97°C. MS (% intensity, *m*/*z*): 237.9 (84.17), 236.9 (10.34), 191.0 (47.24), 178.9 (14.99), 151.9 (100.00), 106.0 (20.76), 100.0 (17.40), 86.0 (63.64), 77.9 (15.30), 76.9 (10.69), 57.5 (35.32).

2.2.6. *1-(n-Morpholinomethyl)-2-naphthol (**1e**)*

Yield: 9.0 g (93%), m.p. (dec.) 109–110°C (Ref. [16]. 119–121°C). MS (% intensity, *m*/*z*): 242.8 (4.57), 155.9 (59.44), 127.9 (100.00), 126.9 (21.94), 101.9 (14.69), 86.9 (26.44), 85.9 (19.48), 76.9 (10.21), 57.5 (38.58).

2.3. *Synthesis of dimethylgallium complexes*

2.3.1. *Dimethylgallium-[2-(n-morpholinomethyl)-1-phenoxide] (**2a**)*

To a solution of **1a** (0.58 g, 3 mmol) in 10 ml benzene, 0.33 ml (3 mmol) $GaMe_3$ was added dropwise at r.t. The mixture was then heated to reflux for 2 h, the solvent was removed by vacuum distillation. The pale yellow oil residue was recrystallized in petroleum ether to give colorless crystals (0.81 g, 92%), m.p. (dec.) 94–96°C. Found: C, 53.36; H, 6.85; N, 4.92 (Anal. Calc. for $C_{13}H_{20}GaNO_2$: C, 53.47; H, 6.91; N, 4.80%). ^1H-NMR (δ): 7.43–7.57 (m, 1H); 6.67–7.27 (m, 3H); 3.67–4.23 (m, 6H); 2.40–3.37 (b, 4H); -0.23 (s, 6H). IR (cm^{-1}): 3050, 1600, 1485, 1460, 1355, 1260, 1200, 1120, 1075, 875, 810, 765, 590, 540. MS (% intensity, *m*/*z*): 292.8 (7.44), 290.9 (11.31), 277.9 (66.71), 275.9 (100.00), 219.9 (2.27), 217.9 (3.54), 192.9 (41.57), 190.8 (48.11), 100.9 (29.98), 98.9 (47.90), 91.0 (2.55), 77.0 (9.91).

2.3.2. *Dimethylgallium-[4-methyl-2-(n-morpholinomethyl)-1-phenoxide] (**2b**)*

Compound **2b** was prepared analogously to **2a**. After the solvent was removed in vacuo, a pale yellow oil was left. The residue was recrystallized in petroleum to give colorless crystals (0.82 g, 89%), m.p. (dec.) 88–90°C. Found: C, 55.12; H, 7.48; N, 4.57 (Anal. Calc. for $C_{14}H_{22}GaNO_2$: C, 54.94; H, 7.25; N, 4.58%). ^1H-NMR (δ): 7.33–7.40 (m, 1H); 6.73–7.27 (m, 2H); 3.57–4.07

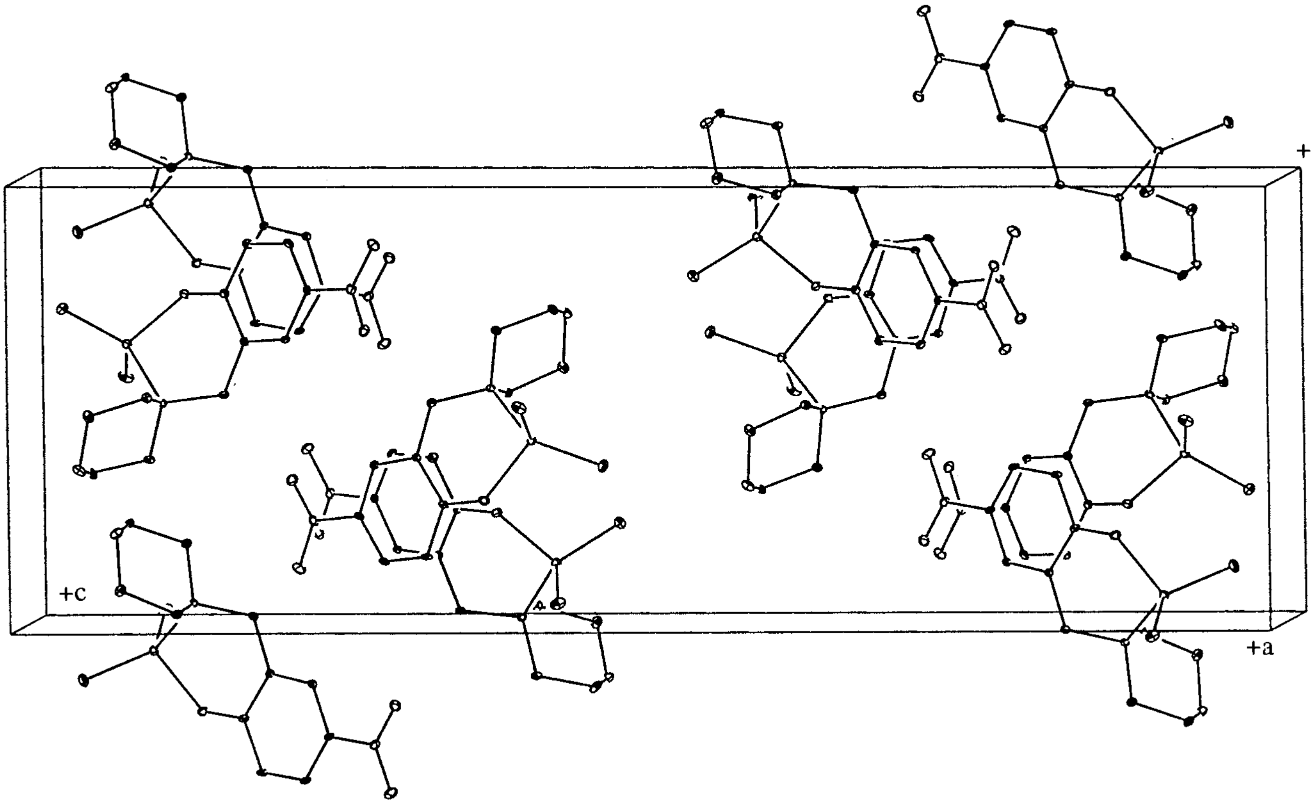

Fig. 2. The unit cell packing diagram of compound **2d**.

(b, 6H); 2.40–3.33 (b, 4H); −0.23 (s, 6H). IR (cm^{-1}): 3020, 1600, 1490, 1445, 1340, 1260, 1110, 1065, 990, 910, 875, 770, 575, 535. MS (% intensity, *m*/*z*): 306.8 (11.97), 304.8 (17.19), 291.8 (68.36), 289.8 (100.00), 277.7 (6.50), 275.7 (10.21), 233.9 (2.09), 231.8 (3.26), 100.9 (35.13), 98.9 (53.26), 91.0 (11.18), 77.0 (5.94).

2.3.3. Dimethylgalium-[4-chloro-2-(n-morpholinomethyl)-1-phenoxide] (2c)

Compound **2c** was prepared analogously to **2a**. Removal of the solvent resulted in a white powder which was recrystallized in benzene:petroleum ether to give colorless transparent crystals (0.92 g, 94%), m.p. (dec.) 84–86°C. Found: C, 47.92; H, 5.77; N, 4.37 (Anal. Calc. for $C_{13}H_{19}ClGaNO_2$: C, 47.82; H, 5.87; N, 4.29%). ^{1}H-NMR (δ): 6.91–7.15 (m, 2H); 6.65–6.81 (m, 1H); 3.41–3.93 (b, 6H); 2.25–3.25 (b, 4H); −0.25 (s, 6H). IR (cm^{-1}): 3020, 1600, 1480, 1350, 1290, 1105, 1075, 890, 835, 740, 560, 540. MS (% intensity, *m*/*z*): 326.9 (12.51), 324.9 (12.18), 311.9 (97.12), 309.9 (100.00), 253.9 (3.57), 251.9 (3.57), 226.9 (36.59), 224.9 (25.02), 100.9 (43.43), 99.0 (67.29), 91.0 (3.53), 77.0 (16.99).

2.3.4. Dimethylgallium-[4-nitro-2-(n-morpholinomethyl)-1-phenoxide] (2d)

Compound **2d** was prepared analogously to **2a**. The yellow powder was recrystallized in benzene to give pale yellow transparent crystals (0.96 g, 95%), m.p. (dec.) 186–188°C. Found: C, 46.32; H, 5.70; N, 8.38 (Anal. Calc. for $C_{13}H_{19}GaN_2O_4$: C, 46.33; H, 5.69; N, 8.31%). ^{1}H-NMR(δ): 7.96–8.26 (m, 2H); 6.73–6.86 (m, 1H); 3.63–4.36 (b, 6H); 2.40–3.53 (b, 4H); −0.19 (s, 6H). IR (cm^{-1}): 3020, 1600, 1570, 1480, 1320, 1250, 1120, 1070, 980, 910, 865, 760, 545, 520. MS (% intensity, *m*/*z*): 337.7 (2.26), 335.7 (2.92), 322.7 (69.20), 320.7 (100.00), 264.7 (2.51), 262.7 (3.97), 237.8 (16.58), 235.8 (17.22), 100.9 (33.02), 98.9 (50.43), 91.0 (1.40), 77.0 (3.99).

2.3.5. Dimethylgallium-[1-(n-morpholinomethyl)-2-naphthoxide] (2e)

Compound **2e** was also prepared analogously to **2a**. Removal of the solvent resulted in a white powder which was recrystallized in benzene:petroleum ether to

Table 3
Distances of C atoms on one phenyl ring to another (Å)[a]

C_{21}–Face 1	3.479	C_{22}–Face 1	3.403
C_{23}–Face 1	3.551	C_{24}–Face 1	3.724
C_{25}–Face 1	3.786	C_{26}–Face 1	3.634
C_8–Face 2	3.657	C_9–Face 2	3.569
C_{10}–Face 2	3.392	C_{11}–Face 2	3.273
C_{12}–Face 2	3.367	C_{13}–Face 2	3.551

[a] Face 1: $C_8C_9C_{10}C_{11}C_{12}C_{13}$; Face 2: $C_{21}C_{22}C_{23}C_{24}C_{25}C_{26}$.

give colorless transparent crystals (0.96 g, 94%), m.p. (dec.) 194–196°C. Found: C, 59.64; H, 6.64; N, 4.16 (Anal. Calc. for $C_{17}H_{22}GaNO_2$: C, 59.69; H, 6.49; N, 4.09%). ^{1}H-NMR(δ): 7.67–8.03 (m, 3H); 7.13–7.60 (m, 3H); 3.57–4.33 (b, 6H); 2.53–3.50 (b, 4H); -0.23 (s, 6H). IR (cm^{-1}): 3050, 1620, 1590, 1500, 1460, 1370, 1280, 1170, 1100, 1010, 965, 890, 830, 750, 680, 580, 545, 515. MS (% intensity, *m*/*z*): 342.9 (20.96), 340.9 (29.82), 327.8 (62.22), 325.8 (90.60), 299.9 (1.95), 297.8 (3.19), 242.9 (29.09), 240.9 (14.84), 179.9 (6.76), 178.00 (10.30), 155.9 (14.60), 153.9 (1.06), 100.9 (64.32), 98.9 (100.00), 77.0 (2.76).

2.4. *X-ray structure determination of dimethylgallium-[4-nitro-2-(n-morpholi-nomethyl)-1-phenoxide] (**2d**)*

Single crystals of **2d** were grown from benzene solution at r.t. for 12 h. A single crystal suitable for X-ray determination was mounted in a thin-walled capillary tube in a glove box, plugged with grease, removed from the glove box, then flame sealed. Data were collected at 291 K on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromate Mo–K$_\alpha$ ($\lambda = 0.7170$ Å) radiation to a maximum 2θ value of 55.1°. Readout was performed in the 0.100 mm pixel mode. The data were corrected for Lorentz and Polarization effects during data reduction. A correction for secondary extinction was applied (coefficient = 1.25940e07). A total of 4448 reflections were collected. The structure was solved by direct methods and expanded using Fourier techniques. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2731 observed reflections [$I > 3.00\sigma(I)$] and 362 variable parameters and converged with unweighted and weighted agreement factor of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.069$, $R_w = \{\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w F_o^2\}^{1/2} = 0.100$. The standard deviation of an observation of unit weight was 1.25. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.66 and -0.64 e Å^{-3}, respectively. Crystal data and details on refinement are presented in Table 1. Selected bond lengths and bond angles without hydrogen atoms are shown in Table 2. Additional data are available from the authors.

3. Results and discussion

3.1. *Synthesis and characterization*

3.1.1. *Ligands*

The yields are high in the syntheses of the Mannich bases (**1a**–**1e**). Effects of substitutes on the yields are small. Even compound **1d**, with a strong electron-withdrawing substitute, the yield is 88%. Reaction of 2-naphthol with paraformaldehyde and morpholine in dry benzene only gave a 1-substituted product, this is due to the relatively high reactivity of the α-H in the *ortho*-position of the hydroxyl group.

3.1.2. *Complexes*

Trimethylgallium reacted with ligands **1a**–**1e** in a 1:1 ratio to give only elimination complexes. These complexes are less air-sensitive than free $GaMe_3$. Only after being reposed in air for several hours do they begin to decompose slowly. In the mass spectra, these complexes all show parent molecular ion peak $[M]^+$, indicating that the molecules are stable. All the complexes have $[M-15]^+$, $[M-17]^+$, $[M-73]^+$, $[M-100]^+$ and $[100.9]^+$ fragments, and isotopic peaks indicate that these fragments all include Ga. This suggests that these complexes all fragment in the same way.

In the ^{1}H-NMR spectrum, there is a single peak of six protons in the region of -0.25 to -0.19 ppm, which is the absorption of the six protons on the two methyl groups connecting to Ga. Aromatic protons resonate in the region 6.65–8.25 ppm. Ten protons on the five methylenes are divided into two groups. One group of six protons (3.41–4.36 ppm) includes $-CH_2-O-CH_2-$ and $Ar-CH_2-N<$ in low field, another group in high field (2.25–3.53 ppm) belongs to the four protons of $-CH_2-\underline{CH_2}-N<$. In compound **2b**, the chemical shift of protons of the methyl linking to AR is 2.30 ppm. All complexes have a moderate absorption near 530 cm^{-1} in IR spectra, which is the Ga–N stretching vibration frequency [12].

3.2. *X-ray crystal structure of dimethylgallium-[4-nitro-2-(n-morpholinomethyl)-1-phenoxide] (**2d**)*

The structure of compound **2d** was determined by X-ray crystallography. The complex crystallized in the monoclinic space group $P2_1/c$ with two chemically identical, crystallographically independent, and conformationally only slightly different molecules in the asymmetric unit. The molecular structure and atom-numbering scheme of the two molecules in one unit is shown in Fig. 1. The unit cell packing diagram is shown in Fig. 2. The complex crystallized in such a way that one unit has two identical molecules. It can be seen from Fig. 2 that there are some intermolecular contacts. The two phenyl rings overlap with each other, with a dihedral angle of 7.71°. The distances between the two phenyl rings from one end to the other vary from 3.273 to 3.786 Å. Since there is no H-bonding and van der Waals interactions between the two molecules, we conclude that these are π–π stacking interactions [13], with a typical phenyl face to face π–π arrangement.

Usually, the reaction of alcohols or phenols with trimethylgallium results in a dimeric product with a five-coordinate gallium center containing a planar Ga_2O_2 ring [14]. In our experiment, we only get monomers, each with a four-coordinate gallium center. This is due to the phenyl π–π stacking interactions and the relatively more bulky ligands than those previously reported [14].

The coordinate spheres around the four-coordinate gallium atoms with Ga_1 linking to N_1, O_3, C_1, C_2 and Ga_2 linking to N_3, O_7, C_{14}, C_{15} are nearly tetrahedral. However, there are some distortions in the bond angles. The angle of $O_3–Ga_1–N_1$ reduces to 95.6°, much less than the ideal value of 109.5°. This is caused by the strain in the ring $Ga_1N_1C_7C_8C_{13}O_3$ (Face 1) (Table 3). The angle of $C_1–Ga_1–C_2$ increases to 123.8°, this is because that methyl group is bigger than the O_3 atom. The situation for Ga_2 is the same as that of Ga_1.

The four atoms $C_7C_8C_{13}O_3$ are nearly planar in the seven-numbered ring $Ga_1N_1C_7C_8C_{13}O_3$, whereas $Ga_1N_1C_7$ have some distortions to make a boat-configuration. The six-membered ring $O_4C_5C_4N_1C_3C_4$ is in a chair-configuration.

It is interesting to note that the Ga–O bond distances are 1.903 and 1.895 Å for $Ga_1–O_3$ and $Ga_2–O_7$, respectively. These Ga–O bond distances in the title compound are much shorter than in other dimethylgallium phenoxides reported. They are similar to the Ga–O bond distances in the compound $CH_3Ga(CH_3COO)_2$ [15]. This indicates that there is a strong interaction between the Ga and O atoms.

The Ga–N bond distances are 2.092 and 2.112 Å for $Ga_1–N_1$ and $Ga_2–N_3$, respectively, similar to those in other four-coordinate Ga–N bond distances reported [14c].

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