

# Aluminum, gallium and copper complexes of 2,2-dimethyl-1,3-propanediamine

Stephen J. Obrey<sup>a</sup>, Simon G. Bott<sup>b</sup>, Andrew R. Barron<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, TX 77005, USA

<sup>b</sup> Department of Chemistry, University of Houston, Houston, TX 77204, USA

Received 29 May 2001; accepted 30 July 2001

Dedicated to François Mathey for his achievements in main group chemistry

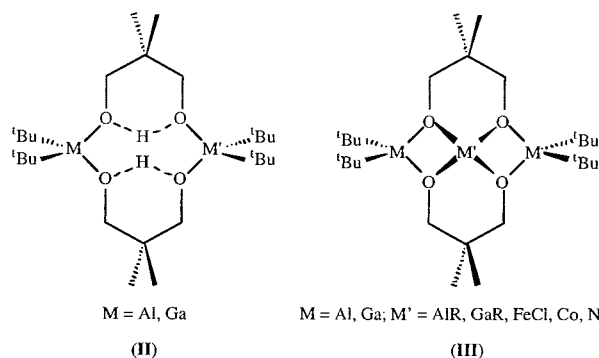
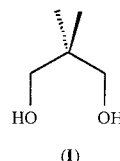
## Abstract

Reaction of  $M(\text{tBu})_3$  ( $M = \text{Al}, \text{Ga}$ ) with 2,2-dimethyl-1,3-propanediamine ( $\text{dmpa-H}_4$ ) yields the thermally stable Lewis acid–base complexes  $(\text{tBu})_3M(\text{dmpa-H}_4)$ ,  $M = \text{Al}$  (**1**) and  $\text{Ga}$  (**2**), respectively. The reaction of **2** with  $\text{Ga}(\text{tBu})_3$  yields the formation of  $[(\text{tBu})_3\text{Ga}]_2(\text{dmpa-H}_4)$  (**3**). In contrast, reaction of  $\text{dmpa-H}_4$  with  $\text{AlMe}_3$  yields the tri-aluminum compounds  $[\text{Al}_3\text{Me}_3(\text{dmpa-H}_2)_2]$  (**4**). Reaction of  $\text{dmpa-H}_4$  with  $\text{CuCl}_2$  in  $\text{MeOH-THF}$  yields the neutral complex,  $[\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2]$  (**5**), while the reaction in the presence of  $\text{NaBPh}_4$  and  $\text{MeCN}$  yields the ionic complex  $[\text{Cu}(\text{dmpa})_2(\text{MeCN})_2][\text{BPh}_4]_2$  (**6**). Compound **6** may also be formed directly from compound **5**. The molecular structures of compounds **2–6** have been determined by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Aluminum complexes; Copper complexes; Gallium complexes; Lewis acid–base complexes; X-ray crystallography

## 1. Introduction

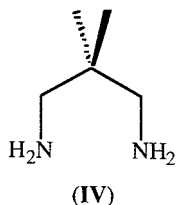
We have recently reported that the reaction of  $M(\text{tBu})_3$  ( $M = \text{Al}, \text{Ga}$ ) with 2,2-dimethyl-1,3-propanediol ( $\text{neol-H}_2$ , **I**) yields  $[\text{M}_2(\text{tBu})_4(\text{neol-H}_2)]$  (**II**) [1]. These compounds may be considered bifunctional (two OH groups) tetradentate (4O) ligands (i.e. **III**), as highlighted by their reactivity with Group 13 hydrides and alkyls [1], as well as transition metal complexes [2].



\* Corresponding author. Tel.: +1-713-348-5610; fax: +1-713-348-5619; [url:www.rice.edu/barron](http://www.rice.edu/barron).

E-mail address: [arb@rice.edu](mailto:arb@rice.edu) (A.R. Barron).

In order to extend this chemistry to bifunctional (two NH groups) tetradentate (4N) ligands we have investigated the reactivity of 2,2-dimethyl-1,3-propanediamine (dmpa-H<sub>4</sub>, **IV**) with aluminum and gallium alkyls, as well as directly with copper dichloride.



## 2. Results and discussion

The reaction of M(<sup>t</sup>Bu)<sub>3</sub> (M = Al, Ga) with H<sub>2</sub>NCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (dmpa-H<sub>4</sub>, **IV**) yields the Lewis acid–base adducts (<sup>t</sup>Bu)<sub>3</sub>Al(dmpa-H<sub>4</sub>) (**1**) and (<sup>t</sup>Bu)<sub>3</sub>Ga(dmpa-H<sub>4</sub>) (**2**), respectively. Compounds **1** and **2** have been characterized spectroscopically and by X-ray crystallography. Furthermore, as was observed for (<sup>t</sup>Bu)<sub>3</sub>Al[NH(Me)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>] and (<sup>t</sup>Bu)<sub>3</sub>Al[NH(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>], compounds **1** and **2** are stable with respect to alkane elimination in solution up to 110 °C for extended periods of time (2 days) [3].

The molecular structure of (<sup>t</sup>Bu)<sub>3</sub>Ga(dmpa-H<sub>4</sub>) (**2**) is shown in Fig. 1; selected bond lengths and angles are given in Table 1. The diamine ligands adopt a configuration to allow hydrogen bonding between the coordinated amine's hydrogen atom and the other NH<sub>2</sub> residue. The diamine exhibits a 'slinky' disorder [4] in which N(1) and C(2) are positioned on opposite sides of the Al(1)⋯C(3) vector. Thus, the ligand makes a Z

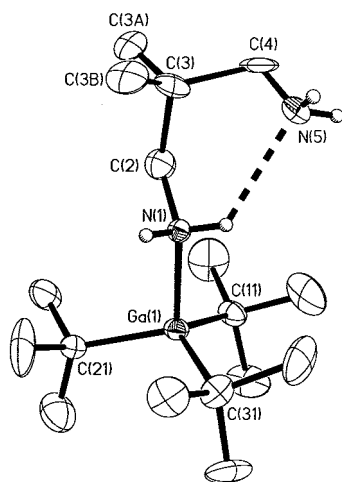


Fig. 1. The molecular structure of (<sup>t</sup>Bu)<sub>3</sub>Ga(dmpa-H<sub>4</sub>) (**2**). Thermal ellipsoids are shown at the 15% level and hydrogen atoms attached to carbon are omitted for clarity.

Table 1  
Selected bond lengths (Å) and bond angles (°) for (<sup>t</sup>Bu)<sub>3</sub>Ga(dmpa-H<sub>4</sub>) (**2**)

Ga(1)–N(1)	2.16(1)	Ga(1)–C(11)	2.062(8)
Ga(1)–C(21)	2.03(2)	Ga(1)–C(31)	2.08(2)
N(1)–Ga(1)–C(11)	111.0(4)	N(1)–Ga(1)–C(21)	107.1(5)
N(1)–Ga(1)–C(31)	87.9(6)	C(11)–Ga(1)–C(21)	109.7(8)
C(11)–Ga(1)–C(31)	122.4(9)	C(21)–Ga(1)–C(31)	115.5(4)

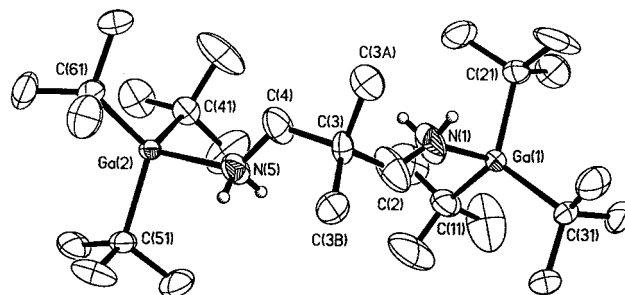


Fig. 2. The molecular structure of [(<sup>t</sup>Bu)<sub>3</sub>Ga]<sub>2</sub>(dmpa-H<sub>4</sub>) (**3**). Thermal ellipsoids are shown at the 20% level and hydrogen atoms attached to carbon are omitted for clarity.

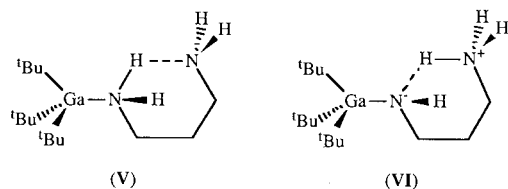
Table 2  
Selected bond lengths (Å) and bond angles (°) in [(<sup>t</sup>Bu)<sub>3</sub>Ga]<sub>2</sub>(dmpa-H<sub>4</sub>) (**3**)

Ga(1)–N(1)	2.109(6)	Ga(1)–C(11)	2.070(8)
Ga(1)–C(21)	2.023(6)	Ga(1)–C(31)	2.042(5)
Ga(2)–N(5)	2.166(5)	Ga(2)–C(41)	2.026(6)
Ga(2)–C(51)	2.034(5)	Ga(2)–C(61)	2.048(6)
N(1)–Ga(1)–C(11)	104.3(4)	N(1)–Ga(1)–C(21)	97.1(3)
N(1)–Ga(1)–C(31)	102.6(3)	C(11)–Ga(1)–C(21)	116.1(3)
C(11)–Ga(1)–C(31)	117.0(3)	C(21)–Ga(1)–C(31)	115.6(3)
N(5)–Ga(2)–C(41)	102.9(2)	N(5)–Ga(2)–C(51)	96.7(2)
N(5)–Ga(2)–C(61)	103.3(2)	C(41)–Ga(2)–C(51)	116.1(3)
C(41)–Ga(2)–C(61)	117.6(3)	C(51)–Ga(2)–C(61)	115.7(3)

shape between Ga(1) and C(3). Despite this disorder, the Ga–N bond lengths [2.16(1) and 2.10(1) Å] are similar to those observed previously for amines complexed to gallium [5,6]. As is observed for (<sup>t</sup>Bu)<sub>3</sub>Al[NH(Me)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>] and (<sup>t</sup>Bu)<sub>3</sub>Al[NH(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>], the amine substituents in compound **2** are staggered about the Ga(1)–N(1) bond [C(11)–Ga(1)–N(1)–C(2) = 51.1°] with respect to the gallium substituents, see Fig. 1.

The size of the Ga(1)–N(1) interaction in compound **2**, when compared to the Al–N interaction of that in (<sup>t</sup>Bu)<sub>3</sub>Al[NH(Me)CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>] and (<sup>t</sup>Bu)<sub>3</sub>Al[NH(Me)CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>] [3], indicates the retention of the primary amine/primary amine form (**V**) rather than the Zwitter ionic amide<sup>−</sup>/ammonium<sup>+</sup> form **VI**. The crystal structure of (<sup>t</sup>Bu)<sub>3</sub>Al(dmpa-H<sub>4</sub>) (**1**) is isomorphous to compound **2**, however, the solution of the single crystal X-ray structure exhibits severe disorder

precluding satisfactory structural solution, see Section 3.



When compounds **1** and **2** are reacted with excess  $M(t\text{-Bu})_3$  no reaction is seen at room temperature. Upon refluxing in hexane, compound **2** yields the di-gallium complex  $[(t\text{-Bu})_3\text{Ga}]_2(\text{dmpa-H}_4)$  (**3**). In contrast, compound **1** shows no reaction under similar conditions. This implies a stronger intramolecular  $\text{N} \cdots \text{N}$  inter-

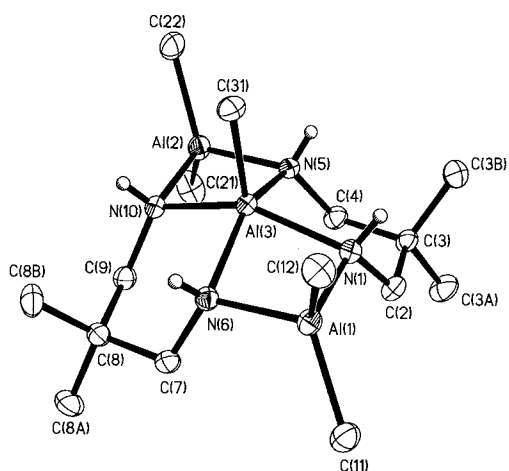


Fig. 3. The molecular structure of  $[\text{Al}_3\text{Me}_5(\text{dmpa-H}_2)_2]$  (**4**). Thermal ellipsoids are shown at the 20% level and hydrogen atoms attached to carbon are omitted for clarity. Hydrogen atoms on nitrogen are in idealized positions.

Table 3  
Selected bond lengths (Å) and bond angles (°) in  $[\text{Al}_3\text{Me}_5(\text{dmpa-H}_2)_2]$  (**4**)

Al(1)–N(1)	1.921(3)	Al(1)–N(6)	1.925(3)
Al(1)–C(11)	1.954(3)	Al(1)–C(12)	1.949(4)
Al(2)–N(5)	1.921(3)	Al(2)–N(10)	1.922(3)
Al(2)–C(21)	1.940(5)	Al(2)–C(22)	1.958(4)
Al(3)–N(1)	2.031(3)	Al(3)–N(5)	2.004(3)
Al(3)–N(6)	2.020(3)	Al(3)–N(10)	2.020(3)
Al(3)–C(31)	1.964(3)		
N(1)–Al(1)–N(6)	86.5(1)	N(1)–Al(1)–C(12)	111.5(2)
N(6)–Al(1)–C(12)	110.5(2)	N(1)–Al(1)–C(11)	113.0(1)
N(6)–Al(1)–C(11)	113.6(2)	C(12)–Al(1)–C(11)	117.6(2)
N(5)–Al(2)–N(10)	86.1(1)	N(5)–Al(2)–C(21)	114.2(2)
N(10)–Al(2)–C(21)	113.3(2)	N(5)–Al(2)–C(22)	111.6(2)
N(10)–Al(2)–C(22)	111.3(2)	C(21)–Al(2)–C(22)	116.6(2)
C(31)–Al(3)–N(5)	106.3(1)	C(31)–Al(3)–N(6)	105.3(2)
N(5)–Al(3)–N(6)	148.4(1)	C(31)–Al(3)–N(10)	103.8(1)
N(5)–Al(3)–N(10)	81.3(1)	N(6)–Al(3)–N(10)	90.7(1)
C(31)–Al(3)–N(1)	105.2(2)	N(5)–Al(3)–N(1)	90.9(1)
N(6)–Al(3)–N(1)	81.2(1)	N(10)–Al(3)–N(1)	150.9(1)

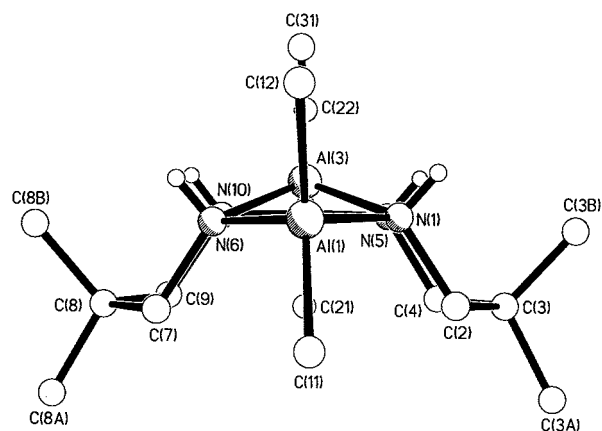


Fig. 4. The structure of  $[\text{Al}_3\text{Me}_5(\text{dmpa-H}_2)_2]$  (**4**) viewed along the  $\text{Al}(1) \cdots \text{Al}(2)$  axis showing the chair conformations of the six-membered  $\text{Al} \cdots \text{N} \cdots \text{C} \cdots \text{C} \cdots \text{N}$  cycles.

action for the aluminum complex as compared to gallium and hence the greater activation (Lewis acidity) of the former [7].

The molecular structure of  $[(t\text{-Bu})_3\text{Ga}]_2(\text{dmpa-H}_4)$  (**3**) is shown in Fig. 2; selected bond lengths and angles are given in Table 2. All key bond lengths and angles are within the ranges previously reported [5,6]. The gallium and nitrogen substituents adopt a staggered *anti* conformation.

Unlike the reaction of  $M(t\text{-Bu})_3$  with *neol-H}\_2, we could not isolate a di-metallic compound  $[\text{M}_2(t\text{-Bu})_4(\text{dmpa-H}_3)_2]$  (cf. **II**) for either aluminum or gallium *tert*-butyl derivatives. Based upon the assumption that the steric bulk of the *tert*-butyl groups may be responsible, we investigated the reaction with sterically less demanding alkyls. In this regard, the reaction of  $\text{dmpa-H}_4$  with  $\text{AlMe}_3$  (16 h at 110 °C) yields the tri-aluminum compound  $[\text{Al}_3\text{Me}_5(\text{dmpa-H}_2)_2]$  (**4**) in modest yield (ca. 25%). The major product appears to be an insoluble (polymeric) precipitate. Attempts to isolate the di-aluminum derivative,  $[\text{Al}_2\text{Me}_4(\text{dmpa-H}_3)_2]$ , through the use of excess  $\text{dmpa-H}_4$  were unsuccessful.*

The molecular structure of  $[\text{Al}_3\text{Me}_5(\text{dmpa-H}_2)_2]$  (**4**) is shown in Fig. 3; selected bond lengths and angles are given in Table 3. Compound **4** is structurally related to its *neol* analogs [8] and consists of a tetra-cyclic structure formed from two four-membered and two six-membered rings. The bond lengths and angles are within the ranges observed for related compounds [9–11]. The central aluminum atom adopts a square based pyramidal structure, where four nitrogen atoms occupy the basal site. The central metal atom in compound **4** is displaced out from the  $\text{N}_4$  plane (0.53 Å). Furthermore, as was observed for the *neol* derivatives [1], the quaternary carbons of the *dmpa-H* rings in compound **4** are displaced from the planar arrangement of the remaining atoms of the six-membered  $\text{Al} \cdots \text{N} \cdots \text{C} \cdots \text{C} \cdots \text{N}$  cycles, with the methyl groups adopting axial and equatorial

positions. Both rings adopt a chair conformation, giving the overall structure a bowl geometry, see Fig. 4.

Since we were unable to prepare the bi-metallic compound (cf. **II**) in order to subsequently employ as a ligand to a transition metal (i.e. Eq. (1)), we investigated the use of a transition metal as a template, i.e. Eq. (2). Similar metal template-assisted ring closure reactions have previously been successfully employed [12–14]. Our previous results [12] have shown that the copper(II) complex is the most readily formed of the first row transition metal derivatives.

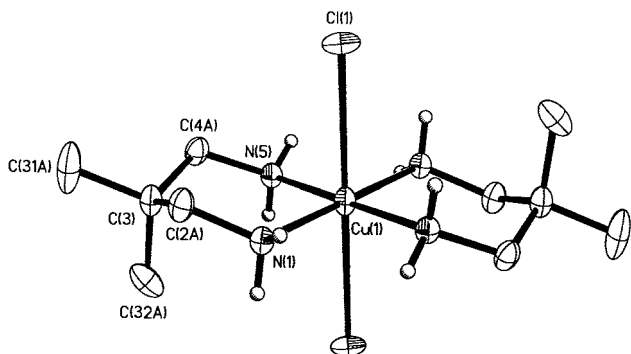
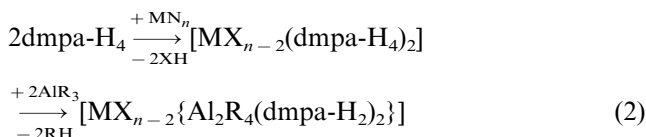
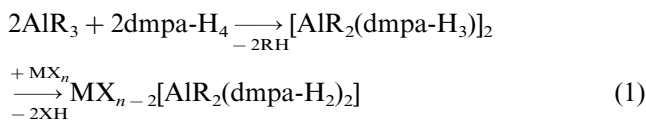


Fig. 5. The molecular structure of  $[\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2]$  (**5**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms attached to carbon are omitted for clarity. Hydrogen atoms on nitrogen are in idealized positions.

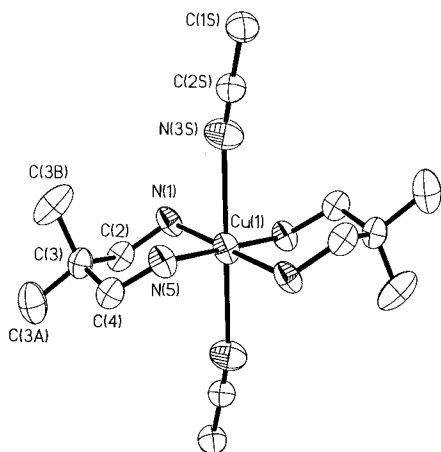


Fig. 6. Structure of cation  $[\text{Cu}(\text{dmpa-H}_4)_2(\text{MeCN})_2]^{2+}$  (**6**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms bound to carbon are omitted for clarity. Hydrogen atoms on nitrogen are in idealized positions.

Table 4

Selected bond lengths (Å) and bond angles (°) for  $\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2$  (**5**) and  $[\text{Cu}(\text{dmpa})_2(\text{MeCN})_2]^{2+}$  (**6**)

	$\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2$ ( <b>5</b> )	$[\text{Cu}(\text{dmpa})_2(\text{MeCN})_2]^{2+}$ ( <b>6</b> )
Cu(1)–N(1)	2.015(2)	1.989(4)
Cu(1)–N(5)	2.021(2)	2.005(4)
Cu(1)–X	2.848(3) <sup>a</sup>	2.708(4) <sup>b</sup>
N(1)–Cu(1)–N(5)	92.79(9)	89.3(2)
N(1)–Cu(1)–N(1')	180 <sup>c</sup>	180 <sup>c</sup>
N(1)–Cu(1)–N(5')	87.21(9)	90.7(2)
N(5)–Cu(1)–N(5')	180 <sup>c</sup>	180 <sup>c</sup>
N(1)–Cu(1)–X	92.3(9) <sup>a</sup>	84.7(3) <sup>b</sup>
N(5)–Cu(1)–X	92.2(3) <sup>a</sup>	83.8(3) <sup>b</sup>
X–Cu(1)–X'	180 <sup>a,c</sup>	180 <sup>b,c</sup>

<sup>a</sup> X = Cl(1).

<sup>b</sup> X = N(3S).

<sup>c</sup> Values constrained by symmetry.

Reaction of two molar equivalents of  $\text{dmpa-H}_4$  with  $\text{CuCl}_2$  yields the bright purple *bis*-diamine complex  $[\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2]$  (**5**). The molecular structure was determined by X-ray crystallography, see below. As expected for octahedral Cu(II), the magnetic susceptibility is consistent with a  $d^9$  ( $s = 1/2$ ) configuration [15]. The UV–vis spectrum shows a band at 648 nm which is similar to other Cu(II) amine complexes [16].

Attempts to deprotonate compound **5** via reaction with  $\text{M}(\text{tBu})_3$  ( $\text{M} = \text{Al}, \text{Ga}$ ) were unsuccessful. However, the chloride ligands may be removed by the addition of  $\text{NaBPh}_4$  in MeCN, leading to the formation of the ionic complex  $[\text{Cu}(\text{dmpa-H}_4)_2(\text{MeCN})_2][\text{BPh}_4]_2$  (**6**). Compound **6** may also be formed from the direct reaction of  $\text{dmpa-H}_4$  with  $\text{CuCl}_2$  in the presence of  $\text{NaBPh}_4$ . If the reaction is performed in a MeCN– $\text{H}_2\text{O}$  (50:50) mixture, crystals suitable for X-ray diffraction are obtained. Complex **6** has a  $d^9$  ( $s = 1/2$ ) configuration, and the UV–vis spectrum shows a similar UV–vis spectral band (654 nm) to that observed for compound **5**. Attempts to use compound **6** as a reagent with  $\text{M}(\text{tBu})_3$  ( $\text{M} = \text{Al}, \text{Ga}$ ) were unsuccessful.

The structures of  $[\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2]$  (**5**) and the cation  $[\text{Cu}(\text{dmpa-H}_4)_2(\text{MeCN})_2]^{2+}$  (**6**) are shown in Figs. 5 and 6, respectively; selected bond lengths and angles are given in Table 4. In both complexes, the copper adopts a highly distorted octahedral structure, where the four  $\text{dmpa-H}_4$  nitrogen atoms occupy the equatorial sites. The equatorial Cu–N bond lengths associated with  $\text{dmpa-H}_4$  ligands [2.015(2)–2.021(2) Å (**5**) and 1.980(4)–2.005(4) Å (**6**)] are within the ranges expected [17,18]. The axial Cu–N bond lengths in compound **6** are significantly longer [2.708(4) Å] due to the large Jahn–Teller distortion for  $d^9$  octahedral coordination [19]. The Cu–Cl bond lengths in compound **5** [2.848(2) Å] are also suitably elongated from the expected range (2.2–2.3 Å), but comparable to other

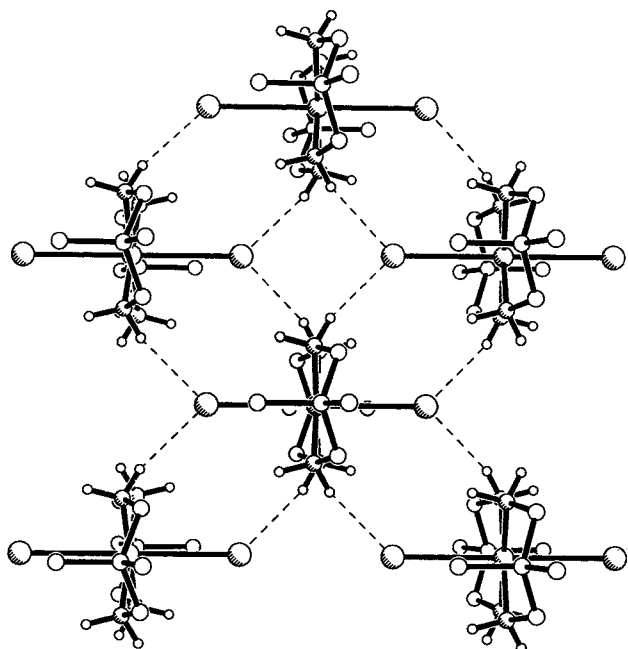


Fig. 7. Structure of the hydrogen bonded sheet of  $[\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2]$  (5). Hydrogen atoms attached to carbon are omitted for clarity.

Jahn–Teller distorted Cu–Cl distances [e.g. 2.64(2)–2.734(4) Å] [20]. The copper atoms in compounds **5** and **6** are essentially co-planar with the  $\text{N}_4$  plane. The

quaternary carbons of the  $\text{dmpa-H}_4$  rings are displaced from a planar arrangement such that both rings adopt a chair conformation. The two rings are *anti* with respect to each other.

Consideration of the crystal packing for compound **5** shows that inter-molecular N–H $\cdots$ Cl hydrogen bonding ( $\text{Cl}\cdots\text{H} = 2.62 - 2.63$  Å) is present within the crystallographic *a/b* plane, resulting in a sheet-like (*secondary* level [21]) structure, see Fig. 7. The sheets are co-planar, but contain no inter-sheet contacts (*tertiary* level), see Fig. 8. The geometry about the chlorides is close to tetrahedral. There exists a 1:1 disorder of the quaternary carbons and associated methyl groups, which is carried over to the inter-molecular hydrogen bonding network. Since inversion of the Cu–N–C–C–N cycle results in the interconversion of the axial/equatorial N–H groups and hence the orientation of the hydrogen bonding network, disorder occurs. Halide hydrogen bonding has been previously proposed to account for stabilization of solid state conformations in transition metal complexes [22,23].

The crystal packing diagram for compound **6** shows the  $\text{BPh}_4$  anions are situated on either side of the equator of the  $[\text{Cu}(\text{dmpa-H}_4)_2(\text{MeCN})_2]^{2+}$  cation. However, no close cation $\cdots$ anion interactions are present.

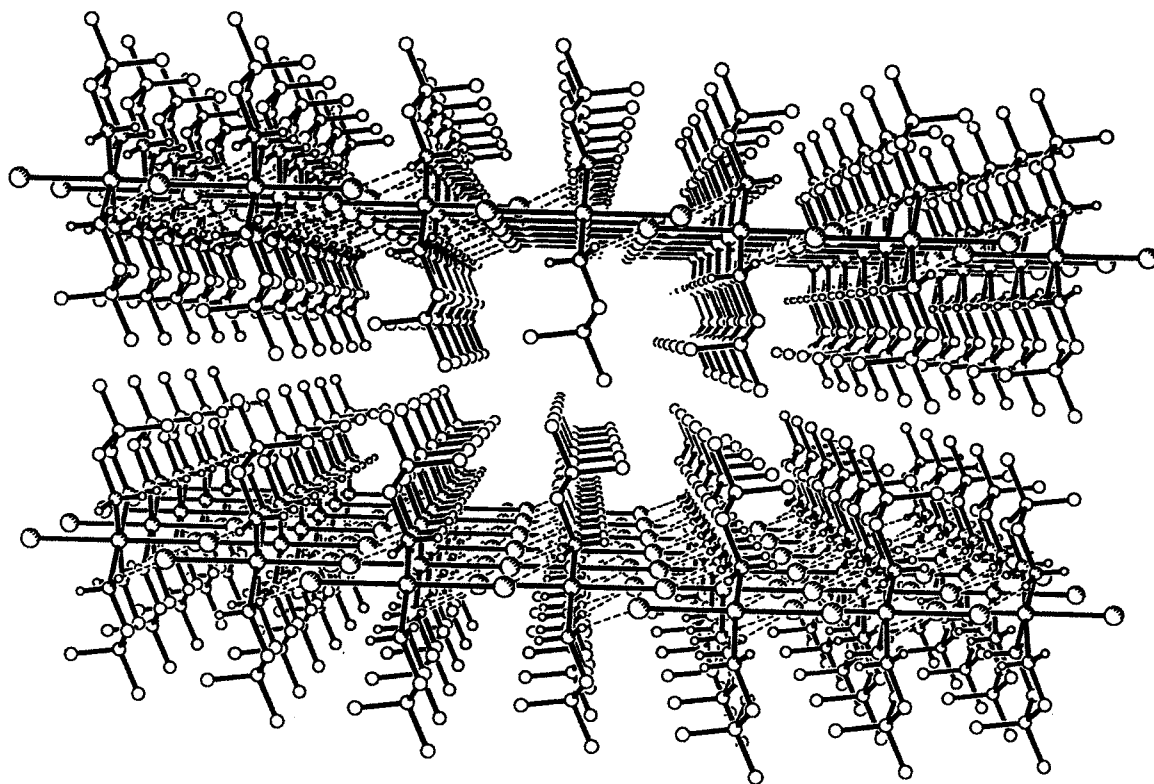


Fig. 8. View along the crystallographic *a*-axis of  $\text{Cu}(\text{dmpa-H}_4)_2\text{Cl}_2$  (5) illustrating the series of layers created by the hydrogen bonded sheets. Hydrogen atoms attached to carbon are omitted for clarity.

### 3. Experimental

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam of 70 eV for EIMS. Evans magnetic susceptibility balance [24] and by use of the Evans solution NMR method [25]. NMR spectra were obtained on a Bruker AM-250, and Avance 200 and 400 MHz spectrometers using (unless otherwise stated)  $C_6D_6$  solutions. Chemical shifts are reported relative to internal solvent resonances ( $^1H$  and  $^{13}C$ ) and external  $[Al(H_2O)_6]^{3+}$  ( $^{27}Al$ ). Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY, USA. IR spectra ( $4000$ – $400\text{ cm}^{-1}$ ) were obtained using a Nicolet 760 FTIR infrared spectrometer. IR samples were prepared as Nujol Mulls between KBr plates unless otherwise stated.  $AlMe_3$  was generously provided by Albemarle Corp. All other chemicals were obtained from Aldrich and used without further purification (unless otherwise noted).

#### 3.1. $(^tBu)_3Al(dmpa-H_4)$ (**1**)

To a solution of  $Al(^tBu)_3$  (1.00 g, 5.05 mmol) in pentane (100 mL) was added  $dmpa-H_4$  (0.504 g, 4.94 mmol). The reaction mixture was stirred for 16 h after which it was concentrated and cooled to  $-33\text{ }^\circ\text{C}$ . The resulting clear colorless crystalline material was isolated by filtration. Yield: 88%. M.p.:  $104$ – $106\text{ }^\circ\text{C}$ . EIMS;  $m/z$  (%): 243 ( $[M^+ - ^tBu]$ , 100).  $^1H$ -NMR:  $\delta$  4.07 (bs, 2H,  $NH_2CH_2$ ), 2.64 (m, 2H,  $Al-NH_2CH_2$ ), 1.97 [t, 2H,  $J(H-H) = 6.6\text{ Hz}$ ,  $CH_2NH_2Al$ ], 1.21 [s, 27H,  $C(CH_3)_3$ ], 0.35 [s, 6H,  $C(CH_3)_2$ ], 0.24 [s, 6H,  $Al-NH_2$ ].  $^{13}C$ -NMR:  $\delta$  54.3 ( $CH_2NH_2$ ), 53.1 ( $Al-NH_2CH_2$ ), 32.8 [ $C(CH_3)_3$ ], 22.6 [ $C(CH_3)_2$ ].  $^{27}Al$ -NMR:  $\delta$  130 ( $W_{1/2} = 2600\text{ Hz}$ ).

#### 3.2. $(^tBu)_3Ga(dmpa-H_4)$ (**2**)

Prepared in a similar manner to compound **1**, but using  $Ga(^tBu)_3$  (1.00 g, 4.15 mmol) and  $dmpa-H_4$  (0.425 g, 4.08 mmol). Yield: 80%. M.p.:  $74$ – $75\text{ }^\circ\text{C}$ . EIMS;  $m/z$  (%): 285 ( $[M^+ - ^tBu]$ , 100).  $^1H$ -NMR:  $\delta$  3.57 (br s, 2H,  $NH_2$ ), 2.77 (br s, 2H,  $NH_2CH_2$ ), 2.00 (br s, 2H,  $Ga-NH_2CH_2$ ), 1.31 [s, 27H,  $C(CH_3)_3$ ], 0.39 [s, 6H,  $C(CH_3)_2$ ], 0.22 (br s, 2H,  $Ga-NH_2$ ).  $^{13}C$ -NMR:  $\delta$  55.1 ( $NH_2CH_2$ ), 52.9 ( $Ga-NH_2CH_2$ ), 33.2 [ $C(CH_3)_3$ ], 22.8 [ $C(CH_3)_2$ ].

#### 3.3. $[(^tBu)_3Ga]_2(dmpa-H_4)$ (**3**)

To a solution of  $(^tBu)_3Ga(dmpa-H_4)$  (0.10 g, 0.29 mmol) in hexane (100 mL) was added  $Ga(^tBu)_3$  (70 mg, 0.29 mmol). The reaction mixture was heated to reflux for 1 h, then concentrated and cooled to  $-33\text{ }^\circ\text{C}$ . The resulting clear colorless crystalline material was isolated by filtration. Yield: 52%. M.p.:  $45$ – $46\text{ }^\circ\text{C}$ .  $^1H$ -NMR:  $\delta$

2.39 [t, 4H,  $J(H-H) = 8.4\text{ Hz}$ ,  $NH_2CH_2$ ], 1.85 [t, 4H,  $J(H-H) = 8.4\text{ Hz}$ ,  $NH_2CH_2$ ], 1.23 [s, 54H,  $C(CH_3)_3$ ], 0.11 [s, 6H,  $C(CH_3)_2$ ].  $^{13}C$ -NMR:  $\delta$  50.9 ( $NH_2CH_2$ ), 35.8 [ $C(CH_3)_2$ ], 32.8 [ $C(CH_3)_3$ ], 21.1 [ $C(CH_3)_2$ ].

#### 3.4. $[Al_3Me_5(dmpa-H_2)]_2$ (**4**)

To a solution of  $AlMe_3$  (1.00 g, 13.89 mmol) in toluene (50 ml) was added  $dmpa-H_4$  (1.275 g, 12.50 mmol). The reaction mixture was stirred for 2 h then heated at reflux for 16 h. After which it was cooled to room temperature (r.t.). Filtration concentration and cooling to  $-33\text{ }^\circ\text{C}$  led to clear colorless crystalline material, which was separated by filtration. Yield: 25%. M.p.:  $132$ – $136\text{ }^\circ\text{C}$ . EIMS (%);  $m/z$ : 341 ( $[M^+ - Me]$ , 75).  $^1H$ -NMR: 2.18 (m, 8H,  $NHCH_2$ ), 0.39 [s, 6H,  $C(CH_3)_2$ ], 0.37 [s, 6H,  $C(CH_3)_2$ ], 0.05 (s, 3H,  $Al-CH_3$ ),  $-0.29$  (s, 6H,  $Al-CH_3$ ),  $-0.26$  (s, 6H,  $AlCH_3$ ).  $^{13}C$ -NMR:  $\delta$  57.3 ( $NHCH_2$ ), 33.6 [ $C(CH_3)_2$ ], 19.4 [ $C(CH_3)_2$ ].

#### 3.5. $Cu(dmpa-H_4)_2Cl_2$ (**5**)

To a solution of  $CuCl_2$  (1.00 g, 7.44 mmol) in MeOH (300 ml) was added  $dmpa-H_4$  (1.518 g, 14.88 mmol) in THF (100 ml). The reaction mixture was stirred for 3 h at r.t., then cooled to  $-33\text{ }^\circ\text{C}$ . Bright purple blocks precipitated overnight. Yield: 95%. M.p.:  $265$ – $267\text{ }^\circ\text{C}$ . Magnetic susceptibility: 1.72. UV-vis (nm):  $\lambda_{max}$  648 ( $\epsilon = 220\text{ l mol}^{-1}\text{ cm}^{-1}$ ).

#### 3.6. $[Cu(dmpa-H_4)_2(MeCN)_2][BPh_4]_2$ (**6**). Method A

To a solution of  $CuCl_2$  (196 mg, 1.46 mmol) in 50:50 MeCN–water (100 ml) was added  $dmpa-H_4$  (298 mg, 2.92 mmol) and  $NaBPh_4$  (1.00 g, 2.92 mmol) in THF (200 ml). The reaction mixture was stirred for 3 h at r.t., then cooled to  $-33\text{ }^\circ\text{C}$ . Bright purple blocks precipitated overnight.

#### 3.7. Method B

To a solution of  $Cu(dmpa-H_4)_2Cl_2$  (500 mg, 1.475 mmol) in MeCN (300 ml) was added  $NaBPh_4$  (1.01 g, 2.95 mmol). The reaction mixture was stirred for 16 h at r.t., then cooled to  $-33\text{ }^\circ\text{C}$ . Bright purple blocks precipitated overnight. Yield: 95%. M.p.:  $90$ – $91\text{ }^\circ\text{C}$ . Magnetic susceptibility: 1.84. UV-vis (nm):  $\lambda_{max}$  654 ( $\epsilon = 155\text{ l mol}^{-1}\text{ cm}^{-1}$ ).

#### 3.8. Crystallographic studies

Crystals were sealed in glass capillaries under Ar. Data were collected on a Bruker CCD SMART system, equipped with graphite monochromated Mo– $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ), and corrected for Lorentz and

Table 5  
Summary of X-ray diffraction data

Compounds	( $\text{Bu}$ ) <sub>3</sub> Ga(dmpa-H <sub>4</sub> ) (2)	[( $\text{Bu}$ ) <sub>3</sub> Ga] <sub>2</sub> (dmpa-H <sub>4</sub> ) (3)	[Al <sub>3</sub> Me <sub>3</sub> (dmpa-H <sub>2</sub> ) <sub>2</sub> ] (4)	[Cu(dmpa-H <sub>4</sub> ) <sub>2</sub> Cl <sub>2</sub> ] (5)	[Cu(dmpa-H <sub>4</sub> ) <sub>2</sub> - (MeCN) <sub>2</sub> ][BPh <sub>4</sub> ] <sub>2</sub> (6)
Empirical formula	C <sub>17</sub> H <sub>41</sub> GaN <sub>2</sub>	C <sub>29</sub> H <sub>68</sub> Ga <sub>2</sub> N <sub>2</sub>	C <sub>15</sub> H <sub>39</sub> Al <sub>3</sub> N <sub>4</sub>	C <sub>10</sub> H <sub>24</sub> Cl <sub>2</sub> CuN <sub>4</sub>	C <sub>62</sub> H <sub>70</sub> B <sub>2</sub> CuN <sub>6</sub>
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions					
<i>a</i> (Å)	8.419(2)	13.789(3)	9.412(2)	6.169(1)	10.833(2)
<i>b</i> (Å)	12.894(3)	17.287(4)	9.753(2)	6.172(1)	11.385(2)
<i>c</i> (Å)	10.744(2)	16.201(3)	13.819(3)	11.817(2)	12.272(3)
$\alpha$ (°)			109.10(3)	99.76(3)	77.85(3)
$\beta$ (°)	111.58(3)	109.43(3)	98.36(3)	103.44(3)	75.38(3)
$\gamma$ (°)			105.42(3)	103.11(3)	75.02(3)
<i>V</i> (Å <sup>3</sup> )	1084.5(4)	3642(1)	1117.4(4)	414.3(1)	1397.7(5)
<i>Z</i>	2	4	2	1	1
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.265	1.066	1.059	1.342	1.170
$\mu$ (cm <sup>-1</sup> )	1.27	1.50	0.17	1.63	0.434
2 $\theta$ range (°)	5.0–46.54	3.6–46.6	4.5–46.6	3.6–46.7	3.48–46.46
No. collected	2810	9290	2951	1893	3027
No. ind.	2251	5147	2332	1183	3020
No. obsd.	1925(  <i>F</i> <sub>o</sub>   > 4.0 $\sigma$   <i>F</i> <sub>o</sub>  )	3181(  <i>F</i> <sub>o</sub>   > 4.0 $\sigma$   <i>F</i> <sub>o</sub>  )	1699(  <i>F</i> <sub>o</sub>   > 4.0 $\sigma$   <i>F</i> <sub>o</sub>  )	1105(  <i>F</i> <sub>o</sub>   > 4.0 $\sigma$   <i>F</i> <sub>o</sub>  )	1690(  <i>F</i> <sub>o</sub>   > 4.0 $\sigma$   <i>F</i> <sub>o</sub>  )
Weights SHELXTL	0.1, 0	0.0837, 0	0.0551, 0	0.0864, 0.0947	0.0628, 0
<i>R</i>	0.0498	0.0523	0.0412	0.0298	0.0512
<i>R</i> <sub>w</sub>	0.1321	0.1322	0.1019	0.0967	0.1079
Largest difference peak (e Å <sup>-3</sup> )	0.59	0.59	0.22	0.46	0.28

polarization effects. Data collection and cell determinations were performed in a manner previously described [26]. The structures were solved using the direct methods program XS [27] and difference Fourier maps and refined by using full-matrix least-squares method [28]. Disorder was noted as follows. The dmpa-H<sub>4</sub> ligand in compound **2** exhibited a 'slinky' disorder between the gallium and quaternary carbon [29]. The thermal parameters of the latter indicate unresolved disorder there also. Both ligands were observed to be statically disordered in compound **5** in a manner previously observed for the O<sub>4</sub> analog [1]. The CuN<sub>4</sub> unit and quaternary carbons remain in fixed positions, while the methylene and methyl groups interchange. The unit cell for this compound could transform to one of higher symmetry. However, solution in this higher symmetry led to extensive disorder. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were placed in calculated positions [*U*<sub>iso</sub> = 0.08; *d*(C–H) = 0.96 Å] for refinement. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 5).

### Acknowledgements

Financial support for this work is provided by the Robert A. Welch Foundation. The Bruker CCD Smart System Diffractometer was funded by the Robert A.

Welch Foundation and the Bruker Avance 200 NMR spectrometer was purchased with funds with ONR Grant N00014-96-1-1146. Halliburton Energy Services and Albemarle Corporation are gratefully acknowledged for the gift of the 400 MHz NMR spectrometer and AlMe<sub>3</sub>, respectively.

### References

- [1] C.N. McMahon, S.J. Obrey, A. Keys, S.G. Bott, A.R. Barron, *J. Chem. Soc. Dalton Trans.* (2001) 2151.
- [2] S.J. Obrey, S.G. Bott, A.R. Barron, *Inorg. Chem.*, in press.
- [3] C.N. McMahon, S.G. Bott, A.R. Barron, *J. Chem. Soc. Dalton Trans.* (1997) 3129.
- [4] C.L. Aitken, A.R. Barron, *J. Chem. Crystallogr.* 26 (1996) 297.
- [5] C.N. McMahon, S.G. Bott, A.R. Barron, *Polyhedron* 16 (1997) 3407.
- [6] Y. Koide, J.A. Francis, S.G. Bott, A.R. Barron, *Polyhedron* 17 (1998) 983 (and references therein).
- [7] D.G. Tuck, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 1, Pergamon Press, Oxford, 1983 (chap. 7).
- [8] W. Ziemkowska, S. Pasykiewicz, T. Glowiak, *J. Organomet. Chem.* 562 (1998) 3.
- [9] G.H. Robinson, S.A. Sangokoya, *J. Am. Chem. Soc.* 109 (1987) 6852.
- [10] G.H. Robinson, S.A. Sangokoya, F. Moise, W.T. Pennington, *Organometallics* 7 (1988) 1887.
- [11] G.H. Robinson, F. Moise, W.T. Pennington, S.A. Sangokoya, *Polyhedron* 8 (1989) 1279.
- [12] L. Fabrizzi, A.M. Lanfredi, P. Pelavicini, A. Perotti, A. Taglietti, F. Ugozzoli, *J. Chem. Soc. Dalton Trans.* (1991) 3263.

- [13] R.W. Hay, A. Danby, P. Lightfoot, Y.D. Lampeka, *Polyhedron* 16 (1997) 2777.
- [14] I.M. Maloshtan, S.V. Rosokha, Y.D. Lampeka, *Zh. Neorg. Khim.* 39 (1994) 792.
- [15] T. Chiang, *J. Chem. Phys.* 48 (1968) 1814.
- [16] G. Marcotrigiano, L. Menabue, G.C. Pellacani, *Inorg. Chim. Acta* 19 (1997) 133.
- [17] D.S. Brown, J.D. Lee, B.G.A. Melson, *Acta Crystallogr. Sect. B* 24 (1968) 730.
- [18] K.R. Maxcy, M.M. Turnbill, *Acta Crystallogr. Sect. C* 55 (1999) 1986.
- [19] J.M. Holland, X. Liu, J.P. Zhao, F.E. Mabbs, C.A. Kilner, M. Thornton-Pett, M.A. Halcrow, *J. Chem. Soc. Dalton Trans.* (2000) 3316.
- [20] H. Grove, J. Sletten, M. Julve, F. Lloret, J. Cano, *J. Chem. Soc. Dalton Trans.* (2001) 259.
- [21] J.A. Zerkowski, J.C. MacDonald, G.M. Whitesides, *Chem. Mater.* 6 (1994) 1250.
- [22] J. Hierso, E. Bouwman, D.D. Ellis, M.P. Cabero, J. Reedijk, A.L. Spek, *J. Chem. Soc. Dalton Trans.* (2001) 197.
- [23] A. Marzotto, D.A. Clemente, F. Benetollo, G. Valle, *Polyhedron* 20 (2001) 171.
- [24] R.S. Drago, *Physical Methods in Chemistry*, Saunders, Philadelphia, 1977, pp. 411–432 and 436–463.
- [25] (a) D.F. Evans, *J. Chem. Soc.* (1959) 2003;  
(b) J. Loliger, R.J. Scheffold, *J. Chem. Educ.* 49 (1972) 646.
- [26] M.R. Marson, J.M. Smith, S.G. Bott, A.R. Barron, *J. Am. Chem. Soc.* 115 (1993) 4971.
- [27] G.M. Sheldrick, *Acta Crystallogr. Sect. A* A46 (1990) 467.
- [28] G.M. Sheldrick, *SHELXTL Bruker AXS, Inc. Madison, WI*, 1997.
- [29] C.L. Aitken, A.R. Barron, *J. Chem. Crystallogr.* 26 (1996) 297.