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A cationic hydroxo-bridged dinuclear gallium complex

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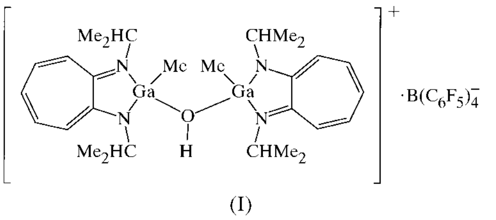
The crystal structure of μ-hydroxo-bis{[*N*-isopropyl-2-(isopropylamino)troponimino-*N*,*N*′](methyl)gallium(II)} tetrakis(pentafluorophenyl)borate (troponimine is 2,4,6-cycloheptatrien-1-imine), $[Ga_2(C_{14}H_{22}N_2)_2(OH)]B(C_6H_5)_4$, is discussed. The two (^{i}Pr$_2$-ATI)GaMe (ATI is aminotroponimime) units of the dinuclear cation are linked by a bridging hydroxo group and are both slightly twisted from planarity.

Comment

In recent reports, we have described the synthesis, structures and reactivity of several classes of cationic group 13 alkyl complexes, some of which polymerize ethylene (Coles & Jordan, 1997; Ihara *et al.*, 1998; Radzewich *et al.*, 1998, 1999; Korolev *et al.*, 1999; Dagorne *et al.*, 2000). During these studies, we found that the cationic Ga methyl complex [(^{i}Pr$_2$-ATI)Ga(Me)(NMe$_2$Ph)][$B(C_6F_5)_4$] is hydrolyzed to the cationic dinuclear Ga–hydroxo complex [{(^{i}Pr$_2$-ATI)GaMe}$_2$(μ-OH)]-[$B(C_6F_5)_4$], (II), the molecular structure of which is presented here.



(I)

Compound (II) crystallizes as discrete [(^{i}Pr$_2$-ATI)GaMe]$_2$-(μ-OH)$^+$ cations and $B(C_6F_5)_4^-$ anions with no close cation–anion contacts. The $B(C_6F_5)_4^-$ anion has a slightly distorted tetrahedral structure. The C29—B—C41 [103.3 (3)°] and C35—B—C47 [101.5 (3)°] bond angles are smaller than the ideal tetrahedral angle (109.47°), which is compensated for by opening of the other C—B—C angles [113.1 (3)° average]. The C_6F_5 rings are normal. The cation of (II) contains two (^{i}Pr$_2$-ATI)GaMe units which are linked through the Ga centers by a hydroxo bridge (Fig. 1). The Ga1—O [1.935 (2) Å] and Ga2—O [1.947 (2) Å] bond distances and the Ga—O—Ga bond angle [140.87 (11)°] are very similar to those in [(^{t}Bu)$_2$Ga(μ-OH)]$_3$ [average Ga—O 1.957 (5) Å; average Ga—O—Ga 143.0 (2)°], which contains three hydroxo bridges (Atwood *et al.*, 1993). The two (^{i}Pr$_2$-ATI)GaMe units of (II) exhibit very similar structures. Both Ga centers adopt a distorted tetrahedral geometry. The N1—Ga1—N2 [84.25 (12)°] and N3—Ga2—N4 [84.44 (11)°] bond angles are comparable to those in (^{i}Pr$_2$-ATI)AlMe$_2$ [83.3 (2)°] and (Me$_2$-ATI)$_2$GaI [80.5 (2)° average] (Dias & Jin, 1995, 1996). The small N—Ga—N bond angles in (II) are compensated for by opening of the N—Ga—C angles [126 (3)° average]. The N—Ga—O [average 105 (2)°] and C—Ga—O [average 107 (1)°] bond angles are similar. The Ga—N bond distances in (II) [average 1.916 (2) Å] are shorter than those in (Me$_2$-ATI)$_2$GaI [average 1.97 (2) Å; Dias & Jin, 1996], which is expected due to the higher charge and lower coordination number of (II). The aminotroponiminate C—N bond distances of (II) fall in the range 1.341 (4)–1.352 (4) Å, and thus are intermediate between the normal Csp^2—N single bond (1.47 Å) and C═N double bond (1.29 Å) distances, which is consistent with significant delocalization of the π-electrons within the ATI unit. However, the five-membered N—C—C—N—Ga rings are slightly twisted as is manifested by the key torsion angles Ga1—N1—C5—C11 [6.0 (4)°] and Ga2—N3—C19—C25 [12.0 (3)°]. Additionally, the seven-membered rings of the ATI ligands are also slightly twisted [torsion angles C9—C10—C11—C5 12.0 (6)° and C23—C24—C25—C19 13.9 (6)°]. The Ga—C bond distances in (II) [average 1.941 (3) Å] are comparable to those in [^{t}BuC(N^{i}Pr)$_2$]Ga-Me$_2$·[^{t}BuC(N^{i}Pr)$_2$]GaMe$^+$ [average 1.950 (3) Å; Dagorne *et al.*, 2000] and are slightly shorter than those in [Me$_2$Ga-(NH$_2$^{t}Bu)$_2$]Br [average 1.98 (2) Å; Atwood *et al.*, 1992].

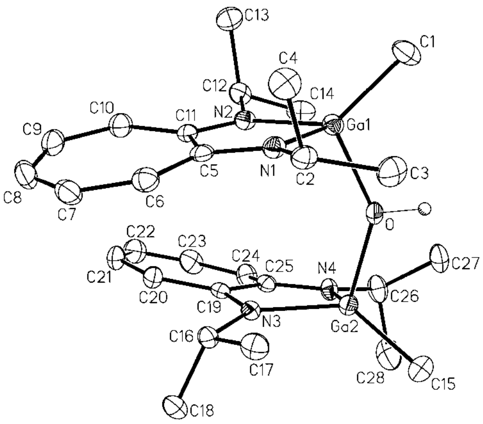


Figure 1
The structure of the cation of (II). Displacement ellipsoids are shown at the 30% probability level.

Experimental

A resealable J-Young NMR tube was charged with (^{i}Pr$_2$-ATI)Ga-Me$_2$ (152 mg, 0.50 mmol) and ($NHMe_2Ph$)[$B(C_6F_5)_4$] (395 mg, 0.50 mmol), and C_6D_5Cl (0.5 ml) was added at 296 K. The tube was shaken to yield a clear orange solution, which was immediately analyzed by ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectroscopy, which showed that quantitative conversion to $[(^i\mathrm{Pr}_2\text{-ATI})\mathrm{Ga(Me)(NMe_2Ph)}][\mathrm{B(C_6F_5)_4}]$, (I), had occurred. The volume of the solution was reduced to *ca* 0.1 ml under vacuum and wet pentane (*ca* 1 ml) was slowly added. Phase separation occurred. The tube was left at 296 K for 3 d which resulted in the formation of yellow–orange crystals of $[\{(^i\mathrm{Pr}_2\text{-ATI})\mathrm{GaMe}\}_2(\mu\text{-OH})][\mathrm{B(C_6F_5)_4}]$, (II), at the phase boundary.

Crystal data

$[\mathrm{Ga_2(C_{14}H_{22}N_2)_2(OH)}](\mathrm{C_{24}F_{20}B})$
$M_r = 1272.17$
Monoclinic, $P2_1/n$
$a = 17.7211$ (8) Å
$b = 16.0050$ (7) Å
$c = 18.5655$ (9) Å
$\beta = 94.904$ (1)°
$V = 5246.4$ (4) Å^3
$Z = 4$
$D_x = 1.611$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7833 reflections
$\theta = 2$–26°
$\mu = 1.142$ mm^{-1}
$T = 173$ (2) K
Block, yellow
0.35 × 0.32 × 0.30 mm

Data collection

Bruker SMART CCD-1000 diffractometer
φ scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{\min} = 0.69$, $T_{\max} = 0.73$
47660 measured reflections
10732 independent reflections
6612 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.064$
$\theta_{\max} = 26.37°$
$h = -22 \rightarrow 22$
$k = -20 \rightarrow 20$
$l = -23 \rightarrow 23$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.054$
$S = 0.996$
10732 reflections
732 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0050P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

All H atoms were included in the structure-factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients (C—H = 0.95–0.99 Å, N—H = 0.88–0.91 Å and B—H = 1.12 Å). The H atom of the hydroxo group was located from the difference map, but was subsequently refined with an idealized geometry (O—H = 0.84 Å).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

Ga1—N1	1.916 (3)	Ga2—N3	1.909 (3)
Ga1—N2	1.917 (3)	Ga2—N4	1.922 (3)
Ga1—O	1.935 (2)	Ga2—C15	1.940 (3)
Ga1—C1	1.943 (3)	Ga2—O	1.947 (2)
N1—Ga1—N2	84.25 (12)	N3—Ga2—C15	128.85 (13)
N1—Ga1—O	104.12 (10)	N4—Ga2—C15	124.42 (14)
N2—Ga1—O	106.83 (10)	N3—Ga2—O	106.14 (10)
N1—Ga1—C1	127.12 (13)	N4—Ga2—O	103.86 (10)
N2—Ga1—C1	123.91 (14)	C15—Ga2—O	105.73 (12)
O—Ga1—C1	107.39 (13)	Ga1—O—Ga2	140.87 (11)
N3—Ga2—N4	84.44 (11)		
N2—Ga1—N1—C5	3.6 (2)	N1—C5—C11—N2	5.7 (4)
N1—Ga1—N2—C12	168.6 (3)	C6—C5—C11—C10	11.5 (5)
N4—Ga2—N3—C19	−10.2 (2)	Ga2—N3—C19—C20	−166.1 (2)
N3—Ga2—N4—C25	6.2 (2)	Ga2—N3—C19—C25	12.0 (3)
Ga1—N1—C5—C11	−6.0 (4)	C19—C20—C21—C22	5.4 (7)
C5—C6—C7—C8	−6.9 (7)	C21—C22—C23—C24	−6.4 (7)
C7—C8—C9—C10	5.8 (7)	C23—C24—C25—C19	13.9 (6)
C9—C10—C11—N2	171.9 (4)	C20—C19—C25—C24	−13.1 (5)
C9—C10—C11—C5	−12.0 (6)		

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1292). Services for accessing these data are described at the back of the journal.

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