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Structure of the Monomethylgallium Derivative of TMTAA (Dibenzotetramethyltetraaza[14]annulene)[†]

N. W. ALCOCK, N. C. BLACKER, W. ERRINGTON AND M. G. H. WALLBRIDGE*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

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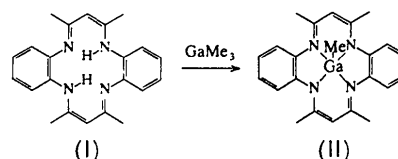
Abstract

The structure consists of a GaCH₃ unit bound symmetrically to the four N atoms of the macrocycle with the metal atom 0.65 (1) Å above the N₄ plane. The four N and C(methyl) atoms form a distorted square-based pyramidal geometry around the Ga atom. The average Ga—N bond distance is 2.016 (5) Å and the Ga—C distance of 1.958 (8) Å is fractionally shorter than the Ga—C distance of 1.967 (2) Å in Ga(CH₃)₃ [Beagley, Schmidling & Steer (1974). *J. Mol. Struct.* **21**, 437–444].

Comment

The reaction of trimethylgallium with the tetraaza macrocycle TMTAA, C₂₂H₂₄N₄ (I), at room temperature results in the loss of one mole of methane and the formation of [(CH₃)₂Ga(C₂₂H₂₃N₄)]. The X-ray crystal structure of this compound shows a Ga(CH₃)₂ group bonded to two N atoms (Alcock, Blacker, Wallbridge & Barker, 1991). Further heating (to 498 K) results in the loss of a second mole of methane and the formation of the title compound (II). The present study was undertaken to determine the structure of this compound and to compare it

with the ethyl aluminium derivative of the same macrocycle (Goedken, Ito & Ito, 1984).



The saddle shape of the free ligand (Goedken, Pluth, Peng & Bursten, 1976) is retained in the metal complex (Fig. 1), with the Ga atom replacing the two H atoms of the two NH groups in the ligand. The metal atom is coordinated essentially symmetrically to the four planar N atoms but is located 0.65 (1) Å above the N₄ plane. This is a significant displacement and is greater than the 0.57 Å observed for the related aluminium compound [(C₂H₅)Al(C₂₂H₂₂N₄)]. However, such displacements are not altogether unexpected since they lie within the range 0.23–0.73 Å observed for cobalt(III), iron(III) and manganese(II) complexes of the same macrocycle (Cotton & Czuchajowska, 1990). It is interesting that the delocalization around the CN framework of the free ligand is not significantly affected by the formation of the metal complex, since the average benzenoid C—N bond distance remains 1.404 (8) Å in both the free ligand and the gallium complex. As expected, the four C—N—C angles in the complex are effectively identical, with mean value 124.8 (5)°, whereas in the free ligand two C—N—C angles are 125° with the other two involving the NH groups opening out to 129°.

Overall, the structure of the title compound shows a close resemblance to that of the free ligand and also to the ethylaluminium derivative. The different distances of the metal atom above the N₄ plane (Ga 0.65, Al 0.57 Å) can be understood in terms of the difference in the respective covalent radii (Ga 1.25, Al 1.18 Å) of the two trivalent metal ions (Alcock, 1990).

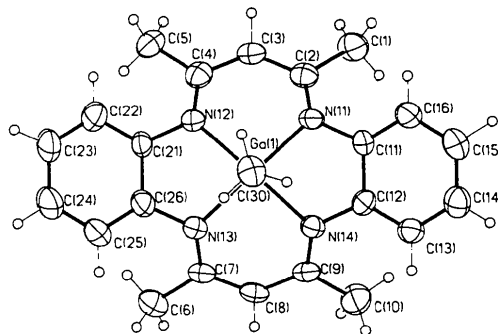


Fig. 1. Face view of (II) showing the atomic numbering with thermal ellipsoids at 50% probability.

[†] TMTAA: 5,14-dihydro-6,8,15,17-tetramethyl-5,9,14,18-tetraazadibenzo[*b,i*]cyclotetradecene.

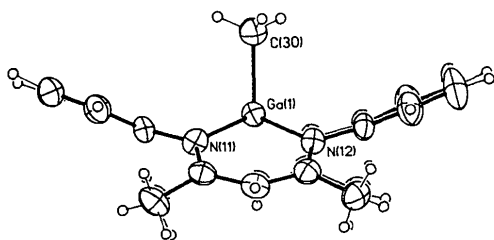


Fig. 2. Side view of (II) showing the saddle conformation adopted by the ligand.

Experimental

Crystal data

[Ga(CH₃)(C₂₂H₂₂N₄)]

M_r = 472.2

Triclinic

*P*1

a = 9.023 (3) Å

b = 11.740 (3) Å

c = 11.861 (3) Å

α = 107.78 (2)°

β = 107.83 (2)°

γ = 107.74 (2)°

V = 1023.3 (5) Å³

Z = 2

D_x = 1.39 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 20 reflections

θ = 9–11°

μ = 1.4 mm⁻¹

T = 290 K

Irregular blocks

0.41 × 0.20 × 0.14 mm

Orange

Data collection

Siemens *R3m* diffractometer

ω–2θ scans

Absorption correction:

Gaussian

T_{min} = 0.78, *T_{max}* = 0.86

3859 measured reflections

3859 independent reflections

2684 observed reflections

[*I*/σ(*I*) ≥ 2.0]

θ_{max} = 25°

h = 0 → 10

k = –13 → 13

l = –13 → 13

3 standard reflections

monitored every 200

reflections

intensity variation: none

Refinement

Refinement on *F*²

Final *R* = 0.053

wR = 0.060

S = 0.84

2684 reflections

268 parameters

w = 1/[σ²(*F*) + *gF*²]

(Δ/σ)_{max} = 0.2

Δρ_{max} = 0.5 e Å⁻³

Δρ_{min} = –0.5 e Å⁻³

Atomic scattering factors

from *SHELXTL-Plus*

(Sheldrick, 1986)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

	$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ga(1)	0.49431 (8)	0.25098 (6)	0.23528 (5)	0.034 (1)
N(11)	0.4226 (6)	0.0864 (4)	0.2658 (4)	0.036 (2)
N(12)	0.2455 (6)	0.2234 (4)	0.1659 (4)	0.036 (2)
N(13)	0.5254 (6)	0.4396 (4)	0.2983 (4)	0.040 (2)
N(14)	0.6993 (6)	0.3062 (4)	0.4041 (4)	0.035 (2)
C(1)	0.2510 (9)	–0.0812 (7)	0.3170 (6)	0.052 (3)
C(2)	0.2710 (7)	0.0184 (5)	0.2608 (5)	0.039 (3)
C(3)	0.1253 (7)	0.0405 (5)	0.2109 (5)	0.039 (2)
C(4)	0.1109 (7)	0.1364 (6)	0.1670 (5)	0.041 (3)
C(5)	–0.0615 (7)	0.1402 (7)	0.1301 (6)	0.049 (3)

C(6)	0.6125 (9)	0.6690 (6)	0.4566 (6)	0.050 (3)
C(7)	0.6284 (7)	0.5406 (5)	0.4181 (5)	0.036 (2)
C(8)	0.7464 (7)	0.5295 (5)	0.5150 (5)	0.040 (2)
C(9)	0.7822 (7)	0.4222 (5)	0.5136 (5)	0.037 (2)
C(10)	0.9057 (9)	0.4366 (7)	0.6408 (6)	0.057 (3)
C(11)	0.5735 (7)	0.0715 (5)	0.3177 (5)	0.036 (3)
C(12)	0.7265 (7)	0.1935 (5)	0.3950 (5)	0.035 (2)
C(13)	0.8858 (8)	0.1901 (6)	0.4394 (5)	0.043 (3)
C(14)	0.8967 (9)	0.0705 (6)	0.4109 (6)	0.049 (3)
C(15)	0.7484 (9)	–0.0475 (6)	0.3328 (6)	0.050 (3)
C(16)	0.5876 (8)	–0.0469 (6)	0.2849 (6)	0.044 (3)
C(21)	0.2415 (7)	0.3240 (5)	0.1264 (5)	0.037 (3)
C(22)	0.1110 (9)	0.3115 (7)	0.0179 (6)	0.055 (3)
C(23)	0.1325 (11)	0.4136 (7)	–0.0189 (7)	0.068 (4)
C(24)	0.2823 (10)	0.5275 (7)	0.0491 (7)	0.074 (4)
C(25)	0.4168 (9)	0.5419 (6)	0.1571 (6)	0.056 (3)
C(26)	0.3950 (8)	0.4420 (6)	0.1972 (5)	0.043 (3)
C(30)	0.5539 (9)	0.2115 (6)	0.0869 (6)	0.050 (3)

Table 2. Selected geometric parameters (Å, °)

Ga(1)—N(11)	2.023 (5)	Ga(1)—N(12)	2.022 (5)
Ga(1)—N(13)	2.005 (5)	Ga(1)—N(14)	2.015 (4)
Ga(1)—C(30)	1.958 (8)	N(11)—C(2)	1.329 (8)
N(11)—C(11)	1.401 (8)	N(12)—C(4)	1.335 (8)
N(12)—C(21)	1.403 (9)	N(13)—C(7)	1.334 (5)
N(13)—C(26)	1.415 (8)	N(14)—C(9)	1.344 (6)
N(14)—C(12)	1.396 (9)		
N(11)—Ga(1)—N(12)	89.6 (2)	N(11)—Ga(1)—N(13)	143.8 (2)
N(12)—Ga(1)—N(13)	78.7 (2)	N(11)—Ga(1)—N(14)	78.8 (2)
N(12)—Ga(1)—N(14)	141.4 (2)	N(13)—Ga(1)—N(14)	89.3 (2)
N(11)—Ga(1)—C(30)	108.6 (3)	N(12)—Ga(1)—C(30)	108.2 (2)
N(13)—Ga(1)—C(30)	107.7 (3)	N(14)—Ga(1)—C(30)	110.4 (3)
C(2)—N(11)—C(11)	125.1 (6)	C(4)—N(12)—C(21)	124.8 (6)
C(7)—N(13)—C(26)	124.6 (6)	C(9)—N(14)—C(12)	124.5 (5)

The compound was prepared according to Alcock, Blacker, Wallbridge & Barker (1991) and recrystallized from a toluene/*n*-pentane mixture. The crystal was mounted in a Lindemann tube. Data were collected with scan speed 4–15° min⁻¹ (in ω), depending on the intensity of a 2 s prescan. Backgrounds were measured at each end of the scan for 25% of the scan time. Reflections were processed using profile analysis. No systematic reflection conditions were observed. The space group *P*1 was selected and shown to be correct by successful refinement. The structure was solved by direct methods using *SHELXTL-Plus* (*TREF*) (Sheldrick, 1986). Anisotropic thermal parameters were used for all non-H atoms. H atoms were given fixed isotropic temperature factors, *U* = 0.08 Å². Those defined by the molecular geometry were inserted at calculated positions and not refined. Methyl groups were treated as rigid CH₃ units, with their initial orientation based on a staggered configuration. Computations were performed with *SHELXTL-Plus* on a DEC MicroVAX II computer.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55997 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1029]

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Structures of Chromium(III) Cyclam Complexes. 5. Structure of *trans*-Dichloro-(1,4,8,11-tetraazacyclotetradecane)-chromium(III) Isothiocyanate

J. BOUCKAERT,* D. MAES AND J. N. LISGARTEN

Department of Ultrastructure, Instituut voor Moleculaire Biologie, Vrije Universiteit Brussel, Paardenstraat 65, B-1640 Sint-Genesius Rode, Belgium

T. K. CHATTOPADHYAY AND R. A. PALMER

Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England

M. A. MAZID

Department of Chemistry, University of Wales College at Cardiff, PO 912, Cardiff CF1 3TB, Wales

D. M. GAZI

Department of Chemistry, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England

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Abstract

The crystal and molecular structure of *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane-*N,N',N'',N'''*)chromium(III) isothiocyanate has been determined. The cyclam (1,4,8,11-tetraazacyclotetradecane) moiety exists in a chair conformation located on a crystallographic centre of symmetry. The equatorial nitrogen ligands and the central chromium ion are exactly coplanar. The isothiocyanate counterion exhibits statistical disorder, the ion being straddled across the inversion centre with the C atom close to (0.5, 0, 0).

Comment

In an attempt to prepare the non-centrosymmetric complex *trans*-[Cr(cyclam)(NCS)Cl]Cl by a substitution method, some dark-red crystals were obtained. Preliminary spectroscopic data suggested that the red compound was the isothiocyanate salt of the complex ion *trans*-[Cr(cyclam)Cl₂]⁺. The crystal structure was determined to confirm this.

The centrosymmetric *trans*-dichloro(cyclam)chromium(III) isothiocyanate can be compared with the enantiomeric *trans*-bromochloro(cyclam)chromium(III) bromide (Chattopadhyay, Palmer, Lisgarten, Wyns & Gazi, 1992), the centrosymmetric *trans*-dibromo(cyclam)chromium(III) bromide (Lisgarten, Palmer, Hemmings & Gazi, 1990), the centrosymmetric *trans*-dichloro(cyclam)chromium(III) bromide (Dealwis, Janes, Palmer, Lisgarten, Maes & Gazi, 1992) and the *trans*-dicyano(cyclam)chromium(III) perchlorate (Hemmings, Lisgarten, Palmer & Gazi, 1990).

The cyclam assumes a chair conformation. The C1—C2 and N3—C4 bond lengths are unusually long for no obvious reason. All other bond lengths and angles in this moiety are normal.

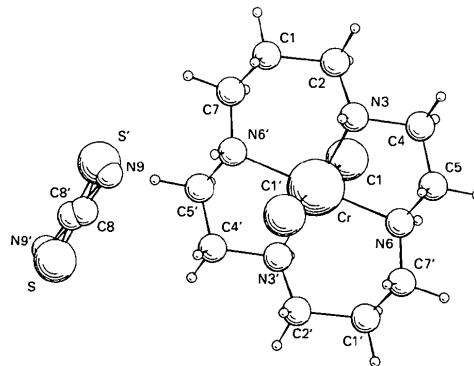


Fig. 1. Minimum overlap view of the molecule. The primed atoms are related by a crystallographic inversion centre via the symmetry operation $1 - x, 1 - y, 1 - z$.

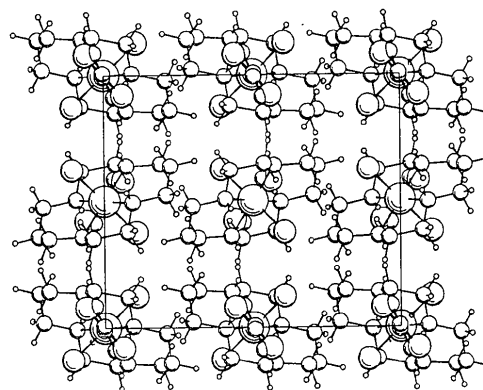


Fig. 2. Crystal packing viewed along *a*.