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Group 13 tetraazamacrocyclic complexes. The synthesis and characterisation of the monomethyl- and dimethyl-aluminium(III) and gallium(III) complexes of the two tetraazamacrocyclic ligands *omtaa*$^{2-}$ (H$_2$*omtaa* = 2,3,6,8,11,12,15,17-octamethyl-5,14-dihydro-5,9,14,18-tetraaza-dibenzo[*a*,*h*]-cyclotetradecene), and *tmtaa*$^{2-}$ (H$_2$*tmtaa* = 6,8,15,17-tetramethyl-5,14-dihydro-5,9,14,18-tetraaza-dibenzo[*a*,*h*]cyclotetradecene), and the crystal structure of [MeGa(*omtaa*)]

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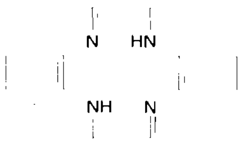
Abstract

Reactions of the tetraazamacrocyclic ligands H$_2$*tmtaa* (**I**) and H$_2$*omtaa* (**II**) with AlMe$_3$ and GaMe$_3$ give the dimethyl metal complexes [Me$_2$Al(H*tmtaa*)] (**III**) and [Me$_2$Ga(H*omtaa*)] (**IV**), respectively. On heating, (**III**) and (**IV**) lose an additional molecule of methane to form quantitatively the respective monomethyl derivatives [MeAl(*tmtaa*)] (**V**) and [MeGa(*omtaa*)] (**VI**). These new macrocyclic complexes have been characterised by ^{1}H and ^{13}C NMR, by FAB mass spectrometry and by elemental analyses. A single crystal X-ray diffraction study of **VI** reveals a five coordinate square-pyramidal coordination geometry, and the usual saddle-shape observed for this type of ligand. The gallium(III) lies 0.656(1) Å above the mean plane of the four nitrogen atoms, with Ga–C 1.966(3) and Ga–N (average) 2.03(1) Å.

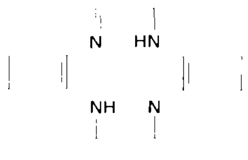
Keywords: Aluminium; Gallium; Macrocycles; Crystal structure

1. Introduction

There have been fairly few studies of the reactions of Group 13 metal alkyls with tetra-azamacrocycles such as H$_2$*tmtaa* (**I**), and H$_2$*omtaa* (**II**) [1–4]. However, there is considerable current interest in these compounds since they act as photocatalysts for polymerisation reactions, and are potential intermediates in the production of semi-conductors [1,2]. So far most of the work carried out with these tetraazamacrocyclic ligands has been concerned with organoaluminium(III) derivatives [3,4], but interest is growing in related compounds of the heavier Group 13 elements.



H$_2$*tmtaa* (**I**)



H$_2$*omtaa* (**II**)

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Table 1

^1H and proton decoupled ^{13}C NMR chemical shifts (δ/ppm) in $CDCl_3$ solution at 25°C for the compounds studied (integrals in parentheses)

(a) ^1H NMR

Compound	NH	phenyl	methine	C–methyl	metal–Me	Reference
H_2*tmtaa*	12.58 (br, 2H)	6.98 (s, 8H)	4.87 (s, 2H)	2.12 (s, 12H)		[8]
[Me_2Al(H*tmtaa*)]	12.54 (br, 1H)	7.18–6.98 (m, 8H)	5.15 (s, 1H) and 4.77 (s, 1H)	2.07 (s, 6H) and 1.68 (s, 6H)	– 0.87 (s, 3H) and – 1.50 (s, 3H)	this work
[Me_2Ga(H*tmtaa*)]	12.43 (br, 2H)	7.13–6.98 (m, 8H)	4.94 (s, 1H) and 4.79 (s, 1H)	2.09 (s, 6H) and 1.64 (s, 6H)	– 0.38 (s, 3H) and – 1.15 (s, 3H)	[5]
[MeAl(*tmtaa*)]		7.15–7.01 (m, 8H)	4.98 (s, 2H)	2.36 (s, 12H)	– 1.58 (s, 3H)	this work
[MeGa(*tmtaa*)]		7.07–6.97 (m, 8H)	4.80 (2H)	2.21 (s, 12H)	– 0.93 (3H)	[5]
H_2*omtaa*	12.56 (br, 2H)	6.76 (s, 4H)	4.83 (2H)	2.22 (s, 12H) and 2.13 (s, 12H)		this work
[Me_2Ga(*omtaa*)]	12.43 (br, 1H)	7.13–6.98 (m, 8H)	4.94 (s, 1H) and 4.79 (s, 1H)	2.09 (s, 6H) and 1.64 (s, 1H)	– 0.38 (s, 3H) and – 1.15 (s, 3H)	this work
[MeGa(*omtaa*)]		6.86 (m, 8H)	4.75 (s, 2H)	2.23 (s, 6H) and 2.22 (s, 6H)	– 0.90 (s, 3H)	this work

(b) ^{13}C NMR

Compound	*C*–N	aromatic *C*–N	aromatic *C*–H	methine–C	C–*Me*	metal–*Me*	Reference
H_2*tmtaa*	158.84(4)	138.38(4)	123.00(4), 122.78(4)	97.84(2)	20.81(4)		[8]
[Me_2Al(H*tmtaa*)]	168.09(2), and 158.23(2)	139.92(2) and 139.84(2)	126.43(2), 125.53(2), 123.67(2), 122.67(2)	99.81(1) and 98.00(1)	22.82(2) and 19.78(2)	– 12.40(1) and – 14.07	this work
[Me_2Ga(H*tmtaa*)]	166.13(2), 158.17(2)	140.95(2) and 139.69(2)	126.20(2), 124.94(2), 123.60(2), 122.56(2)	98.02(1) and 97.95(1)	22.97(2) and 19.84(2)		[10]
[MeAl(*tmtaa*)]	161.20(4)	140.31(4)	123.22(8)	99.19(2)	22.70(4)		this work
[MeGa(*tmtaa*)]	160.69(4)	139.98(4)	123.01(8)	97.28(2)	22.91(4)	– 8.00	[10]
H_2*omtaa*	158.57(4)	136.10(4)	130.87(4), 123.98(4),	97.31(2)	20.80(4), 19.43(4)		this work
[Me_2Ga(H*omtaa*)]	166.13(2), 158.17(2)	140.95(2), 139.68(2)	126.21(2), 124.94(2), 123.61(2), 122.78(2)	98.04(1), 97.96(1)	22.99(2), 19.86(2)		this work
[MeGa(*omtaa*)]	160.18(4)	137.65(4)	130.98(4), 123.65(4)	96.77(2)	22.90(2), 19.68(2)	– 11.04 (br, 1)	this work

In a previous communication [5] we described the reactions of trimethylgallium(III) with **I**:

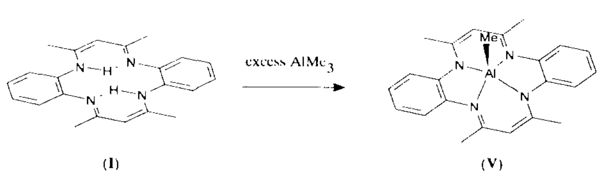
$$[\mathrm{GaMe_3}] + \mathrm{H_2}\mathit{tmtaa} \longrightarrow [\mathrm{Me_2Ga(H}\mathit{tmtaa})] + \mathrm{CH_4} \tag{1}$$

$$[\mathrm{Me_2Ga(H}\mathit{tmtaa})] \longrightarrow [\mathrm{MeGa(}\mathit{tmtaa})] + \mathrm{CH_4} \tag{2}$$

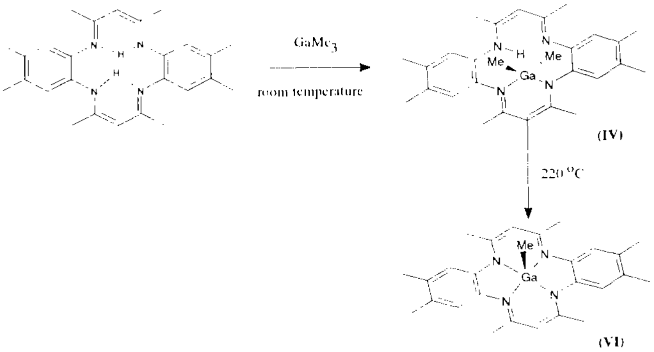
Initial formation of a dimethylgallium macrocyclic complex (Eqn. 1) is followed on heating above 200°C by formation of a monomethylgallium(III) product (eqn. 2). The X-ray crystal structure of the dimethylgallium(III) product shows the gallium atom to have a nearly tetrahedral coordination geometry, with bonding to two of the four nitrogen atoms of the macrocycle and to the two methyl groups. The complex [ClIn(*tmtaa*)] has recently been prepared [6], and here we describe the preparation and isolation of four mono- and dimethylaluminium(III) and -gallium(III) derivatives of macrocycles **I** and **II** by reactions analogous to those shown in Eqns. (1) and (2).

2. Results and Discussion

Reaction of Al_2Me_6 in dry hexane with the macrocycle **I** at room temperature gives [Me_2Al(H*tmtaa*)] (**III**), as expected by analogy with reaction 1. The NMR spectra of **III** (Table 1) clearly indicate two methylaluminium resonances at δ −0.87 and −1.50 ppm in ^{1}H NMR and at δ −12.40 and −14.07 ppm in the ^{13}C NMR, and a decrease in the overall ligand symmetry. Heating **III** in the solid state to 110°C results in quantitative formation of the monomethyl macrocyclic complex [MeAl(*tmtaa*)] **V** and methane. Cowley et al. [7] have recently prepared complex **V** by an alternative route involving transmetallation. One point of interest is that when an excess of trimethylaluminium(III) brought into reaction with **I**, two mols of methane are evolved, and the monomethylaluminium(III) complex is formed immediately (Scheme 1). In contrast, reaction of an excess of trimethylgallium(III) with **I** leads only to the partially inserted species (Eqn. 1). The NMR spectra (Table 1) of **V** shows, as expected, a single methylaluminium resonance at δ −1.58 ppm in the ^{1}H NMR spectrum. Compounds **III** and **V** were further characterised by FAB mass spectra and elemental analyses. The NMR spectra are very similar to those of the analogous ethylaluminium(III) species prepared by Ito et al. [3]. The ^{27}Al NMR spectrum of (**V**) shows a singlet at 57.34 ppm.



Scheme 1. Reaction of free ligand I with excess trimethyl aluminium at 110°C to yield the monomethylaluminium(III) derivative (V).



Scheme 2. Synthesis of organogallium(III) complexes of II.

The reaction of equimolar amounts of trimethylgallium(III) and macrocycle **II** in hexane at room temperature proceeds with the rapid evolution of one mole of methane and precipitation of a yellow solid (Scheme 2). This may be recrystallised from benzene/hexane to yield [Me_2Ga(H*omtaa*)] (**IV**). Although only one of the two macrocycle N–H groups has reacted in this case, no further reaction occurs on addition of an excess of $GaMe_3$.

The spectroscopic properties of **IV** indicate the presence of a single $GaMe_2$ group, and one remaining N–H bond from the macrocycle. The composition of the complex is deduced from the elemental analysis and the ^{1}H and ^{13}C NMR data (Table 1), and by the appearance of the molecular ion (M^+) at m/z 498 (based on ^{69}Ga) in the FAB mass spectrum. When a solid sample of **IV** is heated above 220°C, a further mole of methane is liberated. The resulting orange crystalline solid is the monomethylgallium(III) complex, [MeGa(*omtaa*)] (**VI**). The ^{1}H NMR spectrum of **VI** in $CDCl_3$ shows the absence of an N–H group, and only a singlet in the upfield region attributed to the Ga–Me. In the FAB mass spectrum of **VI** there is a molecular ion at m/z 483 (M^+ based on ^{69}Ga), and elemental analysis is consistent with the above formulation. The structure was finally confirmed by X-ray crystallography (Fig. 1), and reveals a rare example of gallium with a square-based pyramidal coordination geometry. Atomic co-ordinates are in Table 2, and selected bond lengths and angles in Table 3. The structure shows that the metal atom is displaced 0.656(1) Å from the N_4 plane, with the Ga–C bond length 1.966(3) Å and an average Ga–N distance of 2.03(1) Å.

For all the Group 13 metals there is a pronounced displacement of the metal out of the plane of the macrocycle. Table 4 illustrates this, and shows the expected feature that as the metal covalent radii in-

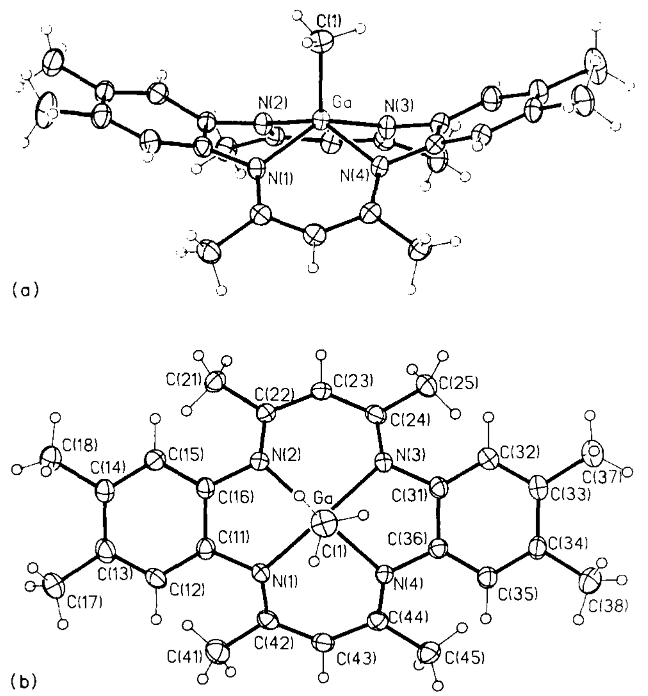


Fig. 1. Two views of the molecular structure of **VI**, illustrating the saddle shape of the ligand.

crease down the Group (Al(118 pm) < Ga(125 pm) < In(141 pm) [8] so the further the metal is from the N_4 plane. Comparison of the data for the complexes of **I** and **II** shows that the addition of the four extra methyl groups of **II** does not greatly influence the distance the metal lies away from the mean nitrogen plane.

We are currently investigating the reactions of these complexes, with the particular aim of assessing the reactivity of the metal–carbon bond.

3. Experimental section

3.1. Starting materials

H_2*tmtaa* (**I**) and H_2*omtaa* (**II**) were prepared by published methods [9]. Me_3Ga was a gift from Johnson Matthey, and other reagents were the best available commercial materials. Their purities were confirmed by their NMR spectra before use.

3.2. Spectroscopy

FTIR spectra were recorded as Nujol mulls with a Perkin Elmer 1720X spectrometer, and Fourier transform ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution with a Bruker AC250 instrument at 250 and 62.66 MHz, respectively. Fast atom bombardment (FAB) mass spectra were obtained in a *p*-nitrobenzyl alcohol (PNBA) matrix with a Kratos MS80 instrument.

Table 2
Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U
Ga	2306.7(2)	1664.8(2)	6212.6(1)	20(1) *
N(1)	2341.3(18)	428.9(16)	6929.0(11)	21(1) *
N(2)	442.2(18)	1322.6(16)	5967.8(12)	22(1) *
N(3)	2084.2(19)	2012.5(17)	5052.0(12)	23(1) *
N(4)	4002.4(17)	1196.6(16)	6059.8(11)	21(1) *
C(1)	2668(3)	2921(2)	6860(2)	36(1) *
C(11)	1240.9(22)	493.8(19)	7208.9(14)	23(1) *
C(12)	1137.9(24)	221.8(20)	7959.4(14)	27(1) *
C(13)	52(3)	386(2)	8199(2)	29(1) *
C(14)	−981(2)	862(2)	7679(2)	26(1) *
C(15)	−870(2)	1185(2)	6942(2)	25(1) *
C(16)	205.6(23)	984.9(18)	6683.8(14)	22(1) *
C(17)	12(3)	106(3)	9033(2)	46(1) *
C(18)	−2179(3)	1060(2)	7927(2)	35(1) *
C(21)	−1667(2)	784(2)	5157(2)	27(1) *
C(22)	−379.0(22)	1244.6(19)	5256.2(14)	22(1) *
C(23)	−71(2)	1518(2)	4555(2)	25(1) *
C(24)	1086(2)	1836(2)	4445(2)	24(1) *
C(25)	1176(3)	1880(2)	3596(2)	31(1) *
C(31)	3280.5(23)	2346.2(19)	4974.7(14)	24(1) *
C(32)	3498(3)	3102(2)	4467(2)	29(1) *
C(33)	4698(3)	3443(2)	4491(2)	31(1) *
C(34)	5731(2)	3055(2)	5073(2)	27(1) *
C(35)	5518.5(23)	2306.2(19)	5590.9(14)	25(1) *
C(36)	4324.7(23)	1918.5(19)	5540.6(14)	22(1) *
C(37)	4879(3)	4242(3)	3898(2)	48(1) *
C(38)	7042(3)	3464(2)	5152(2)	39(1) *
C(41)	2947(3)	−1294(2)	7531(2)	35(1) *
C(42)	3157.1(23)	−348.4(19)	7074.8(14)	23(1) *
C(43)	4227(2)	−380(2)	6788(2)	26(1) *
C(44)	4624.9(22)	329.1(20)	6298.0(13)	23(1) *
C(45)	5773(2)	7(2)	6030(2)	30(1) *

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

3.3. Preparation of [Me_2Al(*tmtaa*)] (**III**)

To a solution of (**I**) (2.01 g, 5.83 mmol) in dry hexane (40 ml) in a Schlenk tube under N_2 at room temperature was added Al_2Me_6 (0.42 g, 2.92 mmol). A yellow precipitate of [Me_2Al(H*tmtaa*)] was formed and was filtered off, washed with petroleum ether and dried in

Table 3
Selected bond lengths (Å) and angles (°) for [MeGa(*omtaa*)] with estimated standard deviations in parentheses

Ga–N(1)	2.030(3)	Ga–N(2)	2.030(3)
Ga–N(3)	2.027(3)	Ga–N(4)	2.044(3)
Ga–C(1)	1.966(3)	N(1)–C(11)	1.422(4)
N(1)–C(42)	1.330(3)	N(2)–C(16)	1.413(4)
N(2)–C(22)	1.333(3)	N(3)–C(24)	1.328(3)
N(3)–C(31)	1.425(4)	N(4)–C(36)	1.413(4)
N(4)–C(44)	1.328(3)	C(11)–C(12)	1.391(4)
N(1)–Ga–N(2)	79.0(1)	N(1)–Ga–N(3)	140.4(1)
N(2)–Ga–N(3)	89.4(1)	N(1)–Ga–N(4)	88.6(1)
N(2)–Ga–N(4)	144.3(1)	N(3)–Ga–N(4)	79.0(1)
N(1)–Ga–C(1)	109.6(1)	N(2)–Ga–C(1)	110.0(1)

Table 4
Distance the metal atom is displaced from the N_4 plane of macrocycles (**I**) (*tmtaa*) and (**II**) (*omtaa*) for Group 13 metal alkyls and chlorides

Complex	Distance/(Å)	Reference
[EtAl(*tmtaa*)]	0.57	[3]
[MeGa(*tmtaa*)]	0.65	[5]
[MeGa(*omtaa*)]	0.66	this work
[ClGa(*tmtaa*)]	0.48	[7]
[ClIn(*tmtaa*)]	0.74	[6]

vacuo (yield: 1.92 g, 82.6%). IR (Nujol) 1622 cm^{-1} (C=N). FAB-MS: *m/z* 400 $[M^+]$. ^{13}C and ^1H NMR are in Table 1. Anal. Calc. for $C_{24}H_{29}N_4Al$: C, 72.0; H, 7.3; Found: C, 71.7; H, 7.2%.

3.4. *Preparation of* $[Me_2Ga(H$*omtaa*$)]$ (**IV**)

To a solution of (**II**) (1.00 g, 2.50 mmol) in dry hexane (30 ml) in a Schlenk tube under N_2 at room temperature was added $GaMe_3$ (0.29 g, 2.50 mmol). A yellow precipitate of $[Me_2Ga(H$*tmtaa*$)]$ was formed immediately, and was filtered off and recrystallised from hexane/benzene (yield: 0.98 g, 88.5%). IR (Nujol) 1621 cm^{-1} (C=N). FAB-MS: *m/z* 498 $[M^+]$. ^{13}C and ^1H NMR are in Table 1. Anal. Calc. for $C_{28}H_{37}N_4Ga$: C, 67.4; H, 7.3; Found: C, 67.1; H, 7.3%.

3.5. *Preparation of* [MeAl(*tmtaa*)] (**V**)

Complex **IV** may be obtained by heating **III** in the solid phase at 110°C or by the reaction of (**I**) with 1.25 molar equivalents of Al_2Me_6. To a solution of (**I**) (1.00 g, 2.91 mmol) in dry hexane (30 ml) in a Schlenk tube under N_2 at room temperature was added Al_2Me_6 (0.52 g, 3.64 mmol). An orange precipitate of [MeAl(*tmtaa*)] was immediately formed and was filtered off, and recrystallised from hexane/benzene (yield: 0.74 g, 77.1%). IR (Nujol) 1619 cm^{-1} (C=N). FAB-MS *m/z* 384 $[M^+]$. ^1H and ^{13}C NMR are in Table 1. Anal. Calc. for $C_{23}H_{25}N_4Al$: C, 71.9; H, 6.5. Found C, 71.7; H, 6.5%.

3.6. *Preparation of* [MeGa(*omtaa*)] (**VI**)

Complex **VI** was obtained quantitatively by heating **IV** in the solid phase at 220°C. IR (Nujol) 1622 cm^{-1} (C=N). FAB-MS *m/z* 483 $[M^+]$. ^1H and ^{13}C NMR are in Table 1.

3.7. *X-ray crystallography*

Orange crystals of [MeGa(*omtaa*)] suitable for crystallography were grown by slow diffusion of a concentrated hexane solution of the compound into toluene. $C_{27}H_{33}GaN_4$, M = 483.29, monoclinic space group $P2_1/c$, $a = 10.994(11)$, $b = 12.998(4)$, $c = 17.462(7)$ Å, $\beta = 105.32(6)$ $U = 2406.7(14)$ $Å^3$, $Z = 4$, $D_c = 1.33$ g cm^{-3}, T = 220 K, Mo Kα radiation, $\lambda = 0.71073$ Å, μ(Mo Kα) = 1.25 mm^{-1}. Data were collected with a Siemens $P2_1$ four-circle diffractometer in the ω-2θ mode. Maximum 2θ was 50°, with scan range ±1.5° around $K_{\alpha 1}$-$K_{\alpha 2}$ angles, scan speed 4–15°(ω) min^{-1} depending on the intensity of a 2 s pre-scan; backgrounds were measured at the end of each scan for 0.25 of the scan time. The *hkl* ranges were *h* (0–10), *k* (0–15) and *l* (−20 to +20). Three standard reflections were monitored every 200 reflections, and showed no change during data collection. Unit cell dimensions were obtained by a least-squares fit to 15 reflections ($15 < 2\theta < 18°$). Using profile analysis, 4507 reflections were processed to give 4270 unique reflections; 3696 were considered observed ($I/\sigma(I) > 2.0$) and used in refinement; they were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method; maximum and minimum transmission factors were 0.79 and 0.72. Crystal dimensions were 0.36 × 0.27 × 0.16 mm. Systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ indicate space group $P2_1/c$. The Ga atom was located by the Patterson interpretation section of SHELXTL, and light atoms were then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-hydrogen atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.08$ $Å^3$. They were inserted at calculated positions and not refined, except for that attached to N(1). Final refinement was on *F* by least-squares methods, refining 200 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height ±0.5 e $Å^{-3}$. A weighting scheme of the form $w = 1/(\sigma^2(F) + gF^2)$, where $g =$ 0.0023, was used, and shown to be satisfactory by a weight analysis. Final $R = 0.034$ ($R_w = 0.055$). Maximum shift/error in the final cycle was 0.001. Computing was with SHELXTL PLUS [10] on a DEC Microvax II. Scattering factors in the analytical form and anomalous dispersion factors were taken from the stored values of the programs. Final atomic co-ordinates are in Table 2, and selected bond lengths and angles are in Table 3. The molecular geometry of the cation is shown in Fig. 1. Tables of H-atom co-ordinates and thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

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