

Benzamidinium tetrachlorogallate(III)

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Key indicators

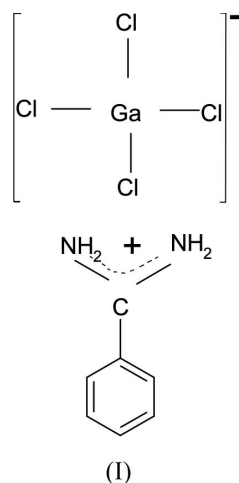
Single-crystal X-ray study
 T = 180 K
 Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
 R factor = 0.043
 wR factor = 0.079
 Data-to-parameter ratio = 21.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The synthesis of the title compound, $(\text{C}_7\text{H}_9\text{N}_2)[\text{GaCl}_4]$, is described. The N—C—N fragment involves delocalized bonding, which does not extend to the adjacent C—C bond. The N—C—N plane is aligned at $39.6(2)^\circ$ to the mean plane through the phenyl group. The GaCl_4^- anion is tetrahedral, with Ga—Cl bonds in the range 2.165(1)–2.180(1) Å. Intermolecular hydrogen bonding is postulated between the N and Cl atoms.

Comment

Interest in the pharmaceutical effects provided by gallium and amidine ligands (Yoshida *et al.*, 2004) continues, particularly with regard to antiviral and antitumour activity (Fimiani *et al.*, 1990; Sharma *et al.*, 1997; Kratz *et al.*, 1992). This fact has directed us to extend our previous work in the area (Barker *et al.*, 1996) to encompass systems containing gallium chloride and the amidinium ion. The crystal structure of the title compound, (I), has been determined since it affords an opportunity to study the structural features of a benzamidinium cationic system, which has no substituents on the N atoms, in combination with the tetrachlorogallate anion.



The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The benzamidinium, in its cationic form, shows protonation at the imino N atom, yielding a more delocalized N—C—N fragment [C—N = 1.304(5) and 1.317(5) Å] than found in the parent benzamidine [1.294(3) and 1.344(3) Å; Barker *et al.*, 1996], but similar to those found in benzamidinium acetylacetonatotetracarboxylrhodate(II) (Lenhert *et al.*, 1984). The C—C_{amidine} distances of the parent amidine [1.489(3) Å; Barker *et al.*, 1996] and the cation [1.475(5) Å] show little

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difference, indicating that the delocalization is restricted to the N—C—N fragment. The latter point is confirmed by the C6—C1—C7—N1 torsion angle of 140.1 (4)°, which shows that the cation is non-planar and thus involves a C1—C7 single bond. The angle between the N—C—N unit and the mean plane through the benzene ring is 39.6 (2)° and compares favourably with that reported previously in benzamidine hydrochloride monohydrate [36.6 (8)°; Thailambal *et al.*, 1986]. In the N—C—N group, a three-centre four π -electron system (Kapp *et al.*, 1996), the stable benzamidinium fragment is reliant on the π -donation of the nitrogen lone pair into the formally unfilled $2p$ π orbital of the adjacent carbon centre, which compensates for the σ -attracting effect from the electronegativity of the nitrogen. The planarity contrasts with the situation calculated for the theoretical diphosphorus analogue, which has proven to be an elusive synthetic goal (Kato *et al.*, 2002).

The GaCl₄[−] anion is essentially tetrahedral, with Ga—Cl distances (Table 1) within the expected range; an examination of the Cambridge Structural Database (Version 5.23; Allen, 2002; Fletcher *et al.*, 1996) shows that, for 37 structures containing the GaCl₄[−] unit (*e.g.* Hausen *et al.*, 1978; Jakubas *et al.*, 1997), the average Ga—Cl bond length is 2.162 (12) Å, with a range from 2.087 to 2.222 Å.

Varying degrees of hydrogen bonding between the NH groups and the Cl atoms is indicated from an examination of the intermolecular geometry (Table 2). The observed N...Cl separations (with the exception of that between N2 and Cl2) are comparable with the sum of the van der Waals radii for nitrogen and chlorine (1.55 + 1.75 = 3.30 Å), whilst the N—H...Cl angles are approximately as expected for conventional two-centre hydrogen bonding. Thus, it would appear that the packing in this structure is significantly influenced by the hydrogen bonding; this effect would be absent in *N*-substituted benzamidinium systems.

Experimental

Anhydrous gallium(III) chloride (1.33 g, 7.6 mmol) was weighed into a round-bottomed flask containing dry toluene (100 ml) and then benzamidine hydrochloride (2.40 g, 15.4 mmol) was added. The resultant suspension was refluxed for 2 h. The solution was filtered hot through a No. 3 frit under nitrogen into a Schlenk tube. The solvent was removed by slow nitrogen flow to yield white crystals [yield 0.14 g, 6%; m.p. (DSC) 394 K]. Calculated for C₇H₈Cl₄GaN₂: C 25.35; H 2.43; N 8.45; found: C 25.42; H 2.93; N 8.62%. ¹³C NMR (50.3 MHz, D₂O): δ 167.0 (N—C—N), 136.2, 131.4, 130.8, 129.4 (Ar). ¹H NMR (200 MHz, D₂O): δ 7.52–6.72. IR: 3415 (*vs* broad), 1688 (*s*), 1642 (*s*), 1161 (*s*), 778 (*s*), 691 (*s*).

Crystal data

(C₇H₈N₂)[GaCl₄]
M_r = 332.68
 Monoclinic, *P*2₁/*c*
a = 13.986 (2) Å
b = 10.8228 (19) Å
c = 9.0976 (16) Å
 β = 108.474 (4)°
V = 1306.1 (4) Å³
Z = 4

D_x = 1.692 Mg m^{−3}
 Mo *K* α radiation
 Cell parameters from 3209 reflections
 θ = 2.4–28.0°
 μ = 2.89 mm^{−1}
T = 180 (2) K
 Needle, white
 0.38 × 0.06 × 0.06 mm

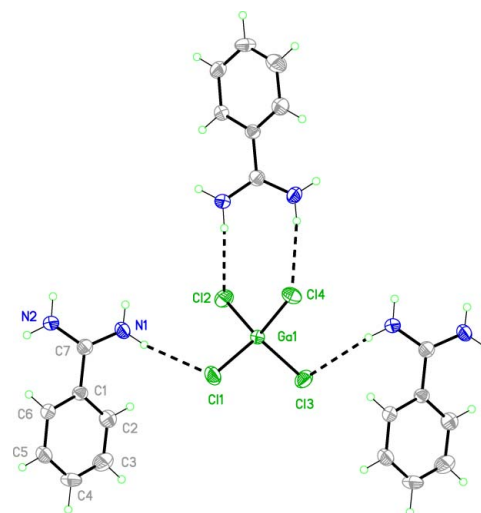


Figure 1

The asymmetric unit of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms are shown as spheres of arbitrary radii.

Data collection

Bruker SMART CCD area-detector diffractometer	3024 independent reflections
ω scans	1892 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.406$, $T_{\text{max}} = 0.846$	$\theta_{\text{max}} = 28.0^\circ$
7620 measured reflections	$h = -18 \rightarrow 13$
	$k = -14 \rightarrow 10$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2]$
$wR(F^2) = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3024 reflections	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
143 parameters	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ga1—Cl3	2.1647 (10)	N1—C7	1.304 (5)
Ga1—Cl2	2.1652 (11)	N2—C7	1.317 (5)
Ga1—Cl1	2.1758 (11)	C1—C7	1.475 (5)
Ga1—Cl4	2.1803 (10)		
Cl3—Ga1—Cl2	114.40 (4)	Cl3—Ga1—Cl4	106.56 (4)
Cl3—Ga1—Cl1	107.62 (5)	Cl2—Ga1—Cl4	108.21 (5)
Cl2—Ga1—Cl1	109.78 (4)	Cl1—Ga1—Cl4	110.20 (4)
C7—C1—C2—C3	−179.7 (3)	C2—C1—C7—N2	141.0 (4)
C6—C1—C7—N1	140.2 (4)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...Cl1	0.82 (3)	2.52 (3)	3.321 (4)	164 (4)
N1—H1B...Cl4 ⁱ	0.83 (3)	2.53 (3)	3.343 (4)	165 (3)
N2—H2A...Cl2 ⁱ	0.85 (3)	2.85 (3)	3.578 (4)	145 (3)
N2—H2B...Cl3 ⁱⁱ	0.85 (2)	2.67 (3)	3.470 (4)	157 (3)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x, y - 1, z$.

C-bound H atoms were placed in calculated positions (C–H = 0.95 Å) and refined using a riding model; those attached to the N atoms were located in an electron-density map and restrained in pairs to give equal N–H distances (0.82–0.85 Å). H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times U_{eq} of their parent atoms.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL97*.

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