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Benzamidinium tetrachlorogallate(III)

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.006 Å
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.

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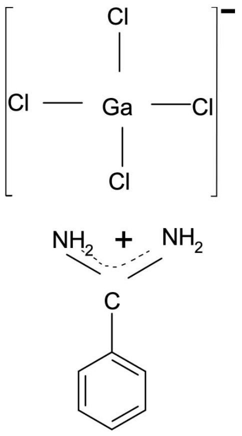
The synthesis of the title compound, $(C_7H_9N_2)[GaCl_4]$, is described. The N—C—N fragment involves delocalized bonding, which does not extend to the adjacent C—C bond. The N—C—N plane is aligned at 39.6 (2)° to the mean plane through the phenyl group. The $GaCl_4^-$ anion is tetrahedral, with Ga—Cl 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.



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The benzamidine, 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 acetylacetonatotetracarbonylrhenate(II) (Lenhert *et al.*, 1984). The C—C$_{\text{amidine}}$ distances of the parent amidine [1.489 (3) Å; Barker *et al.*, 1996] and the cation [1.475 (5) Å] show little 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 $2p\ \pi$ 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 $GaCl_4^-$ 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 $GaCl_4^-$ 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 $C_7H_8Cl_4GaN_2$: C 25.35; H 2.43; N 8.45; found: C 25.42; H 2.93; N 8.62%. ^{13}C NMR (50.3 MHz, D_2O): δ 167.0 (N—C—N), 136.2, 131.4, 130.8, 129.4 (Ar). ^{1}H NMR (200 MHz, D_2O): δ 7.52–6.72. IR: 3415 (*vs* broad), 1688 (*s*), 1642 (*s*), 1161 (*s*), 778 (*s*), 691 (*s*).

Crystal data

$(C_7H_9N_2)[GaCl_4]$
$M_r = 332.68$
Monoclinic, $P2_1/c$
$a = 13.986$ (2) Å
$b = 10.8228$ (19) Å
$c = 9.0976$ (16) Å
$\beta = 108.474$ (4)°
$V = 1306.1$ (4) Å^3
$Z = 4$
$D_x = 1.692$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3209 reflections
$\theta = 2.4$–28.0°
$\mu = 2.89$ mm^{-1}
$T = 180$ (2) K
Needle, white
0.38 × 0.06 × 0.06 mm

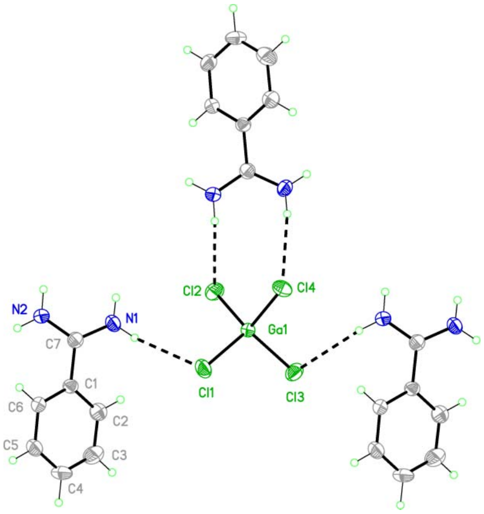


Figure 1
The asymmetric unit of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms are shown as spheres of arbitrary radii.

Data collection

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

Refinement

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1	0.82 (3)	2.52 (3)	3.321 (4)	164 (4)
N1—H1*B*···Cl4^{i}	0.83 (3)	2.53 (3)	3.343 (4)	165 (3)
N2—H2*A*···Cl2^{i}	0.85 (3)	2.85 (3)	3.578 (4)	145 (3)
N2—H2*B*···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) $x, y - 1, z$.

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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: *SAINT* (Siemens, 1995); data reduction: *SAINT*; 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*.

We acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen, 2002).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Barker, J., Phillips, P. R., Wallbridge, M. G. H. & Powell, H. R. (1996). *Acta Cryst.* C**52**, 2617–2619.

Fimiani, V., Ainis, T., Cavellero, A. & Piraino, P. (1990). *J. Chemother.* **2**, 319–326.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Hausen, H. D., Binder, H. & Schwarz, W. (1978). *Z. Naturforsch. Teil B*, **33**, 567–569.

Jakubas, R., Bator, G., Gosniowska, M., Ciunik, Z., Baran, J. & Lefebvre, J. (1997). *J. Phys. Chem. Solids*, **58**, 989–998.

Kapp, J., Schade, C., El-Nahasa, A. & Schleyer, P. *v.* R. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 2236–2238.

Kato, T., Gornitzka, H., Baceiredo, A., Schoeller, W. W & Bertrand, G. (2002). *J. Am. Chem. Soc.* **124**, 2506–2512.

Kratz, F., Nuber, B., Weiss, J. & Keppler, B. K. (1992). *Polyhedron*, **11**, 487–498.

Lenhert, P. G., Lukehart, C. M., Sotiropoulos, P. D. & Srinivasan, K. (1984). *Inorg. Chem.* **23**, 1807–1810.

Sharma, V., Beatty, A., Goldberg, D. E. & Piwnica-Worms, D. (1997). *J. Chem. Soc. Chem. Commun.* pp. 2223–2224.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Siemens (1994). *SMART* and *SHELXTL/PC* (Version 5.0). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SAINT*. Version 4.021. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thailambal, V. G., Pattabhi, V. & Guru Row, T. N. (1986). *Acta Cryst.* C**42**, 587–589.

Yoshida, K., Nakagawa, T. & Kayahara, T. (2004). US Patent No. 6 784 191.

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supporting information

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.986\ (2)$ Å
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$c = 9.0976\ (16)$ Å
$\beta = 108.474\ (4)°$
$V = 1306.1\ (4)$ Å^3
$Z = 4$

$F(000) = 656$
$D_x = 1.692$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3209 reflections
$\theta = 2.4–28.0°$
$\mu = 2.89$ mm^{-1}
$T = 180$ K
Needle, white
0.38 × 0.06 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
Detector resolution: 8.192 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.406$, $T_{max} = 0.846$

7620 measured reflections
3024 independent reflections
1892 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.4°$
$h = -18 \rightarrow 13$
$k = -14 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.079$
$S = 0.99$
3024 reflections
143 parameters
2 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Special details

Experimental. The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 96% complete to at least 28° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Ga1	0.16826 (3)	0.92057 (4)	0.74486 (5)	0.03015 (13)
Cl1	0.27698 (8)	0.79163 (9)	0.89026 (12)	0.0506 (3)
Cl2	0.05578 (8)	0.82047 (9)	0.56531 (12)	0.0469 (3)
Cl3	0.25131 (8)	1.05637 (9)	0.65941 (12)	0.0451 (3)
Cl4	0.09184 (8)	1.02105 (9)	0.88292 (11)	0.0417 (3)
N1	0.1590 (3)	0.5256 (4)	0.7733 (4)	0.0410 (9)
H1B	0.097 (2)	0.533 (3)	0.749 (4)	0.038 (12)*
H1A	0.193 (3)	0.589 (3)	0.788 (4)	0.046 (14)*
N2	0.1424 (3)	0.3159 (3)	0.7645 (5)	0.0474 (10)
H2B	0.170 (2)	0.246 (3)	0.767 (4)	0.024 (10)*
H2A	0.081 (2)	0.321 (3)	0.760 (4)	0.043 (13)*
C1	0.3071 (3)	0.4024 (3)	0.8015 (4)	0.0300 (9)
C2	0.3551 (3)	0.4837 (4)	0.7281 (4)	0.0425 (10)
H2	0.3179	0.5478	0.6636	0.051*
C3	0.4564 (4)	0.4703 (4)	0.7497 (5)	0.0559 (13)
H3	0.4889	0.5249	0.6990	0.067*
C4	0.5110 (3)	0.3789 (4)	0.8439 (5)	0.0516 (12)
H4	0.5810	0.3705	0.8584	0.062*
C5	0.4642 (3)	0.2993 (3)	0.9174 (5)	0.0429 (11)
H5	0.5023	0.2365	0.9834	0.051*
C6	0.3628 (3)	0.3101 (3)	0.8961 (4)	0.0348 (9)
H6	0.3308	0.2542	0.9462	0.042*
C7	0.1984 (3)	0.4158 (4)	0.7784 (4)	0.0333 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.0253 (2)	0.0264 (2)	0.0385 (2)	−0.00007 (19)	0.00972 (18)	−0.00214 (19)
Cl1	0.0382 (7)	0.0343 (6)	0.0656 (7)	0.0094 (5)	−0.0031 (5)	−0.0015 (5)
Cl2	0.0371 (7)	0.0455 (6)	0.0522 (6)	−0.0094 (5)	0.0057 (5)	−0.0122 (5)
Cl3	0.0476 (7)	0.0414 (6)	0.0549 (6)	−0.0122 (5)	0.0283 (6)	−0.0066 (5)

Cl4	0.0376 (7)	0.0505 (6)	0.0407 (6)	0.0084 (5)	0.0177 (5)	−0.0020 (5)
N1	0.032 (3)	0.030 (2)	0.054 (2)	0.0052 (19)	0.004 (2)	−0.0029 (17)
N2	0.027 (2)	0.032 (2)	0.082 (3)	−0.0022 (18)	0.015 (2)	−0.0070 (19)
C1	0.025 (2)	0.032 (2)	0.031 (2)	−0.0011 (17)	0.0061 (17)	−0.0052 (17)
C2	0.040 (3)	0.040 (2)	0.046 (2)	0.002 (2)	0.011 (2)	0.0042 (19)
C3	0.051 (3)	0.057 (3)	0.067 (3)	−0.009 (2)	0.029 (3)	0.008 (3)
C4	0.024 (3)	0.060 (3)	0.070 (3)	0.001 (2)	0.014 (2)	−0.004 (2)
C5	0.035 (3)	0.035 (2)	0.053 (3)	0.0066 (19)	0.006 (2)	0.0002 (19)
C6	0.030 (2)	0.029 (2)	0.044 (2)	−0.0012 (17)	0.010 (2)	0.0005 (18)
C7	0.032 (2)	0.033 (2)	0.032 (2)	−0.0011 (19)	0.0070 (18)	−0.0035 (18)

Geometric parameters (Å, º)

Ga1—Cl3	2.1647 (10)	C1—C2	1.398 (5)
Ga1—Cl2	2.1652 (11)	C1—C7	1.475 (5)
Ga1—Cl1	2.1758 (11)	C2—C3	1.375 (5)
Ga1—Cl4	2.1803 (10)	C2—H2	0.9500
N1—C7	1.304 (5)	C3—C4	1.372 (6)
N1—H1B	0.83 (3)	C3—H3	0.9500
N1—H1A	0.82 (3)	C4—C5	1.377 (5)
N2—C7	1.317 (5)	C4—H4	0.9500
N2—H2B	0.85 (2)	C5—C6	1.375 (5)
N2—H2A	0.85 (3)	C5—H5	0.9500
C1—C6	1.386 (5)	C6—H6	0.9500

Cl3—Ga1—Cl2	114.40 (4)	C1—C2—H2	120.2
Cl3—Ga1—Cl1	107.62 (5)	C4—C3—C2	120.6 (4)
Cl2—Ga1—Cl1	109.78 (4)	C4—C3—H3	119.7
Cl3—Ga1—Cl4	106.56 (4)	C2—C3—H3	119.7
Cl2—Ga1—Cl4	108.21 (5)	C3—C4—C5	119.9 (4)
Cl1—Ga1—Cl4	110.20 (4)	C3—C4—H4	120.0
C7—N1—H1B	120 (3)	C5—C4—H4	120.0
C7—N1—H1A	122 (3)	C6—C5—C4	120.4 (4)
H1B—N1—H1A	118 (4)	C6—C5—H5	119.8
C7—N2—H2B	118 (2)	C4—C5—H5	119.8
C7—N2—H2A	121 (3)	C5—C6—C1	120.0 (4)
H2B—N2—H2A	121 (3)	C5—C6—H6	120.0
C6—C1—C2	119.4 (4)	C1—C6—H6	120.0
C6—C1—C7	120.6 (3)	N1—C7—N2	120.9 (4)
C2—C1—C7	120.0 (3)	N1—C7—C1	119.9 (4)
C3—C2—C1	119.6 (4)	N2—C7—C1	119.2 (4)
C3—C2—H2	120.2		

C6—C1—C2—C3	0.5 (6)	C2—C1—C6—C5	0.2 (5)
C7—C1—C2—C3	−179.7 (3)	C7—C1—C6—C5	−179.5 (3)
C1—C2—C3—C4	−0.7 (6)	C6—C1—C7—N1	140.2 (4)
C2—C3—C4—C5	0.2 (7)	C2—C1—C7—N1	−39.6 (5)
C3—C4—C5—C6	0.6 (6)	C6—C1—C7—N2	−39.3 (5)

C4—C5—C6—C1	−0.8 (6)	C2—C1—C7—N2	141.0 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1	0.82 (3)	2.52 (3)	3.321 (4)	164 (4)
N1—H1*B*···Cl4^{i}	0.83 (3)	2.53 (3)	3.343 (4)	165 (3)
N2—H2*A*···Cl2^{i}	0.85 (3)	2.85 (3)	3.578 (4)	145 (3)
N2—H2*B*···Cl3^{ii}	0.85 (2)	2.67 (3)	3.470 (4)	157 (3)

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+3/2; (ii) *x*, *y*−1, *z*.