organic compounds

1,4-Diazoniabicyclo[2.2.2]octane tetrachloroiodate(III) chloride

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In the title compound, $C_6H_{14}N_2^{2+}\cdot Cl_4I^-\cdot Cl^-$, the dication and the anions lie on special positions. The dication has $mm2$ symmetry with two bonded C atoms and the two N atoms located on a crystallographic mirror plane parallel to bc, and with a mirror plane parallel to ab passing through the mid points of the three C—C bonds. In the square-planar Cl_4I^- anion, two Cl atoms and the I atom are located on the $mm2$ axis; the other two Cl atoms are disordered over two postions of equal occupancy (0.25) across the mirror parallel to the ab plane. The Cl^- anion is located on the $mm2$ axis. The crystal structure is stabilized by intermolecular N—H···Cl hydrogen bonds.

Related literature

For ferroelectric materials, see: Scott (2007); Katrusiak & Szafrański (2006).
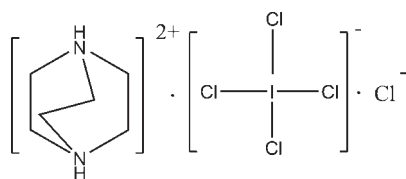
Experimental

Crystal data

$C_6H_{14}N_2^{2+}\cdot Cl_4I^-\cdot Cl^-$	$V = 1377.8$ (5) Å^3
$M_r = 418.34$	$Z = 4$
Orthorhombic, $Cmcm$	Mo $K\alpha$ radiation
$a = 8.1496$ (16) Å	$\mu = 3.26$ mm^{-1}
$b = 21.904$ (4) Å	$T = 293$ K
$c = 7.7184$ (15) Å	$0.28 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer	7175 measured reflections
Absorption correction: multi-scan	908 independent reflections
(CrystalClear; Rigaku, 2005)	882 reflections with $I > 2\sigma(I)$
$T_{min} = 0.85$, $T_{max} = 0.90$	$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	48 parameters
$wR(F^2) = 0.045$	H-atom parameters constrained
$S = 1.25$	$\Delta\rho_{max} = 0.44$ e Å^{-3}
908 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl4^i	0.91	2.29	3.028 (2)	138

Symmetry code: (i) $x, y, z + 1$.

Data collection: CrystalClear (Rigaku, 2005); cell refinement: CrystalClear; data reduction: CrystalClear; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

References

Katrusiak, A. & Szafrański, M. (2006). J. Am. Chem. Soc. **128**, 15775–15785
Rigaku (2005). CrystalClear. Rigaku Corporation, Tokyo, Japan.
Scott, J. F. (2007). Science, **315**, 954–959.
Sheldrick, G. M. (2008). Acta Cryst. A**64**, 112–122.

supporting information

1,4-Diazoniabicyclo[2.2.2]octane tetrachloroiodate(III) chloride

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S1. Comment

Ferroelectric materials continue to attract much attention due to their potential applications in memory devices (Scott, 2007). Recently, diazabicyclo[2.2.2]octane (dabco) salts with inorganic tetrahedral anions having potassium dihydrophosphate-type (KDP-type) structures have been found to exhibit exceptional dielectric properties (Katrusiak & Szafrański, 2006). In our laboratory, the title compound containing a diprotonated cation, $C_6H_{14}N_2^{2+}$, a tetrachloroiodate and a Cl$^-$ anions, has been synthesized. In this article, the crystal structure of the title compound is reported.

In the title compound (Fig. 1), all the species lie on special positions with only one quarter of each being part of the asymmetric unit. The I(III) ion in a square-planar coordination environment. The Cl3 atom is disordered. The crystal structure is stabilized by intermolecular N—H⋯Cl hydrogen bonds (Table 1).

S2. Experimental

KI (0.5 g) and I_2 (0.7 g) were dissolved in a solution of ethanol (30 ml) and conc. HCl (13 ml) (36%). After addition of 1,4-diazoniabicyclo[2.2.2]octane (1 g) to the above solution, the mixture was stirred for 1 h and then filtered. The filtrate was left at room temperature to allow the solvent to evaporate. Yellow transparent block crystals were obtained after one weeks.

S3. Refinement

All H atoms were placed in calculated positions with C—H = 0.97 Å and N—H = 0.91 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C/N)$. The Cl3 atom was disordered over two sites
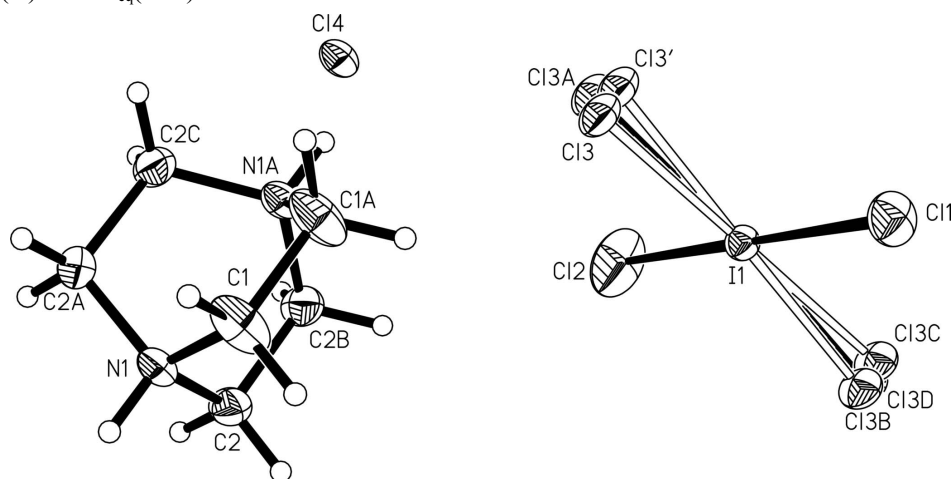
Figure 1

The title compound with atomic labels; displacement ellipsoids were drawn at the 30% probability level.

1,4-Diazoniabicyclo[2.2.2]octane tetrachloroiodate(III) chloride

Crystal data

$C_6H_{14}N_2^{2+} \cdot Cl_4I^- \cdot Cl^-$	$F(000) = 808$
$M_r = 418.34$	$D_x = 2.017$ Mg m^{-3}
Orthorhombic, *Cmcm*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2c 2	Cell parameters from 882 reflections
$a = 8.1496$ (16) Å	$\theta = 3.2$–27.5°
$b = 21.904$ (4) Å	$\mu = 3.26$ mm^{-1}
$c = 7.7184$ (15) Å	$T = 293$ K
$V = 1377.8$ (5) Å^3	Block, yellow
$Z = 4$	$0.28 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer	7175 measured reflections
Radiation source: fine-focus sealed tube	908 independent reflections
Graphite monochromator	882 reflections with $I > 2\sigma(I)$
Detector resolution: 13.6612 pixels mm^{-1}	$R_{int} = 0.028$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan	$h = -10 \rightarrow 10$
(*CrystalClear*; Rigaku, 2005)	$k = -28 \rightarrow 27$
$T_{min} = 0.85$, $T_{max} = 0.90$	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.019$	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 1.0795P]$
$wR(F^2) = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.25$	$(\Delta/\sigma)_{max} < 0.001$
908 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
48 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick,
Primary atom site location: structure-invariant direct methods	2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0042 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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_{iso}*/U_{eq}	Occ. (<1)
N1	0.0000	0.34601 (10)	0.9105 (3)	0.0342 (5)	
H1	0.0000	0.3460	1.0284	0.041*	
C1	0.0000	0.41040 (14)	0.8486 (4)	0.0590 (10)	
H1A	0.0965	0.4315	0.8915	0.071*	0.50
H1B	−0.0965	0.4315	0.8915	0.071*	0.50
C2	0.1498 (3)	0.31364 (11)	0.8488 (3)	0.0442 (5)	
H2A	0.1502	0.2720	0.8917	0.053*	
H2B	0.2472	0.3341	0.8917	0.053*	
I1	0.5000	0.453833 (11)	0.2500	0.03008 (11)	
Cl1	0.5000	0.56970 (5)	0.2500	0.0529 (3)	
Cl2	0.5000	0.34147 (6)	0.2500	0.0918 (6)	
Cl3	0.1864 (17)	0.4465 (8)	0.2500	0.0442 (7)	0.50
Cl3′	0.2037 (18)	0.4541 (8)	0.223 (2)	0.0442 (7)	0.25
Cl4	0.0000	0.27673 (5)	0.2500	0.0396 (2)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0441 (13)	0.0360 (12)	0.0226 (11)	0.000	0.000	0.0025 (9)
C1	0.109 (3)	0.0320 (15)	0.0356 (17)	0.000	0.000	−0.0016 (13)
C2	0.0339 (11)	0.0605 (14)	0.0381 (12)	0.0051 (10)	−0.0025 (9)	0.0047 (10)
I1	0.02875 (15)	0.03053 (15)	0.03098 (15)	0.000	0.000	0.000
Cl1	0.0619 (8)	0.0343 (5)	0.0624 (7)	0.000	0.000	0.000
Cl2	0.0792 (11)	0.0290 (6)	0.167 (2)	0.000	0.000	0.000
Cl3	0.025 (2)	0.055 (3)	0.052 (4)	−0.005 (3)	0.000	0.000
Cl3′	0.025 (2)	0.055 (3)	0.052 (4)	−0.005 (3)	0.000	0.000
Cl4	0.0516 (6)	0.0410 (5)	0.0261 (4)	0.000	0.000	0.000

Geometric parameters (Å, º)

N1—C1	1.489 (4)	I1—Cl3′	2.424 (16)
N1—C2	1.490 (2)	I1—Cl3′iii	2.424 (16)
N1—C2i	1.490 (2)	I1—Cl3′iv	2.424 (16)
N1—H1	0.9100	I1—Cl3′v	2.424 (16)
C1—C1ii	1.522 (7)	I1—Cl2	2.4612 (14)
C1—H1A	0.9700	I1—Cl1	2.5379 (13)
C1—H1B	0.9700	I1—Cl3	2.561 (15)
C2—C2ii	1.525 (4)	I1—Cl3iv	2.561 (15)
C2—H2A	0.9700	Cl3′—Cl3′v	0.42 (4)
C2—H2B	0.9700		
C1—N1—C2	110.37 (15)	Cl3′iv—I1—Cl3′v	179.7 (8)
C1—N1—C2i	110.37 (15)	Cl3′—I1—Cl2	90.2 (4)
C2—N1—C2i	110.0 (2)	Cl3′iii—I1—Cl2	90.2 (4)
C1—N1—H1	108.7	Cl3′iv—I1—Cl2	90.2 (4)

C2—N1—H1	108.7	Cl3$^{\prime v}$—I1—Cl2	90.2 (4)
C2^i—N1—H1	108.7	Cl3$^\prime$—I1—Cl1	89.8 (4)
N1—C1—C1^{ii}	108.72 (16)	Cl3$^{\prime iii}$—I1—Cl1	89.8 (4)
N1—C1—H1A	109.9	Cl3$^{\prime iv}$—I1—Cl1	89.8 (4)
C1^{ii}—C1—H1A	109.9	Cl3$^{\prime v}$—I1—Cl1	89.8 (4)
N1—C1—H1B	109.9	Cl2—I1—Cl1	180.0
C1^{ii}—C1—H1B	109.9	Cl3$^{\prime iii}$—I1—Cl3	173.9 (4)
H1A—C1—H1B	108.3	Cl3$^{\prime iv}$—I1—Cl3	173.9 (4)
N1—C2—C2^{ii}	108.65 (12)	Cl2—I1—Cl3	86.4 (4)
N1—C2—H2A	110.0	Cl1—I1—Cl3	93.6 (4)
C2^{ii}—C2—H2A	110.0	Cl3$^\prime$—I1—Cl3^{iv}	173.9 (4)
N1—C2—H2B	110.0	Cl3$^{\prime v}$—I1—Cl3^{iv}	173.9 (4)
C2^{ii}—C2—H2B	110.0	Cl2—I1—Cl3^{iv}	86.4 (4)
H2A—C2—H2B	108.3	Cl1—I1—Cl3^{iv}	93.6 (4)
Cl3$^\prime$—I1—Cl3$^{\prime iii}$	179.7 (9)	Cl3—I1—Cl3^{iv}	172.8 (7)
Cl3$^\prime$—I1—Cl3$^{\prime iv}$	170.0 (8)	Cl3$^{\prime v}$—Cl3$^\prime$—I1	85.0 (4)
Cl3$^{\prime iii}$—I1—Cl3$^{\prime v}$	170.0 (8)		

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl4^{vi}	0.91	2.29	3.028 (2)	138

Symmetry code: (vi) x, y, z+1.