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Bis(1,10-phenanthroline-1-ium) chlorodiodide(1-) dichloriodide(1-)

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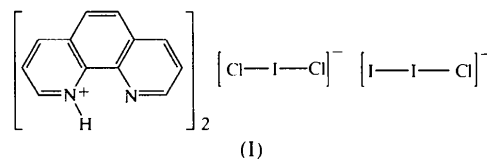
Abstract

The title compound, $2C_{12}H_9N_2^+ \cdot I_2Cl^- \cdot ICl_2^-$, consists of 1,10-phenanthroline-1-ium ($phenH^+$) cations, trihalide anions (ICl_2^-) and the polyanion $[I_2Cl^-]_n$. The $phenH^+$ cations stack in columns and the $[I_2Cl^-]_n$ polyanion forms chains, both running along the *a* direction. The packing of the $phenH^+$ columns produces channels occupied by the $[I_2Cl^-]_n$ chains and cavities occupied by the ICl_2^- anions. Hydrogen bonds between the N—H groups of $phenH^+$ and Cl atoms of the I_2Cl^- chain, along with many weak C—H...X (*X* = Cl, I) interactions, play important roles in the formation of the crystal structure.

Comment

Polyhalides display a variety of structures and belong to a class of long known but poorly understood ma-

terials (Poli *et al.*, 1992; Bailar *et al.*, 1973). During the last decade, various compounds with interesting structures were found when protonated aromatic nitrogen bases were combined with polyhalides. Many of these structures possess interesting hydrogen-bonding patterns. These aromatic nitrogen bases include pyridine (El-Kholi *et al.*, 1988; Hendrixson *et al.*, 1991), bipyridine (Tebbe & Bittner, 1995; Liu *et al.*, 1992) and quinoline (Liu *et al.*, 1991). Rich polyhalide chemistry is found in these simple systems with structures varying from discrete to extended. For example, in the 2,2'-bipyridine- I_2 -HI (Tebbe & Bittner, 1995) system, different polyiodides are produced simply by adjusting the molar ratio of the reactants. We have investigated recently the 1,10-phenanthroline-HCl-KI- I_2 system. At least three different types of crystals have been obtained. The title compound, (I), is one of them, and its crystal structure is reported here.



The asymmetric unit consists of two mono-protonated 1,10-phenanthroline cations ($phenH^+$) and two different trihalide moieties, ICl_2^- and I_2Cl^- (Fig. 1). Both $phenH^+$ cations are planar, with deviations of the non-H atoms from the least-squares plane of less than 0.020 (3) Å in the $phenH^+$ cation (A) consisting of N1, N2, C1 to C12, and 0.039 (4) Å in the $phenH^+$ cation (B) defined by N3, N4, C13 to C24. The angle between the two planar cations in the asymmetric unit is 53.68 (6)°. Compared with the neutral base, 1,10-phenanthroline (Nishigaki *et al.*, 1978), the bond distances in the $phenH^+$ cations show no significant differences, but some internal bond angles vary slightly. The internal

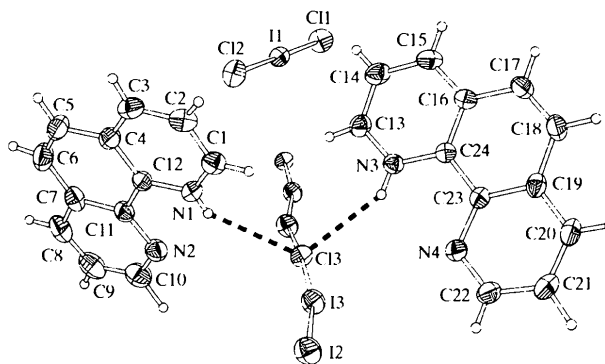


Fig. 1. The molecular structure of (I) drawn with 30% probability displacement ellipsoids.

bond angles at the protonated N atoms (N1 and N3) are *ca* 5° larger than those in neutral 1,10-phenanthroline, while those at the neutral N atoms (N2 and N4) are slightly smaller than those in 1,10-phenanthroline. The enhancement of the internal angles at the protonated N atoms was also reported for quinolinium (quinH⁺; Liu *et al.*, 1991), 8-hydroxyquinolinium (Balasubramanian & Muthiah, 1996*a,b*) and bipyridinium (Liu *et al.*, 1992). This is due to the formation of N—H bonds, which have a less repulsive effect on the N—C bonds than the lone electron pair (Shriver *et al.*, 1994), and the N—H···X hydrogen bond (Jebamony & Muthiah, 1998).

The phenH⁺ cations, *A* and *B*, stack alternately to form columns running along the *a* direction. In one column, the neutral rings of adjacent phenH⁺ cations overlap each other, and are opposite in orientation. They are almost parallel to each other, as the angle between the stacked *A* and *B* cations is 1.35 (10)°. The cations are inclined relative to the stacking direction and are separated by *ca* 3.55 Å.

The ICl₂⁻ anion is almost linear and symmetric, with Cl—I distances of 2.5417 (11) and 2.5575 (10) Å, and a Cl—I—Cl angle of 178.65 (4)°, similar to that reported in the literature (Bailar *et al.*, 1973). The [I₂Cl⁻]_{*n*} polyanion, which is an infinite chain with the I₂Cl⁻ moiety as the chain unit, is the most interesting part of the structure. To the best of our knowledge, this work is the first structural characterization of the I₂Cl⁻ moiety in an organic structure. The I—I distance of 2.7371 (4) Å is obviously smaller than those in I₃⁻ (Tebbe & Bittner, 1995; Liu *et al.*, 1991, 1992), but close to that in neutral iodine (Bailey *et al.*, 1992; Tebbe & Nagel, 1995). The I—Cl distances of 3.0404 (9) and 3.1584 (9) Å indicate that the I—Cl bonds are covalent, as these bond distances are much smaller than the sum of the van der Waals radii (*ca* 4.2 Å). The [I₂Cl⁻]_{*n*} chain propagates along the *a* direction and fluctuates slightly, as the I—Cl—I and I—I—Cl angles differ slightly from 180°.

The packing of the phenH⁺ columns gives two different types of interstices for the occupation of the [I₂Cl⁻]_{*n*} chain and the ICl₂⁻ anion. A large infinite channel is formed by three adjacent phenH⁺ columns and is occupied by the [I₂Cl⁻]_{*n*} chain. The inner wall of the channel is lined with the positive ends, *i.e.* the H atoms of C—H and N—H bonds of the phenH⁺ cations. These C—H and N—H bonds point to the [I₂Cl⁻]_{*n*} chain in the channel. In this combination of positive channel and negative chain, many C—H···X (X = Cl, I) and N—H···Cl interactions exist. Each Cl atom of the [I₂Cl⁻]_{*n*} chain forms two N—H···Cl hydrogen bonds with two phenH⁺ cations in the two adjacent phenH⁺ columns. The N···Cl distances of 3.181 (3) and 3.162 (3) Å, and the N1···Cl···N3 angle of 103.78 (8)°, are comparable to those found in [(quinH⁺)₃Cl(I₃)₂] (Liu *et al.*, 1991). The Cl atom is also involved in one C—H···Cl interaction or hydrogen bond, with a

short H···Cl contact, from the third phenH⁺ column. The Cl atom is therefore surrounded by three H atoms with short H···Cl contacts of 2.53 (4) and 2.48 (4) Å for two N—H groups, and 2.82 (5) Å for the C—H group. The three H···Cl···H angles are 117 (1), 102 (1) and 140 (1)°. The I atoms of the [I₂Cl⁻]_{*n*} chain are also involved in some C—H···I interactions, with short H···I distances ranging from 3.05 (5) to 3.13 (5) Å. The other interstices are small long-shaped cavities. They are formed between another three adjacent phenH⁺ columns and are occupied by ICl₂⁻ anions. Each ICl₂⁻ anion is surrounded by nine phenH⁺ cations, and the two negative ends of the ICl₂⁻ anion, *i.e.* the Cl atoms, point to the two positive pyridinium rings of the two cations at the top and the bottom of the cavity. The inner side wall of the cavity is also built by the H atoms of C—H groups provided by seven surrounding phenH⁺ cations in a style similar to those found in the aforementioned channel. So there are also many C—H···X (X = Cl, I) interactions in this part of the structure, with short H···Cl distances ranging from 2.84 (4) to 2.93 (4) Å and H···I distances ranging from 3.24 (4) to 3.31 (4) Å. These intermolecular interactions certainly have an important role in and give interesting characteristics to the packing of the crystal structure (Fig. 2).

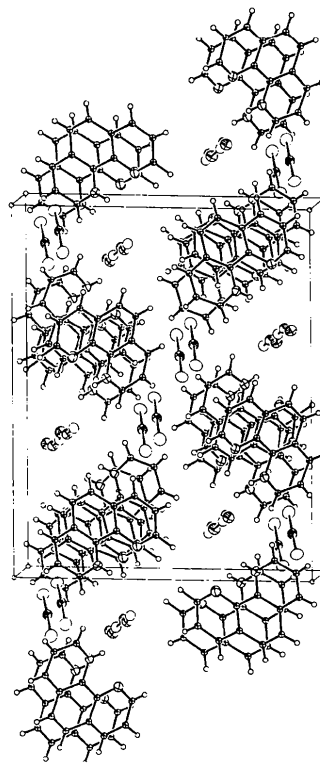


Fig. 2. A packing diagram for (I) viewed along the *a* direction. H atoms have been omitted for clarity.

Experimental

KI (1.17 g) and I₂ (1.36 g) were dissolved in a mixed solution of ethanol (70 ml) and concentrated hydrochloric acid (30 ml) (36%). On addition of 1,10-phenanthroline (0.50 g) to the above solution (10 ml), a dark-red precipitate formed. The mixture was stirred for 48 h, then filtered. The filtrate was left at room temperature to allow the solvent to evaporate. Light-yellow transparent rectangular crystals were obtained after two weeks and dark-red transparent columnar crystals of the title compound were obtained after one month. Elemental analysis, found: C 33.93, H 2.00, N 6.67%; analysis calculated for C₂₄H₁₈Cl₃I₃N₄: C 33.90, H 2.12, N 6.50%.

Crystal data

2C₁₂H₉N₂⁺·I₂Cl⁻·ICl₂⁻
M_r = 849.47
 Monoclinic
*P*2₁/*c*
a = 8.9031 (4) Å
b = 15.7897 (6) Å
c = 20.0697 (7) Å
 β = 99.569 (4)°
V = 2782.09 (19) Å³
Z = 4
D_x = 2.028 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 11.46–13.75°
 μ = 3.679 mm⁻¹
T = 293 (2) K
 Column
 0.40 × 0.19 × 0.19 mm
 Dark red

Data collection

Enraf–Nonius CAD-4
 MACH3 diffractometer
 θ – 2θ scans
 Absorption correction:
 ψ scan (North *et al.*,
 1968)
 T_{\min} = 0.441, T_{\max} = 0.497
 7821 measured reflections
 7376 independent reflections

5866 reflections with
 $I > 2\sigma(I)$
 R_{int} = 0.009
 θ_{max} = 28.99°
 h = –12 → 0
 k = 0 → 21
 l = –26 → 27
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.033
 $wR(F^2)$ = 0.075
 S = 1.084
 7376 reflections
 379 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 2.6180P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}}$ = 0.003
 $\Delta\rho_{\text{max}}$ = 0.617 e Å⁻³
 $\Delta\rho_{\text{min}}$ = –0.783 e Å⁻³
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|------------|-------------|-------------|------------|
| I1—C11 | 2.5417 (11) | I3—C13 | 3.0404 (9) |
| I1—C12 | 2.5575 (10) | C13—I2' | 3.1584 (9) |
| I2—I3 | 2.7371 (4) | | |
| C11—I1—C12 | 178.65 (4) | I3—C13—I2' | 174.44 (3) |
| I2—I3—C13 | 172.11 (2) | C13''—I2—I3 | 168.68 (2) |

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$.

Table 2. Hydrogen-bonding geometry (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|------------------|----------|----------|-----------|---------|
| N1—H1...C13 | 0.76 (4) | 2.53 (4) | 3.162 (3) | 142 (4) |
| N3—H10...C13 | 0.80 (4) | 2.48 (4) | 3.181 (3) | 148 (4) |
| C1—H2...C11' | 0.88 (4) | 2.90 (4) | 3.606 (4) | 138 (4) |
| C5—H5...C11'' | 0.93 (5) | 2.90 (5) | 3.667 (5) | 141 (4) |
| C6—H6...I2''' | 0.92 (5) | 3.05 (5) | 3.813 (4) | 142 (4) |
| C13—H11...C12 | 0.86 (4) | 2.93 (4) | 3.531 (4) | 128 (3) |
| C14—H12...I1 | 0.89 (4) | 3.24 (4) | 3.900 (4) | 133 (3) |
| C15—H13...C13'' | 0.87 (5) | 2.82 (5) | 3.634 (4) | 158 (4) |
| C18—H15...I3' | 0.95 (5) | 3.13 (5) | 3.956 (4) | 146 (4) |
| C21—H17...C12'' | 1.04 (5) | 2.84 (4) | 3.722 (4) | 143 (3) |
| C22—H18...I1'''' | 0.86 (4) | 3.31 (4) | 3.983 (4) | 137 (4) |

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (vi) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; (vii) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

All H atoms were located by difference Fourier synthesis, and refined isotropically. C—H distances are in the range 0.84 (4)–1.09 (6) Å.

Data collection: CAD-4 ARGUS Software (Nonius, 1996). Cell refinement: CAD-4 ARGUS Software. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: SHELXTL/PC (Sheldrick, 1990) and ZORTEP (Zsolnai, 1998). Software used to prepare material for publication: SHELXL97.

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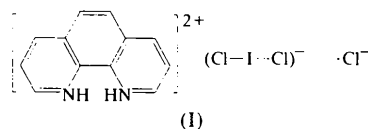
Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1070). Services for accessing these data are described at the back of the journal.

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or diprotonated resulting in diverse structures. In the system 1,10-phenanthroline–HCl–KI–I₂, several compounds have been obtained under different conditions (Wang *et al.*, 1999), of which the title compound, (I), is one example.



The crystal structure of (I) consists of diprotonated 1,10-phenanthroline cations (phenH_2^{2+}), and Cl^- and ICl_2^- anions (Fig. 1). In the phenH_2^{2+} cations, the bond lengths are very similar to those in neutral 1,10-phenanthroline (Nishigaki *et al.*, 1978), but the C—N angles [both $122.7(3)^\circ$] are significantly greater than the corresponding values in the neutral species [$117.2(6)$ – $117.9(5)^\circ$], in agreement with other structures containing protonated 1,10-phenanthroline (Hensen *et al.*, 1998; Lis, 1979). The enlargement of the internal angles at the protonated N atoms was also reported for quinolinium (Liu *et al.*, 1991), 8-hydroxyquinolinium (Balasubramanian & Muthiah, 1996) and bipyridinium (Liu *et al.*, 1992). The phenH_2^{2+} cation is planar and parallel to the *ac* plane, with deviations from the least-squares plane of less than $0.057(3) \text{ \AA}$.

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1,10-Phenanthroline(2+) dichloroiodide(1-) chloride

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Abstract

The title compound, $\text{C}_{12}\text{H}_{10}\text{N}_2^{2+} \cdot \text{ICl}_2^- \cdot \text{Cl}^-$, consists of 1,10-phenanthroline(2+) cations (phenH_2^{2+}), and ICl_2^- and Cl^- anions. The ICl_2^- anions occupy two crystallographic sites, one on a twofold axis and the other on a centre of symmetry. The phenH_2^{2+} cations build up positive columns along the *b* direction, while the ICl_2^- anions form infinite branched zigzag chains running along the *a* direction. The Cl^- anions embedded in the interstices of the positive columns form N—H...Cl hydrogen bonds, which contribute to the stabilization of the structure.

Comment

During the last decade, there has been considerable interest in the structure and properties of species obtained by combining protonated aromatic nitrogen bases with halide or polyhalide ions (El-Kholi *et al.*, 1988; Hendrixson *et al.*, 1991; Liu *et al.*, 1991, 1992; Tebbe *et al.*, 1995). Among these aromatic nitrogen bases, 1,10-phenanthroline is a good candidate for study as it has two close aromatic N atoms which can be neutral, mono-

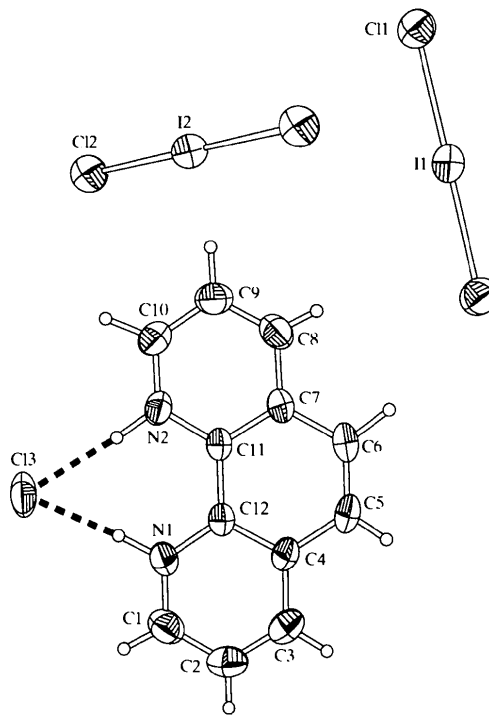


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.