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The Polyiodide Salts: Pyridinium Pentaiodide; β-Naphthylammonium Pentaiodide; and *N*-Methyl-γ-Picolinium Heptaiodide. Structures with Channel Inclusion Features*

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Abstract. The crystal structures of three polyiodode salts are reported (pyridinium pentaiodide, monoclinic, $P2_1/m$, $a = 9.221(5)$, $b = 12.918(5)$, $c = 6.026(4)$ Å, $\beta = 103.60(7)°$, $Z = 2$, $R_F = 0.087$ for 1187 intensities; β-naphthylammonium pentaiodide, triclinic, $P\bar{1}$, $a = 10.390(5)$, $b = 9.502(5)$, $c = 4.462(3)$ Å, $\alpha = 99.19(7)$, $\beta = 90.40(7)$, $\gamma = 108.49(8)°$, $Z = 2$, $R_F = 0.059$ for 1319 intensities; *N*-methyl-γ-picolinium heptaiodide, monoclinic, $C2/c$, $a = 19.315(7)$, $b = 12.714(5)$, $c = 8.442(4)$ Å, $\beta = 107.26(7)°$, $Z = 4$, $R_F = 0.065$ for 1336 intensities). All three structures can be described as having channel inclusion features; the cations are contained in channels in polyiodide frameworks based on different arrangements of I_2 molecules and I_3^- anions. This structural type is the converse of the more widespread kind where polyiodide anions are contained in an organic matrix (e.g., cyclodextrin polyiodides).

Key words: Polyiodide salts, pyridinium pentaiodide, β-naphthylammonium pentaiodide, *N*-methyl-γ-picolinium heptaiodide, channel inclusion arrangement, crystal structure.

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1. Introduction

Crystalline polyiodides have been known for about 170 years [1] and a rich structural chemistry has developed [2–4]. A variety of geometrical arrangements has been found, generally based on similar first-neighbour interactions but with overall structures which depend on the cation present. Some of these structures belong to the channel inclusion category, particularly when the polyiodide is quasi-linear. Typical examples with linear chains of triiodides are $(n\text{—}C_4H_7)_4NI_3$, bis(benzamide) hydrogen triiodide and caffeine monohydrate hydrogen triiodide [5]. Higher polyiodides are found in [α-cyclodextrin (CD)]$_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$, $(\alpha\text{-CD})_2Cd_{0.5}I_5 \cdot 26H_2O$ [6], $(\beta\text{-CD})_2 \cdot KI_7 \cdot 9H_2O$ [7] and trimesic acid $0.7H_2O \cdot 0.09HI_5$ and analogues [8]. These crystals have one structural feature in common – the polyiodide anion is enclosed within a framework formed by the organic moieties. We now report the structures of three polyiodide salts in which the converse situation

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holds – the organic cations are held within a framework formed by the polyiodide anions, which themselves are composed of iodine molecules and triiodide anions linked together in various ways.

2. Experimental

2.1. PREPARATION OF CRYSTALS

(a) Preparation of pyridinium pentaiodide: Crystals were obtained by the method of Prescott and Trowbridge [9–11]. The most common crystals were black prisms or plates which were found to be orthorhombic. Although no unusual features could be detected by Weissenberg photography, all attempts to solve the structure by means of ordered models have failed so far. In one preparation, a second, *monoclinic*, modification was obtained with a unit cell volume half that of the orthorhombic phase. This structure was solved without difficulty and refined in routine fashion.

(b) Preparation of β-naphthylammonium pentaiodide: β-naphthylamine was dissolved in ethanol and an ethanol solution containing 1 : 1 HI/I_2 added. The oily residue remaining after evaporation of the solvent solidified within a few days. Inspection under the microscope showed small single crystals of good diffraction quality growing out of the bulk. These were shown to be β-naphthylammonium pentaiodide.

(c) Preparation of *N*-methyl-γ-picolinium heptaiodide: Following Murrill [12] 250 mg of *N*-methyl-γ-picolinium iodide (prepared and purified by standard procedures from γ-picoline and methyl iodide) was refluxed for 30 min in I_2-saturated ethanol. Slow cooling of the solution in a Dewar container yielded two types of crystals: brown plates (presumably the triiodide salt but not examined further) and black crystals of either platelike or needle-shaped appearance. Diffraction photography showed that the needles and plates had the same cell dimensions; the needles were twinned while no such problems were encountered with the plates.

2.2. CRYSTALLOGRAPHIC MEASUREMENTS AND RESULTS

(a) *Diffraction studies*

All the crystals were deeply colored. After preliminary diffraction photography to check crystal quality and determine unit cell symmetry and approximate dimensions, suitable crystals were sealed into thin-walled glass capillaries and mounted on a Philips PW-1100 four-circle diffractometer. Elemental analyses were not made as the compositions emerged from the crystal data and were substantiated by the structure analyses. Crystal data and details of the intensity measurements are given below. Graphite-monochromated Mo$K\alpha$ (λ = 0.71069 Å) was used for all diffractometer measurements.

(b) *Solution and refinement of structures*

The crystal structures were generally solved by a combination of Patterson and direct methods, and refined by standard least-squares techniques, using MULTAN [13] and the SHELX-77 [14] program set. Hydrogen atoms were not located in any of the structure analyses. The structure factors and anisotropic temperature factors for the three structure analyses have been deposited.

(c) *Pyridinium pentaiodide*

Monoclinic, $P2_1/m$, $a = 9.221(5)$, $b = 12.918(5)$, $c = 6.026(4)$ Å, $\beta = 103.60(7)°$, $V = 697.7(5)$ Å^3, $Z = 2$, Mo$K\alpha$ ($\lambda = 0.71069$ Å), $\mu = 104.0$ cm^{-1}, $F(000) = 616$, $T = 298$ K, $R_F = 0.087$ for 1187 intensities. Cell dimensions from 25 strong, high-angle reflections, intensities of 1396 reflections ($-10 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 7$) measured, $\omega/2\theta$ measurement mode, no absorption correction, scan range, speed and width $5° < 2\theta < 45°$, $3.0°\ \omega$ min^{-1} and $1.3°\ \omega$, respectively, standard reflections 103, 211, 110; refinement on F converged after inclusion of all nonhydrogen atoms, 1187 reflections used (reflections for which $F_o < 1.5\sigma(F_o)$ suppressed), 56 parameters refined in final cycle, unit weights, final difference synthesis revealed excursions between 2.6 and -2.7 eÅ^{-3} (in the vicinity of the I atoms).

Atomic parameters are listed in Table I.

Table I. Pyridinium pentaiodide – atomic parameters (× 10^4 for the iodine atoms and × 10^3 for the rest). $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Atom	x	y	z	U_{eq} (Å^2)
I(1)	4606(2)	4271(2)	−3559(3)	440(4)
I(2)	3911(3)	2500	274(4)	402(6)
I(3)	7257(3)	2500	2191(4)	408(6)
I(4)	10430(3)	2500	3589(6)	614(9)
C(1)[a]	907(3)	47(3)	−178(6)	67(9)
C(2)	847(3)	2(2)	−23(5)	50(7)
C(3)	943(3)	−51(3)	164(5)	64(10)

[a] The pyridinium ring was rotationally disordered and the nitrogen atom could not be identified; thus the atoms designated as C were treated as (5/6C + 1/6N).

(d) *β-Naphthylammonium pentaiodide*

Triclinic, $P\bar{1}$, $a = 10.390(5)$, $b = 9.502(5)$, $c = 4.462(3)$ Å, $\alpha = 99.19(7)$, $\beta = 90.40(7)$, $\gamma = 108.49(8)°$, $V = 411.6(7)$ Å^3, $Z = 2$, Mo$K\alpha$($\lambda = 0.71069$ Å), $\mu = 88.2$ cm^{-1}, $F(000) = 342$, $T = 298$ K, $R_F = 0.051$ ($R_w = 0.059$) for 1319 intensities. Cell dimensions from 25 strong high-angle reflections, intensities of 1435 reflections ($-12 \leq h \leq 12$, $-11 \leq k \leq 11$, $0 \leq l \leq 5$) measured, $\omega/2\theta$ measurement mode, no absorption correction; scan range, speed and width $5° < 2\theta < 50°$, $2.4°\ \omega$ min^{-1} and $1.3°\ \omega$, respectively, standard reflections 101, 230, 410; refinement on F converged after inclusion of all nonhydrogen atoms, 1319 reflections used (reflections for which $F_o < 1.5\sigma(F_o)$ suppressed), 79 parameters refined in final cycle; weighting scheme $w = 1.189/[\sigma^2(F_o)]$, final difference synthesis revealed excursions between 1.7 and -1.9 eÅ^{-3} (in the vicinity of the I atoms).

Atomic parameters are in Table II.

(e) *N-methyl-γ-picolinium heptaiodide*

Monoclinic, $C2/c$, $a = 19.315(7)$, $b = 12.714(5)$, $c = 8.442(4)$ Å, $\beta = 107.26(7)°$, $V = 1979.7(5)$ Å^3, $Z = 4$, μ(Mo$K\alpha$) $= 102.6$ cm^{-1}, $F(000) = 1720$, $T = 298$ K, $R_F = 0.065$ ($R_w = 0.058$) for 1336 intensities. Cell dimensions from 25 strong, high-angle reflections, intensities of 1680 unique reflections ($-21 \leq h \leq 21$; $0 \leq k \leq 15$; $0 \leq l \leq 9$) measured, $\omega/2\theta$

Table II. β-Naphthylammonium pentaiodide-atomic parameters ($\times 10^4$ for the iodine atoms and $\times 10^3$ for the rest)

Atom	x	y	z	U_{eq} (Å^2)
I(1)	0	0	0	495(3)
I(2)	620(1)	- 2776(1)	75(2)	568(2)
I(3)	6265(1)	699(1)	6363(2)	449(2)
C(1)	419(1)	603(1)	- 226(3)	46(3)
C(2)	313(1)	486(1)	- 360(3)	50(3)
C(3)	285(1)	337(1)	- 312(3)	51(3)
C(4)	374(1)	310(1)	- 121(2)	45(3)
C(5)	513(1)	577(1)	- 27(2)	37(2)
N(1)	227(2)	515(3)	- 555(4)	57(6)

measurement mode, no absorption correction; scan range, speed and width $5° < 2\theta < 50°$, $1.5°\omega\ \mathrm{min}^{-1}$ and $1.10°\omega$, respectively, standard reflections 031, 231, 233; refinement on F converged after inclusion of all nonhydrogen atoms, 1336 reflections used (reflections for which $F_o < 1.5\sigma(F_o)$ supressed), 70 parameters refined in final cycle; weighting scheme $1.664/[\sigma^2(F_o)]$, final difference synthesis revealed excursions between ± 1.2 eÅ^{-3} (in the vicinity of the I atoms).

Atomic parameters are listed in Table III.

Table III. N-methyl-γ-picolinium heptaiodide-atomic parameters ($\times 10^4$ for the iodine atoms and $\times 10^3$ for the rest)

Atom	x	y	z	U_{eq} (Å^2)
I(1)	5695(1)	4510(1)	- 1484(1)	585(3)
I(2)	9260(1)	4488(1)	2160(2)	758(4)
I(3)	7400(1)	4521(1)	1549(2)	732(3)
I(4)	7500	2500	0	688(5)
C(1)[a]	649(1)	752(1)	952(3)	86(6)
C(2)	572(1)	754(1)	850(2)	59(4)
C(3)	516(1)	750(1)	919(2)	71(6)
C(4)	557(1)	752(1)	681(3)	71(5)

[a] Treated as ($\frac{1}{2}$C + $\frac{1}{2}$N).

3. Descriptions of the Crystal Structures

3.1. PYRIDINIUM PENTAIODIDE

The crystal packing (ORTEP [15] stereodiagram in Figure 1) can be described as an arrangement of pleated sheets of iodines pierced by channels of almost square cross-section which extend along the c-axis. The iodine arrangement (Figure 2) is based on zigzag chains of I_2 molecules (at centres of symmetry) linked through terminal I atoms of I_3^- ions (in mirror planes). The other terminal I of I_3^- makes a van der Waals contact ($d = 4.160(4)$ Å) with a terminal I of an I_3^- from an adjacent chain. The pleated sheet formed in this way has pleat lines along [100], with the planes of the pleats along (021) and ($02\bar{1}$).

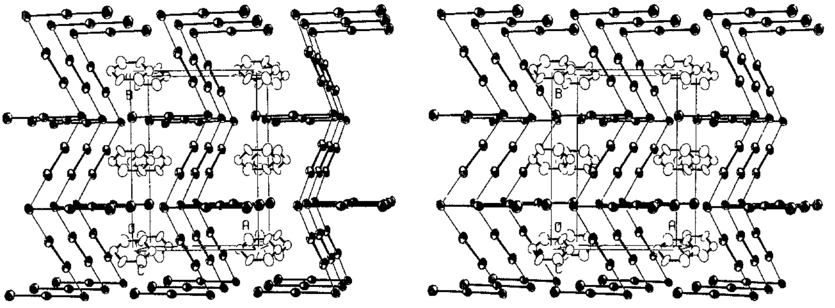

Fig. 1. Pyridinium pentaiodide – ORTEP stereoview of overall structural arrangement. The thermal motion ellipsoids represent 50% probability distributions.

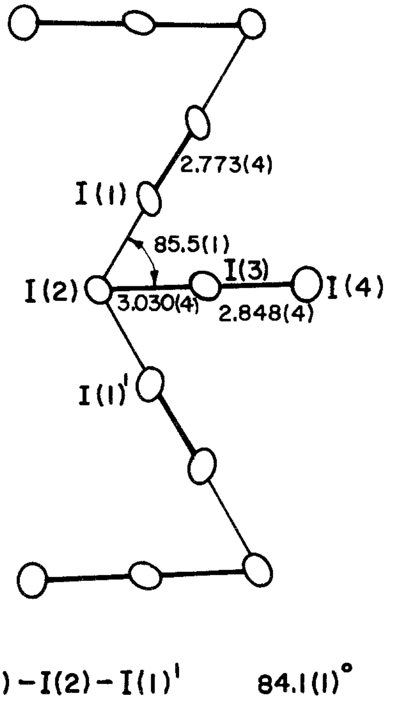

Fig. 2. Pyridinium pentaiodide – arrangement of I_2 and I_3^- in the framework motif. The independent iodine atoms of the reference molecule (coordinates in Table I) are labelled.

The $I_3^- \cdots I_2$ units are not coplanar but rather define two parallel planes above and below the inversion center around which the pyridinium ion is located (and thus has at least a twofold disorder imposed by crystal symmetry). Attempts made to identify the nitrogen *via* thermal parameters and possible $N—H \cdots I$ hydrogen bonds were not successful.

The $I_2 \cdots I_3^-$ interaction is fairly strong as is shown by elongation of I_2 to 2.773(4) Å (compared to the gas-phase distance of 2.667 Å – see reference 16 of Herbstein and Schwotzer [16] for summary of earlier results) and also by the appreciable asymmetry of the bond lengths in the triiodide ion (3.030(4), 2.848(4) Å). The total length of the I_3^- ion here is 5.878 Å, which is close to the longest I_3^- ion on record (5.904 Å in NH_4I_3 [17] and ~0.08 Å longer than the shortest I_3^- ions on record (5.802(5) and 5.804(5) Å in $[MoCl_4(diars)_2]I_3$ [18] and $[Mo(diars)_2(CO)_2Cl]I_3 \cdot 2CHCl_3$ [19]). The degree of asymmetry ($|[d(I(1)\text{-}I(2))]—[d(I(2)\text{-}I(3))]|$) is 0.182(6) Å in pyridinium pentaiodide, compared to 0.322(6) Å in NH_4I_3. The $I_2 \cdots I_3^-$ distance of 3.417(4) Å lies at the lower end of the range of distance found for such interactions. The iodines are bicoordinate except for one of the terminal iodines of I_3^-, which is pyramidally tricoordinate with bond angles of 85.5(1)° and 84.1(1)°.

3.2. β-NAPHTHYLAMMONIUM PENTAIODIDE

The iodine arrangement consists of zigzag chains (propagation vector [101]) of I_2 and I_3^- moieties, both at centres of symmetry (Figure 3). The dimensions of the chain fall into the range found in analogous arrangements. There is a weak $I_3^- \cdots I_3^-$ interaction between adjacent chains ($dI \cdots I$) = 3.998(2) Å). If this interaction is ignored, then the iodines are all bicoordinate and the I—I—I bond angles are either ~90° or ~180°. The adjacent chains are so disposed as to form a rhomboid 12-membered ring of iodines about an inversion centre, which is occupied by the β-naphthylammonium ion, the cation taking up a disordered superposition of two orientations. There are hydrogen bonds between the NH_3^+ group and the terminal atom of the I_3^- unit, the observed distance ($N \cdots I$) of 3.52(1) Å being substantially shorter than the sum of the van der Waals radii. The overall structure is that of a channel inclusion complex, with the channel axis along *c*.

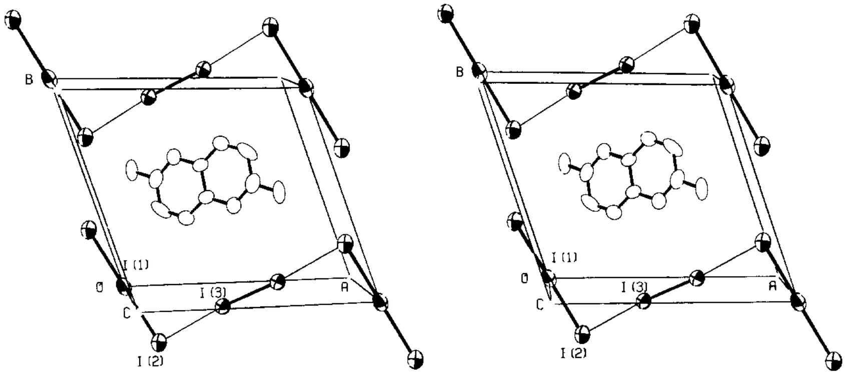

Fig. 3. β-Naphthylammonium pentaiodide – ORTEP stereodiagram of the structure. The thermal motion ellipsoids represent 50% probability distributions. The independent iodine atoms of the reference molecule (coordinates in Table II) are labelled. Relevant distances and angles are:

(i) I_3^- ion $d(I(1)\text{-}I(2)) = 2.912(1)$ Å.

(ii) I_2 molecule $d(I(3)\text{-}I(3')) = 2.716(1)$ Å.

(iii) Intermoiety interactions: distance between terminal iodines in two I_3^- ions separated by translation along [010] is 3.998(2) Å.

$\angle I(1)\text{-}I(2) \cdots I(3) = 89.4(1)°$
$\angle I(2) \cdots I(3)\text{-}I(3') = 174.5(1)°$
$\angle I(1)\text{-}I(2') \cdots I(2'') = 150.1(1)°$.

3.3. *N*-METHYL-γ-PICOLINIUM HEPTAIODIDE

The basic structural unit has the form of a twisted ladder in which I_3^- ions bridge between two zigzag chains of I_2 molecules (Figure 4). The propagation vector of the ladder is parallel to [101].

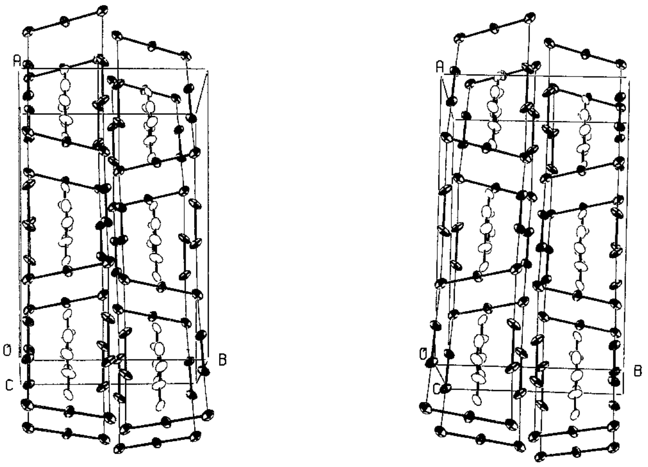

Fig. 4. *N*-methyl-γ-picolinium heptaiodide – ORTEP stereodiagram of the unit cell. The thermal motion ellipsoids represent 50% probability distributions.

The I_3^- ion is at the centre of symmetry on the *n* glide plane (*not* at the origin in the standard setting of the *C*2/*c* space group) and the two iodine molecules of the asymmetric unit are each bisected by two-fold axes. The chains of I_2 molecules extend along [101] and the bridging I_3^- ions approximately along [010]. The interatomic distances (Figure 5) fall within the

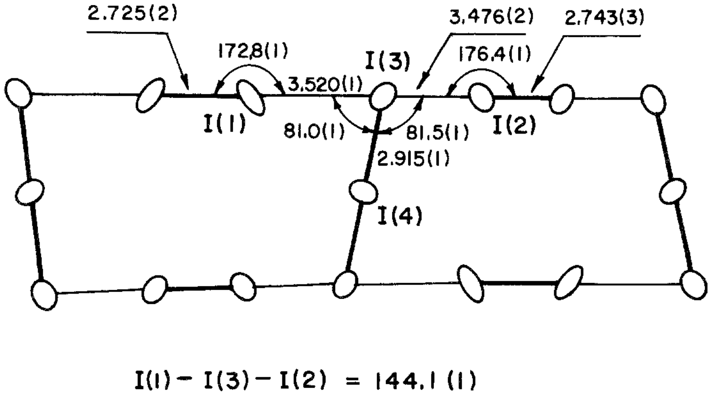

Fig. 5. *N*-methyl-γ-picolinium heptaiodide – the structural motif shown as a twisted ladder which extends along [100]. The independent iodine atoms of the reference molecule (coordinates in Table III) are labelled.

accepted limits. The twisted ladders contain 10-membered rings annulated *via* triiodide ions. The iodines of the I_2 molecules are bicoordinate but the exterior iodines of the triiodides are pyramidally tricoordinate with bond angles of 81.0(1), 81.5(1), and 144.1(1)°.

Channels with axes along [101] are formed by superimposed twisted ladders separated by translation along *c*. The *N*-methyl-γ-picolinium cations are lined up within the channel with an intermolecular contact distance of 3.73(4) Å between adjacent methyl groups. The picolinium cations are found to be planar (mean *y* coordinate is 0.752(2) (Table III)) in accordance with chemical expectations. Furthermore, the crystallographic two-fold axis normal to be ring plane leads to effective $2/m$ symmetry for the cation, although this is not required crystallographically. Thus the cation is lengthwise disordered, the methyl substituted carbon and nitrogen atoms being indistinguishable.

There are two twisted ladders per unit cell, related by the *c* glide; it is their mutual displacement along *z* which gives rise to formation of chains rather than sheets of cations. The size of the iodine atoms is such that they largely fill the interstices of the twisted ladder structure and prevent any egress of cations in the *z* direction.

4. Discussion

4.1. OVERALL ARRANGEMENTS

The structures of all three salts reported here can be described in terms of inclusion of cations in the channels formed by networks of I_2 molecules and I_3^- ions. In the pyridinium pentaiodide and *N*-methyl-γ-picolinium heptaiodide structures there are only Coulombic interactions between included cations and surrounding anions and these are thus ionic channel inclusion complexes where host···host interactions (here between I_2 and I_3^-) predominate. They are analogous to the urea-hydrocarbon channel inclusion complexes [20, 21] where, however, the moieties are not charged. In β-naphthylammonium pentaiodide the Coulombic interactions are supplemented by host-guest hydrogen bonding; thus the resemblance here is to the Heilbron complex DHDK: *p*-dimethylaminobenzaldehyde which can be formally described as a channel inclusion complex with host-guest hydrogen bonding [22].

Only a few other examples of polyiodide inclusion complexes are known in which the cations are contained in the polyiodide framework; among these are bis(pyridine)iodinium heptaiodide [23], quinuclidinium pentaiodide [24] and tetraethylammonium heptaiodide [25]. The various types of polyiodide networks are discussed below.

4.2. IODINE ARRANGEMENTS

Polyiodides composed of strongly interacting I_2 and I_3^- subunits are common [26]; the stronger secondary interactions between I_2 and I_3^- are characterized by interatomic distances of 3.4–3.6 Å while weaker interactions are indicated by longer distances which extend up to ~4.2 Å, the sum of the van der Waals radii. The iodine atoms in crystalline I_2 are tricoordinate, with each making two I···I contacts of 3.496(6) Å, the corresponding I—I···I angles being 84.2(1)° and 170.1(1)° [27]. However the iodines of I_2 appear always to be bicoordinate in $I_2 \cdots I_3^-$ salts. The terminal I of I_3^- is tricoordinate in these salts, with $d(\mathrm{I}\cdots\mathrm{I})$ lying in the range from 3.4 to 4.2 Å, and the pyramidal angles varying from ~90° to ~180°.

Zigzag chains of iodine molecules linked through terminal iodines of I_3^- ions are a characteristic feature of the structures of pyridinium pentaiodide, *N*-methyl-γ-picolinium heptaiodide and tetraethylammonium heptaiodide but the ways in which such chains are constructed and connected are quite different in the three salts. In pyridinium pentaiodide adjacent I_3^- ions in the $\cdots I_2 \cdots I \cdots I_2 \cdots$chain are antiparallel and pendant (i.e., only one of the iodines is tricoordinate) with bond angles of 84.1(1) and 85.5(1)°. In both *N*-methyl-γ-picolinium heptaiodide and tetraethylammonium heptaiodide both terminal iodines of I_3^- are tricoordinate, with the I_3^- ions bridging between adjacent zigzag I_2 chains; however this bridging occurs in different ways (cf. Figure 4 here and Figure 2 of reference [25]). One consequence is that tetraethylammonium heptaiodide has a clathrate rather than a channel inclusion complex type structure.

Formation of rings of iodines enclosing a cation has been found in a number of polyiodide salts. There are rather similar 12-membered rhomboid rings in β-naphthylammonium pentaiodide and in diferrocenylselenium iodine triiodide hemi (methylene chloride) [28], while quinuclidinium pentaiodide has 12-membered rings of trapezoidal rather than rhomboid shape [24]. In bis(pyridine)iodinium heptaiodide there are crinkled sheets of I_2 and I_3^- in 2 : 1 ratio; the terminal iodines of the I_3^- ions are tricoordinate and have a distorted pyramidal arrangement of linkages with bond angles of 83.4(3), 108.5(3), and 138.3(3)°. 16-membered rings of roughly rectangular shape are formed and these contain the elongated cations. This salt is a channel inclusion complex in the present sense; not enough detail is available for classification of quinuclidinium pentaiodide.

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