Crystal structures of Zn(cyclam)I₂ (second monoclinic polymorph) and Zn(cyclam)I(I₃)

Sergey P. Gavrish, Sergiu Shova and Yaroslav D. Lampeka

The asymmetric unit of the first title compound iodido(1,4,8,11-tetraazacyclotetradecane-\(\kappa^4N^3,N^4,N^6,N^{11}\))zinc(II) iodide, [ZnI(C₁₀H₂₄N₄)]I, I, consists of the zinc-cyclam macrocyclic cation with one iodide anion coordinated to the metal ion [Zn—I = 2.6619 (5) Å] and the second present as a counter-ion. The asymmetric unit of the second title compound iodido(1,4,8,11-tetraazacyclotetradecane-\(\kappa^6N^3,N^4,N^8,N^{11}\))zinc(II) triiodide, [ZnI(C₁₀H₂₄N₄)]I₃, II, consists of half of the centro symmetric macrocyclic cation, in which the Zn II ion coordinated to an iodide anion [Zn—I = 2.766 (2) Å] is disordered over two positions [Zn—Zn = 0.810 (3) Å], and of the two halves of the crystallographically non-equivalent, non-coordinated, centrosymmetric triiodide anions. In both compounds, the \(\kappa^4\)N,<sub>3</sub>,N<sub>4</sub>,N<sub>6</sub>,N<sub>11</sub>-tetradentate macrocyclic ligand is present in the most energetically favored \(\text{trans-III}\) conformation. In the crystals of I, the [ZnI(C₁₀H₂₄N₄)I]⁺ cations and the non-coordinated iodide anions are linked by N—H—I and bifurcated N—H—I(I,I) hydrogen bonds, resulting in the formation of two-dimensional networks lying parallel to the (001) and (101) planes. In contrast, the crystals of II are built up from infinite chains of the five-coordinate macrocyclic units arranged along the \(b\)-axis direction and perpendicular sheets formed of the triiodide counter-ions without significant hydrogen bonding between them.

1. Chemical context

The 14-membered tetraazamacrocycle 1,4,8,11-tetraazacyclotetradecane (C₁₀H₂₄N₄, cyclam, \(L\)) is one of the most useful and widely studied ligands because of a number of unique properties, such as exceptionally high thermodynamic stability, kinetic inertness and unusual redox properties inherent to its complexes with transition-metal ions (Melson, 1979; Yatsimirskii & Lampeka, 1985). Typically, cyclam coordinates to the metal ion by its four N atoms in a planar manner, leaving two vacant \(\text{trans}\) binding sites in the coordination sphere for additional ligands, including halide anions as an important class. To date, a number of complexes of \([M(L)]^{1+}\) cations \((M = \text{Cu}^{II}, \text{Ni}^{II}, \text{Zn}^{II})\) with halides \(X^- (X = \text{Cl}, \text{Br}, I)\) have been reported (Ito et al., 1984; Adam et al., 1991; Porai-Koshits et al., 1994; Chen et al., 1996; Makhaev et al., 1996; Ha, 2017; Horii et al., 2020).

Typically, the compounds under consideration are prepared by the direct reaction of \(MX_2\) salts with \(L\). We were interested in the development of alternative methods of synthesizing zinc(II) iodide compounds by anion exchange, starting from the initially formed acetate or nitrate species. It was found in the course of this investigation that precipitation of Zn(\(L\))I₂ from the \textit{in situ} formed acetate complex by potassium iodide
in methanol solution occurs slowly (over several days) and results in the formation of the colorless compound I, the structure of which is different from that described previously (Porai-Koshits et al., 1994). When the metathesis reaction was carried out in aqueous solution, a small amount of the iodide/triiodide salt (compound II) was obtained in the form of intensely colored brown crystals. The lattice parameters for this compound were reported by Heinlein & Tebbe (1985) in an alternate setting of the unit cell (see Database Survey) but no atomic coordinates were established. Here, we report the crystal structures of these two compounds, namely, iodido-(1,4,8,11-tetraazacyclotetradecane-N1N4N8N11)zinc(II) iodide, [ZnI(L)]I, I and iodido-(1,4,8,11-tetraazacyclotetradecane-N1N4N8N11)zinc(II) triiodide, [ZnI(L)]I3, II.

2. Structural commentary

The molecular structure of I is shown in Fig. 1. It represents the square-pyramidal macrocyclic [Zn(L)]+ cation with one iodide anion coordinated in the axial position of the zinc(II) ion, while the second iodide anion acts as a counter-ion.

Thus, I belongs to a rather limited family of [Zn(L)] compounds in which the ZnII ion is five-coordinated. Other distinct examples are complexes with thiolate (Notni et al., 2006) and hexacyanoferrate(3–) (Colacio et al., 2001) axial ligands. In the majority of compounds, the ZnII ion is six-coordinated. Analogously to these complexes, the macrocyclic ligand in I adopts the most energetically favorable trans-III (R,R,S,S) conformation (Bosnich et al., 1965).

The coordination polyhedron of the [Zn(L)]I+ cation in I is characterized by a large deviation [0.4412 (14) Å] of the metal ion from the mean N4 plane of donor atoms toward the coordinated iodide ion and this results in conformational peculiarities, distinguishing it from planar tetra- or hexacoordinated species. In particular, this deviation results in non-equivalence of the six-membered chelate rings in chair conformations with syn and anti directivity of the NH-hydrogen atoms with respect to the displacement of the metal ion. In the first case, the ring becomes more flattened at the Zn side, and in the second more puckered. Simultaneously, the five-membered rings in I adopt gauche-envelope conformation.

Table 1

|   | I          | II         |
|---|------------|------------|
| Zn1—N1    | 2.101 (3)  | Zn1—N1    | 2.014 (10) |
| Zn1—N2    | 2.121 (3)  | Zn1—N2    | 2.014 (10) |
| Zn1—N3    | 2.121 (3)  | Zn1—N1i   | 2.179 (10) |
| Zn1—N4    | 2.110 (3)  | Zn1—N2i   | 2.210 (10) |
| Zn1—I1    | 2.6619 (5) | Zn1—I1    | 2.766 (2)  |
| N1—Zn1—N4| 95.77 (11) | N1—Zn1—N2| 98.9 (5)   |
| N2—Zn1—N3| 88.94 (11) | N1′—Zn1—N2| 88.4 (4)   |
| N1—Zn1—N2| 82.64 (11) | N1′—Zn1—N2| 82.9 (5)   |
| N3—Zn1—N4| 82.61 (11) | N1—Zn1—N2′| 82.2 (5)   |

Symmetry code: (i) −x + 1/2, −y + 1/2, −z + 1/2.

![Figure 1](image1.png)

View of the molecular structure of I showing the atom-labeling scheme with displacement ellipsoids drawn at the 30% probability level. C-bound H atoms are omitted for clarity. Hydrogen-bonding interactions are shown as dashed lines.

![Figure 2](image2.png)

View of the molecular structure of II showing the atom-labeling scheme with displacement ellipsoids drawn at the 30% probability level. C-bound H atoms are omitted for clarity. Symmetry codes: (i) −x + 1/2, −y + 1/2, −z + 1/2; (ii) −x + 1/2, y − 1/2, z + 1/2; (iii) −x + 2, y, −z + 1; (iv) −x + 1, y, −z + 1.)
tions (one of the carbon atoms lies almost in the N—Zn—N plane) in contrast to the symmetric gauche conformations in planar structures.

As expected, the bite angles in the five-membered chelate rings in \( \text{I} \) (ca 82.6°, Table 1) are reduced compared to the typical value of ca 85° in planar structures. At the same time, a considerable decrease in the bite angle occurs only in the ‘anti’ six-membered chelate ring [88.94 (11)° versus ca 95° in planar structures].

The molecular structure of compound \( \text{II} \) is shown in Fig. 2. In this case the [Zn\((L)\)] unit is centrosymmetric but the zinc(II) ion is disordered over two positions with site occupancies of 50% constrained by symmetry with a Zn1···Zn1i distance of 0.810 (3) Å [symmetry code: (i) \(-x, -y, -z + 1/2\)]. Two crystallographically non-equivalent, non-coordinated centrosymmetric triiodide anions serve as counter-ions, with I2 and I4 occupying the inversion centers.

The structural characteristics of the [Zn\((L)\)]+ unit in \( \text{II} \) are in general agreement with those described above for \( \text{I} \), with the deviation of the zinc(II) ion from the mean N₄ plane being 0.381 (2) Å. The ‘syn’ and ‘anti’ six-membered chelate rings are characterized by even higher divergences in their bite angles as compared to \( \text{I} \) (10.5° and 6.8°, respectively, Table 1). The five-membered rings in \( \text{II} \) are also present in gauche–envelope conformations. A notable distinction in \( \text{II} \) is the considerable difference of the Zn—N bond lengths in the ‘syn’ and ‘anti’ six-membered chelate rings [average values = 2.01 (1) and 2.20 (2) Å, respectively], while in \( \text{I} \) this difference is only 0.015 Å.

3. Supramolecular features

The crystals of \( \text{I} \) have dual lamellar structure. The layers parallel to the \( ab \) plane are readily discernible (Fig. 3). They are composed of zigzag chains propagating along the \( b \)-axis direction, in which the links between the [Zn\((L)\)]I⁺ units occur via N—H···I hydrogen bonds between the secondary amino groups of the macrocyclic ligands (N1—H1, N2—H2 and N3—H3) as the donors and the non-coordinated I2 anions as the acceptors (Table 2). These chains are linked in the perpendicular (\( a \)-axis) direction through weak N3—H3···I1 bonds (Fig. 4). At the same time, paired hydrogen-bond contacts involving the coordinated iodide anions I1 and the N4—H4 groups of neighboring macrocycles lead to the formation of another two-dimensional network (Fig. 5).

### Table 2

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···I2i | 0.98 | 2.82 | 3.708 (3) | 151 |
| N2—H2···I2 | 0.98 | 2.78 | 3.634 (3) | 146 |
| N3—H3···I1ii | 0.98 | 3.20 | 3.819 (3) | 123 |
| N3—H3···I2 | 0.98 | 3.13 | 3.897 (3) | 137 |
| N4—H4···I1iii | 0.98 | 2.86 | 3.680 (3) | 142 |

Symmetry codes: (i) \(-x, -y, -z + 1/2\); (ii) \(-x + 1/2, y + 1/2, -z + 1/2\); (iii) \(-x, -y + 1, -z\).

Figure 3

The packing in \( \text{I} \) viewed down the \( b \)-axis direction. Hydrogen-bonding interactions are shown as dashed lines.

Figure 4

The structure of the hydrogen-bonded layer parallel to the \( ab \) plane in \( \text{I} \). Hydrogen-bonding interactions are shown as dashed lines.

Figure 5

The structure of the hydrogen-bonded layer parallel to the (101) plane in \( \text{I} \). Hydrogen-bonding interactions are shown as dashed lines.
the existence of such hydrogen-bonded layers parallel to the (101) plane is not so evident, one of these sheets in Figs. 3 and 4 is highlighted in dark green.

The disordered [Zn(L)]I⁺ cations in the crystal of II are arranged in parallel chains running along the b-axis direction (Fig. 6). The peculiarity of this structure is that all of the iodine atoms, both coordinated (I1) and those of the triiodide anions [I3/I2/I3 and I5/I4/I5i], symmetry codes: (i) −x + 2, y, −z + 1; (ii) −x + 1, y, −z + 1] lie strictly in crystallographic planes parallel to the ac plane, thus forming ‘purely iodide’ layers separated by half of the b unit-cell length (Fig. 7). As can be seen, all of the 13–12–13 triiodide anions are parallel, as well as the 15–14–15 ones, and they form an angle of 71.5 (3°) to each other. The shortest distance between the coordinated iodide and the triiodide anion is 4.803 (3) Å (I1−I5), while the shortest distance between triiodide anions is 4.949 (3) Å [I3⋯I3iii, symmetry code: (iii) −x + 1, y, −z + 1]. Surprisingly, there are no hydrogen-bonding interactions in the crystal of II so its three-dimensional structure is based on weak ionic and van der Waals interactions.

4. Database survey
A search of the Cambridge Structural Database (CSD, version 5.40, last update February 2019; Groom et al., 2016) indicated that a number of compounds of the composition [M(L)]X₂ have been characterized structurally. They include complexes of nickel(II) [refcodes TAZDNCO1 (Ito et al., 1984); TAZDNO02-08 (Horii et al., 2020); RAPKAX (Ha, 2017); JIZTUH (Adam et al., 1991); JIZTUH01-04 (Horii et al., 2020)], copper(II) [TEGRPOK (Chen et al., 1996); TUCQEN (Makhnev et al., 1996)] and zinc(II) [VUSDUI10, HEGNEM and HEGNOW (Porai-Koshits et al., 1994)] cyclam cations with the full series (except for CuLCl₂) of halide anions (X = Cl, Br, I).

In the overwhelming majority of cases, these complexes form monoclinic (space group P2₁/c or P2₁/n) molecular crystals with the same structural motif: the complex moieties form infinite chains, in which they are joined by the pairs of N−H⋯X hydrogen bonds between the NH group of the macrocycle and the coordinated halide ion. On the other hand, in the case of the nickel(II), two other polymorphs of the iodide salt are known. These are also chain structures; however, one of the iodide anions is not coordinated [CAFHUM (Prasad & McAuley, 1983) and JIZTUH05–08 (Horii et al., 2020)]. The peculiarity, characteristic only of zinc(II) complexes, is that quite similar to the situation observed in II, the metal ion is disordered over two positions. It should also be noted that a degree of pyramidalization of the Zn(N₄) chromophore progressively increases on going from Cl to I (the deviation of the ZnIII ion from the mean N₄ plane is 0.237, 0.322 and 0.385 Å, respectively) and the conformations of the chelate rings and their bite angles demonstrate systematic trends consistent with this variation. The structure of the complex [Zn(L)]I₂ is also mentioned (DEHVOB; Heinlein & Tebbe, 1985), but without atomic coordinates. The reported unit-cell parameters (space group C2/m; a = 19.189, b = 12.615, c = 10.072 Å; β = 120.65°) represent an alternative setting of the I2/m unit cell found here for II: the matrix 0 0 1 / 0 1 0 / −1 0 1 transforms the DEHVOB cell to that of II.

5. Synthesis and crystallization
All chemicals and solvents used in this work were purchased from Sigma–Aldrich and were used without further purification.

To prepare I, a solution of 48 mg (0.240 mmol) of cyclam in 2 ml of MeOH was added to a solution of 50 mg (0.228 mmol) of Zn(CH₃CO₂)₂⋅2H₂O in 2 ml of MeOH and the mixture was heated at ca 333 K for 10 h. After cooling, a solution of 0.6 g of KI in 4 ml of MeOH was added and the mixture was left at room temperature. After one week, colorless prismatic crystals formed were filtered off, washed with MeOH and dried in air. Yield: 79 mg (67%). Analysis calculated for C₁₀H₂₂N₂ZnI₂: C 23.12; H 4.66; N 10.78%. Found: C 22.98; H 4.72; N 10.63%. Single crystals of I in the form of colorless prisms suitable for X-ray diffraction analysis were picked from the sample resulting from the synthesis.

Crystals of II were obtained in an experiment when the precipitation of the product was attempted in aqueous solu-
tion. After addition of the solution of 0.5 g ofKI in 0.5 ml of H2O to the solution of the nitrate salt of the macrocyclic cation [obtained in situ from 50 mg (0.25 mmol) of cyclam and 75 mg (0.25 mmol) of Zn(NO3)2·6H2O] in 2 ml of H2O, a white precipitate formed (ca 92 mg), which was filtered off and the mother liquor was left exposed to the air. After several days, a small quantity of brown crystals of II had formed, which were picked for crystallographic investigation.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All of the H atoms in I and II were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.97 Å and N–H = 0.98 Å with Uiso(H) values of 1.2Ueq of the parent atoms.

Table 3

| Experimental details | I | II |
|----------------------|---|----|
| Chemical formula     | [Zn(C10H24N4)]I | [Zn(C10H24N4)]I3 |
| M                    | 519.50 | 773.30 |
| Crystal system, space group | Monoclinic, P21/n | Monoclinic, P2/m |
| Temperature (K)      | 293 | 293 |
| a, b, c (Å)          | 8.3837 (3), 13.7570 (4), 14.6478 (5) | 10.0629 (12), 12.6263 (12), 16.5133 (16) |
| β (°)                | 103.852 (3) | 90.921 (10) |
| V (Å³)               | 1640.25 (9) | 2097.9 (4) |
| Z                    | 4 | 4 |
| Radiation type       | Mo Kα | Mo Kα |
| μ (mm⁻¹)             | 5.25 | 7.05 |
| Crystal size (mm)    | 0.2 × 0.2 × 0.15 | 0.18 × 0.18 × 0.10 |

Data collection

| Diffractometer      | Xcalibur, Eos | Xcalibur, Eos |
|---------------------|---------------|---------------|
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2019) | Multi-scan (CrysAlis PRO; Rigaku OD, 2019) |
| Tmin, Tmax          | 0.650, 1.000  | 0.563, 1.000  |
| No. of measured, independent and observed | 10691, 3785, 2982 | 1931, 1931, 1531 |
| R(F)                | 0.031 | 0.065 |
| ρ(2)max (Å⁻³)       | 0.684 | 0.595 |
| Refinement          | | |
| R(F²) > 2σ(F²), wR(F²), S | 0.033, 0.053, 1.02 | 0.065, 0.209, 1.02 |
| No. of reflections  | 3785 | 1931 |
| No. of parameters   | 155 | 100 |
| H-atom treatment    | H-atom parameters constrained | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.57, −0.83 | 1.86, −2.21 |

Computer programs: CrysAlis PRO (Rigaku OD, 2019), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and publCIF (Westrip, 2010).

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Crystal structures of Zn(cyclam)I₂ (second monoclinic polymorph) and Zn(cyclam)I(I₃)

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Computing details

For both structures, data collection: CrysAlis PRO (Rigaku OD, 2019); cell refinement: CrysAlis PRO (Rigaku OD, 2019); data reduction: CrysAlis PRO (Rigaku OD, 2019); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: publCIF (Westrip, 2010).

Iodido(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)zinc(II) iodide (I)

Crystal data

[ZnI(C₁₀H₂₄N₄)]I
Mr = 519.50
Monoclinic, P2₁/n
a = 8.3837 (3) Å
b = 13.7570 (4) Å
c = 14.6478 (5) Å
β = 103.852 (3)°
V = 1640.25 (9) Å³
Z = 4

\( F(000) = 992 \)
\( D_\text{c} = 2.104 \text{ Mg m}^{-3} \)

Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 3942 reflections
θ = 2.1–27.3°
\( µ = 5.25 \text{ mm}^{-1} \)
\( T = 293 \text{ K} \)
Prism, clear light colourless
0.2 × 0.2 × 0.15 mm

Data collection

Xcalibur, Eos diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1593 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2019)

\( T_{\min } = 0.650, T_{\max } = 1.000 \)
10691 measured reflections
3785 independent reflections
2982 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.031 \)
\( θ_{\text{min}} = 29.1°, θ_{\text{max}} = 2.1° \)
h = −10→10
k = −17→11
l = −18→19

Refinement

Refinement on \( F^2 \)
Least-squares matrix: full
\( R[ F^2 > 2\sigma(F^2) ] = 0.033 \)
\( wR(F^2) = 0.053 \)
\( S = 1.02 \)
3785 reflections
155 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = 1/[ σ^2(F_o^2) + (0.0145P)^2 ] \)
where \( P = (F_o^2 + 2F_c^2)/3 \)
(Δ/σ)max = 0.001
\( Δρ_{\text{max}} = 0.57 \text{ e Å}^{-3} \)

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Δρ_{\text{min}} = -0.83 \text{ e Å}^{-3} \quad \text{Extinction correction: } SHELXL2018/3 \begin{equation} 
 Fc^* = kF_c[1 + 0.001xF_c^2/\sin(2\theta)]^{-1/4} \end{equation} \text{Extinction coefficient: 0.00134 (7)}

**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.

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

| Atom | x        | y        | z        | U_{iso}/U_{eq} |
|------|----------|----------|----------|----------------|
| I1   | 0.16199  | 0.40650  | 0.15018  | 0.03711 (9)    |
| Zn1  | 0.00746  | 0.54540  | 0.22192  | 0.02665 (12)   |
| N1   | -0.2241  | 0.48210  | 0.2122   | 0.0272 (7)     |
| H1   | -0.22647 | 0.423178 | 0.174250 | 0.033*         |
| N2   | 0.0454   | 0.5033   | 0.36481  | 0.0292 (7)     |
| H2   | 0.003393 | 0.556139 | 0.397386 | 0.035*         |
| N3   | 0.1933   | 0.65217  | 0.2632   | 0.0282 (7)     |
| H3   | 0.149659 | 0.704337 | 0.295758 | 0.034*         |
| N4   | -0.0687  | 0.63817  | 0.1048   | 0.0288 (7)     |
| H4   | -0.05478 | 0.601213 | 0.050069 | 0.035*         |
| C1   | -0.2327  | 0.4485   | 0.3069   | 0.0371 (10)    |
| H1A  | -0.306512| 0.393370 | 0.301155 | 0.044*         |
| H1B  | -0.275717| 0.500177 | 0.339202 | 0.044*         |
| C2   | -0.0644  | 0.4196   | 0.3632   | 0.0384 (10)    |
| H2A  | -0.068776| 0.402191 | 0.426776 | 0.046*         |
| H2B  | -0.024607| 0.363962 | 0.334543 | 0.046*         |
| C3   | 0.2174   | 0.4875   | 0.4148   | 0.0410 (10)    |
| H3A  | 0.264794 | 0.437386 | 0.382861 | 0.049*         |
| H3B  | 0.221722 | 0.465027 | 0.478124 | 0.049*         |
| C4   | 0.3177   | 0.5806   | 0.4193   | 0.0463 (11)    |
| C4A  | 0.262635 | 0.631620 | 0.445670 | 0.056*         |
| H4B  | 0.423918 | 0.570130 | 0.462252 | 0.056*         |
| C5   | 0.3457   | 0.6162   | 0.3260   | 0.0415 (10)    |
| H5A  | 0.426638 | 0.667933 | 0.337714 | 0.050*         |
| H5B  | 0.389197 | 0.563309 | 0.295420 | 0.050*         |
| H6B  | 0.288015 | 0.745919 | 0.183961 | 0.047*         |
| C7   | 0.0475   | 0.7213   | 0.1152   | 0.0389 (10)    |
| H7A  | 0.006315 | 0.775097 | 0.145756 | 0.047*         |
| H7B  | 0.056870 | 0.742876 | 0.053664 | 0.047*         |
| C8   | -0.2429  | 0.6695   | 0.0832   | 0.0365 (9)     |
| H8A  | -0.267305| 0.706063 | 0.024857 | 0.044*         |
| H8B  | -0.259879| 0.712074 | 0.132732 | 0.044*         |
| C9   | -0.3590  | 0.5841   | 0.0740   | 0.0393 (10)    |

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### Atomic displacement parameters (Å²)

|       | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| I1    | 0.04629 (18) | 0.03129 (16) | 0.03725 (17) | 0.00582 (11) | 0.01687 (13) | −0.00334 (11) |
| Zn1   | 0.0257 (2) | 0.0263 (2) | 0.0277 (3) | −0.00164 (17) | 0.00594 (19) | 0.00302 (18) |
| N1    | 0.0295 (18) | 0.0244 (16) | 0.0288 (18) | −0.0045 (13) | 0.0095 (14) | −0.0032 (13) |
| N2    | 0.0333 (18) | 0.0282 (17) | 0.0252 (18) | 0.0054 (13) | 0.0054 (14) | −0.0004 (13) |
| N3    | 0.0252 (17) | 0.0267 (17) | 0.0320 (19) | −0.0028 (13) | 0.0054 (14) | −0.0032 (13) |
| N4    | 0.0294 (17) | 0.0297 (17) | 0.0276 (18) | −0.0024 (13) | 0.0073 (14) | −0.0020 (13) |
| C1    | 0.039 (2) | 0.037 (2) | 0.039 (3) | −0.0065 (18) | 0.019 (2) | −0.0012 (19) |
| C2    | 0.048 (3) | 0.037 (2) | 0.032 (2) | −0.0008 (19) | 0.014 (2) | 0.0108 (18) |
| C3    | 0.050 (3) | 0.039 (3) | 0.030 (2) | 0.0088 (19) | 0.001 (2) | 0.0068 (18) |
| C4    | 0.039 (3) | 0.051 (3) | 0.039 (3) | 0.009 (2) | −0.010 (2) | −0.007 (2) |
| C5    | 0.025 (2) | 0.040 (2) | 0.054 (3) | −0.0029 (17) | −0.002 (2) | −0.005 (2) |
| C6    | 0.042 (3) | 0.029 (2) | 0.048 (3) | −0.0098 (18) | 0.016 (2) | −0.0040 (19) |
| C7    | 0.050 (3) | 0.026 (2) | 0.042 (3) | −0.0054 (18) | 0.014 (2) | 0.0059 (18) |
| C8    | 0.037 (2) | 0.036 (2) | 0.034 (2) | 0.0092 (17) | 0.0049 (18) | 0.0057 (18) |
| C9    | 0.027 (2) | 0.048 (3) | 0.037 (3) | 0.0015 (18) | −0.0034 (18) | −0.0012 (19) |
| C10   | 0.025 (2) | 0.047 (3) | 0.044 (3) | −0.0047 (18) | 0.0070 (19) | −0.003 (2) |
| I2    | 0.04667 (19) | 0.03273 (17) | 0.0554 (2) | 0.00644 (12) | 0.00368 (14) | 0.00011 (13) |

### Geometric parameters (Å, °)

|       | I1—Zn1  | Zn1—N1  | Zn1—N2  | Zn1—N3  | Zn1—N4  | N1—H1  | N1—C1  | N1—C10 | N2—H2  | N2—C2  | N2—C3  | N3—H3  | N3—C5  | N3—C6  | N4—H4  | N4—C7  | N4—C8  | C1—H1A |
|-------|----------|---------|---------|---------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|       | 2.6619 (5) | 2.101 (3) | 2.121 (3) | 2.121 (3) | 2.110 (3) | 0.9800 | 1.481 (4) | 1.483 (4) | 0.9800 | 1.471 (4) | 1.468 (4) | 0.9800 | 1.471 (4) | 1.470 (4) | 0.9800 | 1.486 (4) | 1.482 (4) | 0.9700 |
|       | C3—H3A  | C3—H3B  | C3—C4  | C4—H4A  | C4—H4B  | C4—C5  | C5—H5A  | C5—H5B  | C6—H6A  | C6—H6B  | C6—C7  | C7—H7A  | C7—H7B  | C8—H8A  | C8—H8B  | C8—C9  | C9—H9A  | C9—H9B  | 0.9700 |
|       | 0.9700 | 0.9700 | 1.525 (5) | 0.9700 | 0.9700 | 1.522 (6) | 0.9700 | 0.9700 | 0.9700 | 0.9700 | 1.509 (5) | 0.9700 | 0.9700 | 0.9700 | 0.9700 | 1.510 (5) | 0.9700 | 0.9700 | 0.9700 | 0.9700 |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| C1—H1B               | 0.9700       | C9—C10               | 1.516 (5)    |
| C1—C2                | 1.507 (5)    | C10—H10A             | 0.9700       |
| C2—H2A               | 0.9700       | C10—H10B             | 0.9700       |
| N1—Zn1—I1            | 101.81 (8)   | N2—C3—H3B            | 109.4        |
| N1—Zn1—N2            | 82.64 (11)   | N2—C3—C4             | 111.3 (3)    |
| N1—Zn1—N3            | 155.51 (11)  | H3A—C3—H3B           | 108.0        |
| N1—Zn1—N4            | 95.77 (11)   | C4—C3—H3A            | 109.4        |
| N2—Zn1—I1            | 102.79 (8)   | C4—C3—H3B            | 109.4        |
| N2—Zn1—N3            | 88.94 (11)   | C3—C4—H4A            | 108.4        |
| N3—Zn1—I1            | 102.47 (8)   | C3—C4—H4B            | 108.4        |
| N4—Zn1—I1            | 101.21 (8)   | H4A—C4—H4B           | 107.4        |
| N4—Zn1—N2            | 155.76 (11)  | C5—C4—C3             | 115.7 (3)    |
| N4—Zn1—N3            | 82.61 (11)   | C5—C4—H4A            | 108.4        |
| Zn1—N1—H1            | 105.9        | C5—C4—H4B            | 108.4        |
| C1—N1—Zn1            | 108.5 (2)    | N3—C5—C4             | 111.9 (3)    |
| C1—N1—C10            | 111.5 (3)    | N3—C5—H5A            | 109.2        |
| C10—N1—Zn1           | 118.3 (2)    | C4—C5—H5A            | 109.2        |
| C10—N1—H1            | 105.9        | C4—C5—H5B            | 109.2        |
| Zn1—N2—H2            | 107.0        | H5A—C5—H5B           | 107.9        |
| C2—N2—Zn1            | 104.6 (2)    | N3—C6—H6A            | 110.1        |
| C2—N2—H2             | 107.0        | N3—C6—H6B            | 110.1        |
| C3—N2—Zn1            | 115.5 (2)    | N3—C6—C7             | 108.2 (3)    |
| C3—N2—H2             | 107.0        | H6A—C6—H6B           | 108.4        |
| C3—N2—C2             | 115.3 (3)    | C7—C6—H6A            | 110.1        |
| Zn1—N3—H3            | 108.1        | C7—C6—H6B            | 110.1        |
| C5—N3—Zn1            | 114.5 (2)    | N4—C7—C6             | 109.7 (3)    |
| C5—N3—H3             | 108.1        | N4—C7—H7A            | 109.7        |
| C6—N3—Zn1            | 103.3 (2)    | N4—C7—H7B            | 109.7        |
| C6—N3—H3             | 108.1        | C6—C7—H7A            | 109.7        |
| C6—N3—C5             | 114.3 (3)    | C6—C7—H7B            | 109.7        |
| Zn1—N4—H4            | 106.2        | H7A—C7—H7B           | 108.2        |
| C7—N4—Zn1            | 108.6 (2)    | N4—C8—H8A            | 109.2        |
| C7—N4—H4             | 106.2        | N4—C8—H8B            | 109.2        |
| C8—N4—Zn1            | 116.1 (2)    | N4—C8—C9             | 112.0 (3)    |
| C8—N4—H4             | 106.2        | H8A—C8—H8B           | 107.9        |
| C8—N4—C7             | 112.7 (3)    | C9—C8—H8A            | 109.2        |
| N1—C1—H1A            | 109.6        | C9—C8—H8B            | 109.2        |
| N1—C1—H1B            | 109.6        | C9—C9—H9A            | 108.5        |
| N1—C1—C2             | 110.3 (3)    | C8—C9—H9B            | 108.5        |
| H1A—C1—H1B           | 108.1        | C8—C9—C10            | 115.2 (3)    |
| C2—C1—H1A            | 109.6        | H9A—C9—H9B           | 107.5        |
| C2—C1—H1B            | 109.6        | C10—C9—H9A           | 108.5        |
| N2—C2—C1             | 107.6 (3)    | C10—C9—H9B           | 108.5        |
| N2—C2—H2A            | 110.2        | N1—C10—C9            | 112.9 (3)    |
| N2—C2—H2B            | 110.2        | N1—C10—H10A          | 109.0        |
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···I2i | 0.98 | 2.82 | 3.708 (3) | 151 |
| N2—H2···I2 | 0.98 | 2.78 | 3.634 (3) | 146 |
| N3—H3···I1ii | 0.98 | 3.20 | 3.819 (3) | 123 |
| N3—H3···I2 | 0.98 | 3.13 | 3.897 (3) | 137 |
| N4—H4···I1iii | 0.98 | 2.86 | 3.680 (3) | 142 |

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

Iodido(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)zinc(II) triiodide (II)

Crystal data

[ZnI(C₁₀H₂₄N₄)]I₃

Mr = 773.30
Monoclinic, I2/m
a = 10.0629 (12) Å
b = 12.6263 (12) Å
c = 16.5133 (16) Å
β = 90.921 (10)°
V = 2097.9 (4) Å³
Z = 4

Data collection

Xcalibur, Eos diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1593 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2019)

Tmin = 0.563, Tmax = 1.000
1931 measured reflections
1931 independent reflections
1531 reflections with I > 2σ(I)
Rint = 0.065
θmax = 25.0°, θmin = 2.0°
h = −11→11
k = −14→15
l = −19→19

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supporting information

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.065\)
\(wR(F^2) = 0.209\)
\(S = 1.02\)
1931 reflections
100 parameters
0 restraints

Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained

\[ w = 1/[\sigma(F_o)^2 + (0.1207P)^2 + 24.1639P] \]
where \(P = (F_o^2 + 2F_c^2)/3\)

\(\Delta \sigma)_{\text{max}} < 0.001\)
\(\Delta \rho_{\text{max}} = 1.86 \text{ e Å}^{-3}\)
\(\Delta \rho_{\text{min}} = -2.20 \text{ e Å}^{-3}\)

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. Refined as a 2-component twin.

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

|    | x    | y    | z     | \(U_{iso}/U_{eq}\) | Occ. (<1) |
|----|------|------|-------|---------------------|-----------|
| I1 | 0.75984 (13) | 1.000000 | 0.25422 (8) | 0.0546 (4) |
| Zn1 | 0.7426 (3) | 0.78147 (17) | 0.24844 (16) | 0.0313 (6) | 0.5 |
| N1 | 0.5759 (11) | 0.7637 (8) | 0.3129 (7) | 0.054 (3) |
| H1 | 0.547169 | 0.831842 | 0.316695 | 0.065* |
| N2 | 0.6627 (11) | 0.7691 (9) | 0.1362 (6) | 0.052 (2) |
| H2 | 0.638693 | 0.836861 | 0.124367 | 0.062* |
| C1 | 0.5986 (19) | 0.7286 (12) | 0.3953 (8) | 0.071 (4) |
| H1A | 0.592616 | 0.652075 | 0.398272 | 0.085* |
| H1B | 0.532274 | 0.758792 | 0.430502 | 0.085* |
| C2 | 0.4593 (13) | 0.7157 (13) | 0.2742 (11) | 0.071 (4) |
| H2A | 0.382036 | 0.730667 | 0.306679 | 0.085* |
| H2B | 0.471137 | 0.639494 | 0.272985 | 0.085* |
| C3 | 0.4330 (15) | 0.7558 (16) | 0.1869 (12) | 0.088 (6) |
| H3A | 0.344086 | 0.734576 | 0.170108 | 0.106* |
| H3B | 0.435683 | 0.832586 | 0.187081 | 0.106* |
| C4 | 0.5303 (16) | 0.7154 (15) | 0.1257 (9) | 0.076 (5) |
| H4A | 0.541286 | 0.639577 | 0.132177 | 0.091* |
| H4B | 0.495758 | 0.728671 | 0.071478 | 0.091* |
| C5 | 0.7596 (16) | 0.7338 (12) | 0.0779 (7) | 0.063 (4) |
| H5A | 0.737529 | 0.762622 | 0.024916 | 0.076* |
| H5B | 0.757810 | 0.657158 | 0.074099 | 0.076* |
| I2 | 1.000000 | 0.500000 | 0.500000 | 0.0780 (7) |
| I3 | 0.7276 (2) | 0.500000 | 0.55899 (13) | 0.0992 (7) |
| I4 | 0.500000 | 1.000000 | 0.500000 | 0.1262 (15) |
| I5 | 0.3190 (3) | 1.000000 | 0.3615 (2) | 0.1519 (13) |

Atomic displacement parameters (Å²)

|    | \(U^{11}\) | \(U^{22}\) | \(U^{33}\) | \(U^{12}\) | \(U^{13}\) | \(U^{23}\) |
|----|-----------|-----------|-----------|-----------|-----------|-----------|
| I1 | 0.0706 (8) | 0.0283 (6) | 0.0650 (8) | 0.000 | 0.0056 (6) | 0.000 |

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| Atom | U1   | U2   | U3   | U4   | U5   | U6   |
|------|------|------|------|------|------|------|
| Zn1  | 0.0299 (11) | 0.0357 (16) | 0.0285 (10) | 0.0018 (15) | 0.0024 (8) | 0.0004 (15) |
| N1   | 0.061 (6) | 0.032 (5) | 0.070 (7) | 0.005 (5) | 0.028 (5) | 0.001 (5) |
| N2   | 0.067 (6) | 0.041 (6) | 0.048 (5) | −0.005 (5) | −0.008 (5) | 0.002 (4) |
| C1   | 0.109 (12) | 0.056 (8) | 0.049 (7) | −0.003 (9) | 0.028 (8) | 0.002 (6) |
| C2   | 0.036 (6) | 0.062 (9) | 0.115 (13) | −0.002 (6) | 0.017 (7) | 0.003 (9) |
| C3   | 0.049 (8) | 0.084 (13) | 0.131 (16) | 0.014 (8) | −0.031 (10) | −0.002 (11) |
| C4   | 0.084 (10) | 0.078 (11) | 0.064 (9) | −0.008 (9) | −0.034 (8) | 0.009 (8) |
| C5   | 0.104 (11) | 0.056 (9) | 0.030 (6) | −0.004 (8) | 0.010 (7) | −0.004 (5) |
| I2   | 0.1383 (19) | 0.0391 (10) | 0.0555 (10) | 0.000 | −0.0321 (11) | 0.000 |
| I3   | 0.1264 (15) | 0.0671 (11) | 0.1039 (13) | 0.000 | −0.0103 (11) | 0.000 |
| I4   | 0.124 (2) | 0.0324 (10) | 0.227 (4) | 0.000 | 0.123 (2) | 0.000 |
| I5   | 0.1283 (19) | 0.0718 (13) | 0.258 (4) | 0.000 | 0.062 (2) | 0.000 |

**Geometric parameters (Å, °)**

| Bond | Distance (Å) | Angle (°) | Symmetry Code |
|------|--------------|-----------|---------------|
| I1—Zn1 | 2.766 (2) | N2—C4 | 1.502 (19) |
| I1—Zn1 | 2.766 (2) | N2—C5 | 1.451 (17) |
| Zn1—Zn1ii | 0.810 (4) | C1—C5ii | 1.56 (2) |
| Zn1—N1ii | 2.179 (10) | C2—C3 | 1.55 (2) |
| Zn1—N1 | 2.014 (10) | C3—C4 | 1.51 (3) |
| Zn1—N2ii | 2.210 (10) | I2—I3iii | 2.924 (2) |
| Zn1—N2 | 2.014 (10) | I2—I3 | 2.924 (2) |
| N1—C1 | 1.444 (19) | I4—I5vi | 2.901 (4) |
| N1—C2 | 1.458 (19) | I4—I5 | 2.901 (4) |
| Zn1i—I1—Zn1 | 171.86 (12) | C1—N1—Zn1ii | 103.7 (9) |
| Zn1ii—Zn1—I1 | 164.9 (4) | C1—N1—C2 | 113.5 (12) |
| Zn1ii—Zn1—N1ii | 67.6 (4) | C2—N1—Zn1ii | 111.2 (9) |
| Zn1ii—Zn1—N1 | 90.6 (5) | C2—N1—Zn1 | 119.1 (9) |
| Zn1ii—Zn1—N2 | 93.0 (5) | Zn1—N2—Zn1ii | 21.47 (16) |
| Zn1ii—Zn1—N2ii | 65.5 (4) | C4—N2—Zn1 | 118.8 (9) |
| N1ii—Zn1—I1 | 103.0 (3) | C4—N2—Zn1ii | 109.8 (8) |
| N1—Zn1—I1 | 98.3 (3) | C5—N2—Zn1ii | 101.5 (8) |
| N1—Zn1—I1ii | 158.18 (16) | C5—N2—Zn1 | 111.8 (8) |
| N1—Zn1—N2ii | 82.2 (5) | C5—N2—C4 | 112.9 (12) |
| N1ii—Zn1—N2ii | 88.4 (4) | N1—C1—C5ii | 107.7 (11) |
| N2ii—Zn1—I1 | 103.4 (3) | N1—C2—C3 | 113.4 (13) |
| N2—Zn1—I1 | 97.6 (3) | C4—C3—C2 | 114.3 (13) |
| N2—Zn1—N1ii | 98.9 (5) | N2—C4—C3 | 110.8 (13) |
| N2—Zn1—N1ii | 82.9 (5) | N2—C5—C1ii | 109.8 (10) |
| N2—Zn1—I1ii | 158.53 (16) | I3iii—I2—I3 | 180.0 |
| Zn1—I1—Zn1ii | 21.82 (19) | I5vi—I4—I5 | 180.0 |
| C1—N1—Zn1 | 114.3 (10) |

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

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