Organic–inorganic hybrid mixed-halide Zn$^\text{II}$ and Cd$^\text{II}$ tetrahalometallates with the 2-methylimidazo[1,5-a]pyridinium cation

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Three isomorphous 0-D hybrid salts, namely, 2-methylimidazo[1,5-a]pyridinium trichloridoiodidozincate(II), ([C$_8$H$_9$N$_2$]$_2$[ZnCl$_3$.19I$_{0.81}$] or [L]$_2$[ZnCl$_3$.19I$_{0.81}$], (I), 2-methylimidazo[1,5-a]pyridinium dibromidochloridocadmate(II), ([C$_8$H$_9$N$_2$]$_2$[CdBr$_{2.42}$Cl$_{1.58}$] or [L]$_2$[CdBr$_{2.42}$Cl$_{1.58}$], (II), and 2-methylimidazo[1,5-a]pyridinium trichloridoiodidocadmate(II), ([C$_8$H$_9$N$_2$]$_2$[CdCl$_{3.90}$I$_{0.10}$] or [L]$_2$[CdCl$_{3.90}$I$_{0.10}$], (III), are assembled from discrete 2-methylimidazo[1,5-a]-pyridinium cations, L$^+$, and mixed-halide tetrahalometallate anions. In the three structures, there are two crystallographically non-equivalent cations that were modelled as being rotationally disordered by 180°. In the lattices of the three compounds, a disordered state exists involving partial substitution of Cl by I for sites 2–4 in (I), Br by Cl for all four sites in (II) and I by Br for site 2 in (III). In the solid state, the organic and inorganic sheets alternate parallel to the $bc$ plane in a pseudo-layered arrangement. In the organic layer, pairs of centrosymmetrically related trans-oriented cations form $\pi$-bonded chains. The adjacent tetrahalometallate anions in the inorganic layer show no connectivity with the shortest $M\cdots M$ separations being greater than 7 Å. A variety of C–H $\cdots X$–M ($X = \text{Cl, Br, I}$) contacts between the organic and inorganic counterparts provide additional structural stabilization. The title structures are isomorphous with the previously reported structures of the chloride analogues, [L]$_2$[ZnCl$_4$] and [L]$_2$[CdCl$_4$].

1. Chemical context

Hybrid organic–inorganic halide salts have proven to be promising materials for optoelectronic applications spanning light-emitting diodes (LED), lasers, photodetectors and solar cells (Manser et al., 2016; Dou et al., 2014; Stranks et al., 2015). The versatile photophysical properties of these materials are combined with low-temperature solution processability and the tunability of their electronic and crystal structures via chemical composition modification. This research field has been mostly dominated by Pb- and Sn-based hybrid halide perovskites due to their prominent semiconducting properties and large optical absorption. However, water permeability in air and the low thermal stability of these perovskite systems limit their industrial manufacturing (Leijtens et al., 2015). The instability issues have been largely related to the volatility of small organic cations. The introduction of larger organic cations that also lower the dimensionality of a 3-D $MX_6$ ($X = \text{halide ion}$) octahedral halometallate network is expected to improve the air, moisture and thermal stability of the hybrid metal halides (Leblanc et al., 2019).
The selective combination of organic and inorganic components to incorporate other metal polyhedra and connectivity directly impacts the properties exhibited by the organic–inorganic halide materials. Hybrid halometallates containing group 12 (II B) elements have been of increasing research interest in this respect (Yangui et al., 2019). Based on the combined experimental and computational results, (CH₃NH₂)₂CdX₆ (X = Cl, Br, I) and related compounds were found to be potential candidates for broadband white-light emitting phosphors and self-activated scintillators (Roccanova et al., 2017). Engineering hybrid halometallate salts through mixing halogen elements is a recent new strategy that allows fine-tuning of the electronic structure and optoelectronic properties depending on the anionic speciation and ratio (Askar et al., 2018; Rogers et al., 2019).

Recently, we have developed a successful synthetic procedure towards organic–inorganic hybrid halometallates with imidazo[1.5-a]pyridinium-based counter-ions (Buvali et al., 2015; Vassilyeva et al., 2020). The latter represent an important class of fused nitrogen-containing bicyclic systems owing to their biological activity and potential applications in materials chemistry. They show strong fluorescence intensity and high quantum yield (Yagishita et al., 2018). The 2-methylimidazo[1.5-a]pyridinium cation, L⁺, has been synthesized from the oxidative cyclocondensation of equimolar amounts of formaldehyde, methylamine hydrochloride and 2-pyridinecarbaldehyde in an aqueous solution. The incorporation of L⁺ in the metal chloride structure reduced the dimensionality of the PbCl₂ 3-D perovskite framework to a 1-D stepwise chloroplumbate(II) wire arrangement in [PbCl₃]₂[PbCl₄]n and produced [L]₂[MCl₄] (M = Zn, Cd) hybrid salts with tetrahedral anions (Vassilyeva et al., 2020, 2021). The three compounds exhibited intense sky blue-light photoluminescence in the solid state.

In this work, we have explored the possibility of preparing the Br and I analogues of [L]₂[MCl₄] hybrids in an attempt to induce changes of the dimensionality in the resulting structures. In the synthesis, a combination of ZnO and NH₄I was used instead of ZnCl₂, while cadmium chloride was replaced with the corresponding bromide or iodide. This approach appeared to be only partially successful because of the competing Cl⁻ anions from the dissociation of the HCl adduct of methylamine. Herein, we report the preparations, crystal structures and spectroscopic characterization of three isomorphous 0-D hybrid salts [L]₂[ZnCl₃.19I₀.81], (I), [L]₂[CdBr₂.42Cl₁.58], (II), and [L]₂[CdCl₃.90I₀.10], (III).

2. Structural commentary

The organic–inorganic hybrids (I)–(III) crystallize in the triclinic space group P T̅ and are assembled from discrete 2-methylimidazo[1.5-a]pyridinium cations and mixed-halide tetrachalometallate anions. Fig. 1 shows the molecular structure and labelling of (I) taken as a representative example. In the three structures, there are two crystallographically non-equivalent cations (L¹ and L²) with similar structural configurations, which do not differ significantly from those of the isomorphous sister compounds [L]₂[ZnCl₄] (GOTHAB; Vassilyeva et al., 2020) and [L]₂[CdCl₄] (GOTJAD; Vassilyeva et al., 2021). The C–N/C bond distances in the imidazolium entities of the fused cores of the cations vary in the range 1.332 (3)–1.408 (4) Å; bond lengths in the pyridinium rings are as expected; the nitrogen atoms are planar with the sums of the three angles being equal to 360°. The almost coplanar five- and six-membered rings in the cations show dihedral angles between them of about 2° [(I): 0.57 (13), 2.11 (12)°; (II): 0.73 (14), 1.55 (15)°; (III): 0.55 (16), 1.66 (17)°]. The tetrahedral ZnX₄²⁻ and CdX₄²⁻ (X = Cl, Br, I) ions in the hybrid salts are slightly distorted with the M–X distances falling in the ranges 2.2689 (10)–2.5969 (4), 2.380 (4)–2.6029 (11) and 2.4481 (8)–2.747 (4) Å for (I), (II) and (III), respectively (Tables 1–3). The X–M–X angles vary from 104.9 (5) to 117.3 (5)°. In the lattices of the three hybrid salts, a disordered state exists involving partial substitution of Cl by I for sites 2–4 in (I), Br by Cl for all four sites in (II) and Cl by I for site 2 in (III). Such a disorder occurs frequently in compounds containing two different halide ions resulting from the competition between them during the crystals formation (Yang et al., 2010). The Zn–Cl and Cd–Cl bond lengths in (I)–(III) are similar to those of GOTHAB [2.2682 (4)–2.2920 (4) Å] and GOTJAD [2.4477 (5)–2.4719 (5) Å].

3. Supramolecular features

In the crystals of (I)–(III), the organic and inorganic sheets alternate parallel to the bc plane in a pseudo-layered arrangement. Fig. 2 illustrates the crystal packing common for the three compounds. The consecutive inorganic planes are separated by a distance corresponding to the a-axis length [9.4588 (6), 9.5172 (5) and 9.4304 (3) Å for (I)–(III), respectively]. In the organic layer, pairs of centrosymmetrically...
related trans-oriented $L^+$ and $L^2+$ cations form π-bonded chains with the centroid–centroid distances between the pairs being 3.543 (2) Å in (I), 3.569 (2) Å in (II) and 3.559 (2) Å in (III) (Fig. 3). The pairs of equivalent cations in the chains demonstrate stronger and weaker 10πe–10πe stacking with the centroid–centroid distances for (I), (II) and (III) of 3.448 (2), 3.409 (2) Å; 3.496 (2), 4.105 (2) Å and 3.485 (2), 4.017 (2) Å, respectively. The adjacent tetrahalometaallate anions in the inorganic layer show no connectivity with the shortest $M \cdot \cdot \cdot M$ separations being about 7.287 in (I), 7.158 in (II) and 7.046 Å (iodine) (Mantina et al., 2020) published by our research group, there are no structures containing the $L^+\ion{+}{c}$ cation in the Database. The reported compounds with cations similar to $L^+$ of the title hybrid salts are, for example, 2-(2,4,6-trimethylphenyl)-2H-imidazo[1,5-a]-pyridine-4-ium bromide (PARBOA; Burstein et al., 2005) and 2-(4-chlorophenyl)imidazo[1,5-a]pyridinium perchlorate (ETOXEQ; Chattopadhyay et al., 2004) having trimethyl-phenyl and chlorophenyl substituents, respectively, instead of the methyl group in $L^+$. Such organic cations are precursors for N-heterocyclic carbones, which are able to bind metal ions as e.g. bis(2-t-butylimidazo[1,5-a]pyridin-3-yldiene)(η⁵-1,5-cyclooctadiene)rhodium(I) hexafluorophosphate (FOJYAF; Alcarazo et al., 2005) or bis[2-(2-pyridyl)imidazo[1,5-a]-pyridin-2(1H)-yldene]mercury bis(hexafluorophosphate) (IVOWEW; Samanta et al., 2011). The neutral derivatives of the $L^+$ cation lacking the methyl group but possessing other substituents with donor atoms (N, O, S) often act as ligands that coordinate various metal ions: chloro-bis[3-(pyridin-2-yl)imidazo[1,5-a]pyridine]copper(II) chloride ethanol solvate

4. Database survey

More than 300 crystal structures of molecules featuring the imidazo[1,5-a]pyridine core are found in the CSD (Version 5.42, update of February 2021; Groom et al., 2016). Those comprise neutral organic compounds, organic salts and metal complexes with the imidazo[1,5-a]pyridine core having various substituents in the rings. Apart from $[L_2]\text{[CdCl}_4\text{]}$ (GOTJAD; Vassilyeva et al., 2021), $[L_2]\text{[ZnCl}_4\text{]}$ (GOTHAB; Vassilyeva et al., 2020) and $[L_n\text{[PbCl}_3\text{]}]_{n\infty}$ (TURJUO; Vassilyeva et al., 2020) published by our research group, there are no structures containing the $L^+$ cation in the Database. The reported compounds with cations similar to $L^+$ of the title hybrid salts are, for example, 2-(2,4,6-trimethylphenyl)-2H-imidazo[1,5-a]-pyridine-4-ium bromide (PARBOA; Burstein et al., 2005) and 2-(4-chlorophenyl)imidazo[1,5-a]pyridinium perchlorate (ETOXEQ; Chattopadhyay et al., 2004) having trimethyl-phenyl and chlorophenyl substituents, respectively, instead of the methyl group in $L^+$. Such organic cations are precursors for N-heterocyclic carbones, which are able to bind metal ions as e.g. bis(2-t-butylimidazo[1,5-a]pyridin-3-yldiene)(η⁵-1,5-cyclooctadiene)rhodium(I) hexafluorophosphate (FOJYAF; Alcarazo et al., 2005) or bis[2-(2-pyridyl)imidazo[1,5-a]-pyridin-2(1H)-yldene]mercury bis(hexafluorophosphate) (IVOWEW; Samanta et al., 2011). The neutral derivatives of the $L^+$ cation lacking the methyl group but possessing other substituents with donor atoms (N, O, S) often act as ligands that coordinate various metal ions: chloro-bis[3-(pyridin-2-yl)imidazo[1,5-a]pyridine]copper(II) chloride ethanol solvate

Figure 2

Fragment of the crystal packing of (II) viewed along the c axis with the non-equivalent $L^+$ and $L^2+$ cations shown in blue and green, respectively, and $[\text{CdBr}_2.42\text{Cl}_{1.58}]^2-$ anions presented in polyhedral form.

| Table 1  | Selected geometric parameters (Å, °) for (I). |
| --- | --- |
| Zn1−C3 | 2.2689 (10) | Zn1−I3 | 2.542 (4) |
| Zn1−C4 | 2.2780 (11) | Zn1−I4 | 2.568 (3) |
| Zn1−C1 | 2.2884 (6) | Zn1−I2 | 2.5969 (4) |
| Zn2−C2 | 2.346 (3) |
| C3−Zn1−C4 | 112.60 (5) | C3−Zn1−I4 | 107.23 (14) |
| C3−Zn1−C1 | 108.40 (4) | C3−Zn1−I1 | 109.51 (13) |
| C3−Zn1−C2 | 107.71 (4) | C3−Zn1−I2 | 110.37 (19) |
| C3−Zn1−C3 | 110.84 (13) | C3−Zn1−I3 | 110.4 (2) |
| C3−Zn1−C4 | 106.83 (14) | C3−Zn1−I2 | 109.83 (4) |
| C1−Zn1−C1 | 110.41 (12) | C1−Zn1−I2 | 106.78 (4) |
| C1−Zn1−C2 | 115.8 (2) | C1−Zn1−I1 | 115.4 (2) |
| C1−Zn1−C3 | 106.36 (19) | I3−Zn1−I2 | 108.8 (2) |
| C1−Zn1−C4 | 109.7 (2) | I4−Zn1−I2 | 110.22 (13) |

| Table 2  | Selected geometric parameters (Å, °) for (II). |
| --- | --- |
| Cd1−C3 | 2.380 (4) | Cd1−Br3 | 2.5353 (12) |
| Cd1−C2 | 2.460 (5) | Cd1−Br1 | 2.5834 (17) |
| Cd1−C1 | 2.467 (3) | Cd1−Br2 | 2.5950 (5) |
| Cd1−C4 | 2.497 (4) | Cd1−Br4 | 2.6029 (11) |
| C3−Cd1−C2 | 107.3 (10) | Br3−Cd1−Br1 | 106.2 (3) |
| C3−Cd1−C1 | 106.1 (7) | C3−Cd1−Br2 | 108.3 (5) |
| C3−Cd1−C1 | 114.9 (9) | C1−Cd1−Br2 | 112.8 (5) |
| C3−Cd1−C4 | 112.7 (5) | C4−Cd1−Br2 | 110.6 (2) |
| C3−Cd1−C2 | 109.6 (9) | Br3−Cd1−Br2 | 110.34 (14) |
| C3−Cd1−C4 | 106.3 (6) | Br4−Cd1−Br2 | 111.3 (3) |
| C3−Cd1−C3 | 108.4 (9) | Cd1−Cd1−Br4 | 117.3 (5) |
| C3−Cd1−C3 | 105.3 (5) | Cd1−Cd1−Br4 | 106.6 (9) |
| C3−Cd1−C4 | 112.4 (2) | Cd1−Cd1−Br4 | 104.9 (5) |
| C3−Cd1−Br1 | 107.0 (5) | Br3−Cd1−Br4 | 117.00 (15) |
| C3−Cd1−Br2 | 113.4 (8) | Br1−Cd1−Br4 | 105.4 (3) |
| C3−Cd1−Br1 | 106.9 (4) | Br2−Cd1−Br4 | 107.57 (8) |
The very similar IR spectra of hybrid salts (I)–(III) show a distinctive pattern we consider characteristic of the \( L^+ \) cation (Vassilyeva et al., 2020) (Fig. 4). The spectra are distinguished by the very sharp intense peaks in the aromatic \( \nu(C-H) \) stretching region (3130–3012 cm\(^{-1}\)) and the lack of absorbance from 1656 to 1568 cm\(^{-1}\). They include weak bands below 3000 cm\(^{-1}\) due to alkyl C—H stretching, sharp bands of medium intensity at 1654/1654/1656, 1542/1542/1546, 1450/1452/1456 and 1328/1326/1332 cm\(^{-1}\) associated with heterocyclic rings stretching, a very strong band at 1150/1146/1152 cm\(^{-1}\) ascribed to \( \nu(N-C_{	ext{aryl}}) \) vibration and a noticeable set of three very intense absorptions in the out-of-plane C—H bending region 800–600 cm\(^{-1}\) (peaks at 789/800/780, 738/740/734 and 616/624/618 cm\(^{-1}\)) for (I)/(II)/(III), respectively.

6. Synthesis and crystallization

**Synthesis of \([L]_2[ZnCl_{1.98}I_{0.81}]\) (I)**

Solid CH\(_3\)NH\(_2\)·HCl (0.27 g, 4 mmol) was added to the warm formaldehyde solution prepared by dissolving paraform...
Table 4
Experimental details.

| Crystal data | (I) | (II) | (III) |
|--------------|-----|------|------|
| Chemical formula | (C6H11N3)2[ZnCl0.5I0.5] | (C6H11N3)2[CdBr2.4Cl1.6] | (C6H11N3)2[CdCl3] |
| M | 547.59 | 628.14 | 529.69 |
| Crystal system, space group | Triclinic, P1 | Triclinic, P1 | Triclinic, P1 |
| Temperature (K) | 100 | 100 | 100 |
| a, b, c (Å) | 9.4588 (8), 10.8892 (8), 10.8843 (9) | 9.5732 (5), 10.8293 (6), 10.9697 (6) | 9.4304 (3), 10.7968 (3), 10.7565 (3) |
| a, β, γ (°) | 100.305 (7), 110.910 (7), 90.955 (6) | 99.620 (5), 110.413 (5), 90.827 (5) | 99.209 (3), 110.746 (3), 90.837 (2) |
| V (Å³) | 1021.67 (14) | 1014.45 (10) | 1007.97 (5) |
| Z | 2 | 2 | 2 |
| Radiation type | Mo Kα | Mo Kα | Cu Kα |
| μ (mm⁻¹) | 2.85 | 5.90 | 14.69 |
| Crystal size (mm) | 0.68 × 0.48 × 0.20 | 0.36 × 0.28 × 0.11 | 0.25 × 0.08 × 0.04 |

Data collection

| Diffractometer | Oxford Diffraction Xcalibur diffractometer | Oxford Diffraction Gemini diffractometer | Oxford Diffraction Gemini diffractometer |
|----------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|
| Absorption correction | Analytical Crysalis PRO (Rigaku OD, 2016) | Analytical Crysalis PRO (Rigaku OD, 2016) | Analytical Crysalis PRO (Rigaku OD, 2016) |
| Tmin, Tmax | 0.284, 0.592 | 0.206, 0.55 | 0.052, 0.522 |
| No. of measured, independent and observed | 21436, 10105, 8082 | 15893, 6879, 5371 | 18506, 3581, 3309 |
| Rint | 0.028 | 0.036 | 0.041 |
| (sinθ/λ)max (Å⁻¹) | 0.852 | 0.760 | 0.598 |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.044, 0.104, 1.03 | 0.036, 0.068, 1.04 | 0.036, 0.068, 1.06 |
|--------------------------|-------------------|-------------------|-------------------|
| No. of reflections | 10105 | 6879 | 3581 |
| No. of parameters | 241 | 246 | 234 |
| No. of restraints | 6 | 8 | 2 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 1.67, -1.13 | 0.89, -0.77 | 0.79, -0.46 |

(0.13 g, 4.5 mmol) in boiling deionized water (10 ml) in a 50 ml conical flask. The solution was stirred vigorously for 1 h at room temperature, filtered, and 2-pyridinecarbaldehyde (0.19 ml, 2 mmol) was added to the flask, which was then left open overnight. On the following day, ZnO (0.08 g, 1 mmol) and NH4I (0.29 g, 2 mmol) were introduced into the flask and the mixture was magnetically stirred at 323 K for 1.5 h. After that, the turbid orange solution was filtered and allowed to evaporate. Very light brownish prisms of (I) suitable for X-ray crystallography formed within two weeks in the brown solution. The crystals were filtered off, washed with diethyl ether and dried in air. Yield: 83% (based on Zn). FT-IR (v, cm⁻¹): 3436br, 3114s, 3094vs, 3068, 3038vs, 3006, 2972, 2934, 1654, 1562, 1542, 1505, 1376, 1346, 1322, 1262, 1216, 1150vs, 1128, 1036, 986, 918, 789vs, 762, 736, 616vs, 500, 466, 424. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.81 (s, 1H, H Cl13), 8.68 (d, 1H, J = 6.9 Hz, H Cl14), 8.25 (s, 1H, H Cl11), 7.80 (d, 1H, J = 9.2 Hz, H Cl17), 7.21 (t, 1H, J = 8.1 Hz, H Cl13), 7.11 (t, 1H, J = 6.7 Hz, H Cl14), 4.26 (s, 3H, CH3). Analysis calculated for C10H18N2ZnCl3I1 (564.99): C 34.01; H 3.21; N 9.92%. Found: C 35.40; H 2.83; N 7.94%.

Synthesis of [L]_{2}[CdBr2.4Cl1.6] (II)

The compound was prepared by a similar procedure except that CdBr₂·4H₂O (0.34 g, 1 mmol) dissolved in water was used instead of ZnO and NH₄I. Yield: 72% (based on cadmium). FT-IR (v, cm⁻¹): 3428br, 3116s, 3092, 3050s, 3012, 2952, 2910, 1654, 1564, 1542, 1452, 1372, 1350, 1326, 1256, 1220, 1146vs, 1036, 984, 920, 800vs, 762, 740, 624vs, 498, 466, 434, 406. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.75 (s, 1H, H Cl13), 8.64 (d, 1H, J = 7.3 Hz, H Cl14), 8.21 (s, 1H, H Cl11), 7.83 (d, 1H, J = 9.3 Hz, H Cl17), 7.24 (t, 1H, J = 8.1 Hz, H Cl13), 7.14 (t, 1H, J = 6.8 Hz, H Cl14), 4.25 (s, 3H, CH3). Analysis calculated for C10H18N2ZnBrCl3I4 (653.92): C 29.39; H 2.77; N 8.57%. Found: C 28.91; H 2.84; N 8.68%.

Synthesis of [L]_{2}[CdCl3]_{0.0} (III)

The compound was synthesized in a similar way by employing Cd₄ (0.36 g, 1 mmol) dissolved in water in place of ZnO and NH₄I. Yield: 89% (based on cadmium). FT-IR (v, cm⁻¹): 3420br, 3130s, 3098s, 3072, 3054, 2994, 2914, 1656, 1568, 1546, 1456, 1376, 1356, 1332, 1256, 1218, 1152s, 1040, 982, 920, 780vs, 734, 618s, 504, 464, 432, 418. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 9.75 (s, 1H, H Cl13), 8.64 (d, 1H, J = 7.3 Hz, H Cl14), 8.21 (s, 1H, H Cl11), 7.83 (d, 1H, J = 9.3 Hz, H Cl17), 7.25 (t, 1H, J = 7.8 Hz, H Cl13), 7.15 (t, 1H, J = 7.1 Hz, H Cl14), 2.42 (s, 3H, CH3). Analysis calculated for C10H18N2ZnCl3I3 (479.92): C 25.69; H 2.43; N 7.49%. Found: C 22.74; H 1.79; N 6.42%. The iodine content in the bulk sample appeared significantly larger than in the single crystal of (III) used for data collection.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. In all three structures, the cations were modelled as being rotationally disordered by 180°.
site occupancies refined to 0.855 (17) and its complement for both cations in (I), 0.73 (2) and its complement for cation 1 and 0.75 (2) and its complement for cation 2 in (II), and 0.72 (3) and its complement for cation 1 and 0.81 (3) and its complement for cation 2 in (III). In compound (I), the halide atom sites 2, 3 and 4 were modelled as being part Cl and part I, with Cl site occupancies refined to 0.3034 (15), 0.9489 (12) and 0.9343 (12), respectively, with the I site occupancies being the complements. The halide atom sites in compound (II) were modelled as being part Br and part Cl with the Br site occupancies refined to 0.417 (2), 0.857 (2), 0.558 (2) and 0.590 (2) with the Cl occupancies being the complements. Cd–X bond lengths of the disordered atoms were restrained to ideal values. The halide atom site 2 in (III) was modelled as being part Cl and part I, with Cl site occupancies refined to 0.9008 (15) with the I site occupancies being its complement. Cd–X bond lengths of the disordered atoms were restrained to ideal values. The coordinates of the halogens were refined to be independent for all three structures. All hydrogen atoms were included in calculated positions and refined using a riding model with isotropic displacement parameters based on those of the parent atom (C–H = 0.95 Å, \( \nu_{iso}(H) = 1.2 \nu_{eq}(C) \) for CH, C–H = 0.98 Å, \( \nu_{iso}(H) = 1.5 \nu_{eq}(C) \) for CH₂). Anisotropic displacement parameters were employed for the non-hydrogen atoms.

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References

Alcarazo, M., Roseblade, S. J., Cowley, A. R., Fernández, R., Brown, J. M. & Lasaletta, J. M. (2005). J. Am. Chem. Soc. 127, 3290–3291.

Ardizzoia, G. A., Ghiotti, D., Therrien, B. & Brenna, S. (2018). Inorg. Chim. Acta. 471, 384–390.

Askar, A. M., Karmakar, A., Bernard, G. M., Ha, M., Terskikh, V. V., Wiltshire, B. D., Patel, S., Fleet, J., Shankar, K. & Michaelis, V. K. (2018). J. Phys. Chem. Lett. 9, 2671–2677.

Burstein, C., Lehmann, C. W. & Glorius, F. (2005). Tetrahedron. 61, 6207–6217.

Buvayo, E. A., Kokozay, V. N., Linnik, R. P., Vassilyeva, O. Y. & Skelton, B. W. (2015). Dalton Trans. 44, 13735–13744.

Carson, J. J. K., Miron, C. E., Luo, J., Mergny, J. L., van Staalduinen, L., Jia, Z. & Petitjean, A. (2021). Inorg. Chim. Acta. 518, 120236.

Chattopadhyay, S. K., Mitra, K., Biswas, S., Naskar, S., Mishra, D., Adhikary, B., Harrison, R. G. & Cannon, J. F. (2004). Transition Met. Chem. 29, 1–6.

Dou, L., Yang, Y., You, J., Hong, Z., Chang, W.-H., Li, G. & Yang, Y. (2014). Nat. Commun. 5, 1–6.

Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.

Leblanc, A., Mercier, N., Allain, M., Dittmer, J., Pauperté, T., Fernandez, V., Boucher, F., Kepenekian, M. & Katan, C. (2019). Appl. Mater. Interfaces, 11, 20743–20751.

Leijtens, T., Eperon, G. E., Noel, N. K., Habisreutinger, S. N., Petrozza, A. & Snaith, H. J. (2015). Adv. Energy Mater. 5, 1500963.

Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.

Manser, J. S., Christians, J. A. & Kamat, P. V. (2016). Chem. Rev. 116, 12956–13008.

Martina, M., Chamberlin, A. C., Valero, R., Cramer, C. J. & Truhlár, D. G. (2009). J. Phys. Chem. A. 113, 5806–5812.

Rigaku OD (2016). CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, England.

Roccanova, R., Ming, W., Whiteside, V. R., McGuire, M. A., Sellers, I. R., Du, M. H. & Saparov, B. (2017). Inorg. Chem. 56, 13878–13888.

Rogers, R. D., Gurau, G., Kelley, S. P., Kore, R. & Shamshina, J. L. (2019). University of Alabama (UA), US Patent 10, 357, 362.

Samanta, T., Rana, B. K., Roymahapatra, G., Giri, S., Mitra, P., Pallepoug, R., Chattaraj, P. K. & Dinda, J. (2011). Inorg. Chim. Acta. 375, 271–279.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.

Stranks, S. D. & Snaith, H. J. (2015). Nature Nanotech. 10, 391–402.

Vassilyeva, O. Y., Buvayo, E. A., Linnik, R. P., Nesterov, D. S., Trachevsky, V. V. & Skelton, B. W. (2020). CrystEngComm. 22, 5096–5105.

Vassilyeva, O. Y., Buvayo, E. A., Lobko, Y. V., Linnik, R. P., Kokozay, V. N. & Skelton, B. W. (2021). RSC Adv. 11, 7713–7722.

Yagishita, F., Nii, C., Tezuka, Y., Tabata, A., Nagamura, H., Uemura, N., Yoshida, Y., Mino, T., Sakamoto, M. & Kawamura, Y. (2018). Asia. J. Org. Chem. 7, 1614–1619.

Yang, C., Wang, M. S., Cai, L. Z., Jiang, X. M., Wu, M. F., Guo, G. C. & Huang, J. S. (2010). Inorg. Chem. Commun. 13, 1021–1024.

Yangui, A., Roccanova, R., McWhorter, T. M., Wu, Y., Du, M. H. & Saparov, B. (2019). Chem. Mater. 31, 2983–2991.
Organic–inorganic hybrid mixed-halide Zn\textsuperscript{II} and Cd\textsuperscript{II} tetrahalometallates with the 2-methylimidazo[1,5-a]pyridinium cation

Olga Yu. Vassilyeva, Elena A. Buvaylo, Vladimir N. Kokozay and Brian W. Skelton

Computing details

For all structures, data collection: CrysAlis PRO (Rigaku OD, 2016); cell refinement: CrysAlis PRO (Rigaku OD, 2016); data reduction: CrysAlis PRO (Rigaku OD, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2017 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: WinGX (Farrugia, 2012).

Bis(2-methylimidazo[1,5-a]pyridinium) trichloridoiodidozincate(II), (I)

Crystal data

\[ \text{C}_{8}\text{H}_{9}\text{N}_{2})_{2}[\text{ZnCl}_{3.19}\text{I}_{0.81}] \]

\[ \text{Mr} = 547.59 \]

\[ \text{Triclinic, } \text{P} \text{1} \]

\[ a = 9.4588 \text{ (6) Å} \]

\[ b = 10.8892 \text{ (8) Å} \]

\[ c = 10.8343 \text{ (9) Å} \]

\[ \alpha = 100.305 \text{ (7)°} \]

\[ \beta = 110.910 \text{ (7)°} \]

\[ \gamma = 90.955 \text{ (6)°} \]

\[ V = 1021.67 \text{ (14) Å}^3 \]

\[ Z = 2 \]

\[ F(000) = 538 \]

\[ D_\lambda = 1.780 \text{ Mg m}^{-3} \]

Mo Kα radiation, \( \lambda = 0.71073 \text{ Å} \)

Cell parameters from 6804 reflections

\[ \theta = 2.1–36.7° \]

\[ \mu = 2.85 \text{ mm}^{-1} \]

\[ T = 100 \text{ K} \]

Prism, colourless

\[ 0.68 \times 0.48 \times 0.20 \text{ mm} \]

Data collection

Oxford Diffraction Xcalibur diffractometer

Graphite monochromator

Detector resolution: 16.0009 pixels mm\(^{-1}\)

\( \omega \) scans

Absorption correction: analytical

CrysAlis Pro (Rigaku OD, 2016)

\[ T_{\text{min}} = 0.284, T_{\text{max}} = 0.592 \]

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R[F^2 > 2\sigma(F^2)] = 0.044 \]

\[ wR(F^2) = 0.104 \]

\[ S = 1.03 \]

10105 reflections

241 parameters

6 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[ w = 1/[\sigma^2(F_c) + (0.0358P)^2 + 1.1052P] \]

where \( P = (F_c^2 + 2F_s^2)/3 \)

\( \Delta/\sigma)_{\text{max}} = 0.001 \]

\[ \Delta \rho_{\text{max}} = 1.67 \text{ e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -1.13 \text{ e Å}^{-3} \]
Supporting information

**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.** The halogen sites 2,3,4 were modelled as being part Cl and part I, with Cl site occupancies refined to 0.3034 (15), 0.9489 (12) and 0.9343 (12) respectively with the I site occupancies being the complements. The cations were modelled as being rotationally disordered by 180 degrees. The site occupancies refined to 0.855 (17) and its complement for both cations after independent refinement showed insignificant differences in the values for the two cations.

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

|       | x       | y       | z       | U(eq)   | Occupancy (<1) |
|-------|---------|---------|---------|---------|----------------|
| C11   | 0.6600  | 0.6614  | 0.1111  | 0.0248  |                |
| H11   | 0.6464  | 0.7110  | 0.0446  | 0.030   |                |
| N12   | 0.7941  | 0.6239  | 0.1886  | 0.0252  |                |
| C12   | 0.9412  | 0.6546  | 0.1804  | 0.0357  |                |
| H12A  | 0.9462  | 0.6059  | 0.0969  | 0.053   |                |
| H12B  | 1.0226  | 0.6342  | 0.2580  | 0.053   |                |
| H12C  | 0.9531  | 0.7442  | 0.1806  | 0.053   |                |
| C13   | 0.7715  | 0.5545  | 0.2710  | 0.0263  |                |
| H13   | 0.8470  | 0.5171  | 0.3339  | 0.032   |                |
| N13A  | 0.6223  | 0.5472  | 0.2485  | 0.0233  | 0.855 (17)     |
| C13A  | 0.6223  | 0.5472  | 0.2485  | 0.0233  | 0.145 (17)     |
| C14   | 0.5420  | 0.4899  | 0.3113  | 0.0303  |                |
| H14   | 0.5922  | 0.4442  | 0.3791  | 0.036   |                |
| C15   | 0.3917  | 0.5003  | 0.2739  | 0.0334  |                |
| H15   | 0.3358  | 0.4634  | 0.3175  | 0.040   |                |
| C16   | 0.3147  | 0.5662  | 0.1692  | 0.0324  |                |
| H16   | 0.2081  | 0.5711  | 0.1434  | 0.039   |                |
| C17   | 0.3906  | 0.6215  | 0.1063  | 0.0273  |                |
| H17   | 0.3384  | 0.6641  | 0.0361  | 0.033   |                |
| C17A  | 0.5491  | 0.6143  | 0.1470  | 0.0222  | 0.855 (17)     |
| N17A  | 0.5491  | 0.6143  | 0.1470  | 0.0222  | 0.145 (17)     |
| C21   | 0.2953  | 0.9033  | 0.3100  | 0.0312  |                |
| H21   | 0.1976  | 0.9028  | 0.3163  | 0.037   |                |
| N22   | 0.3346  | 0.9439  | 0.2132  | 0.0312  |                |
| C22   | 0.2337  | 0.9986  | 0.1032  | 0.0476  |                |
| H22A  | 0.2012  | 1.0768  | 0.1408  | 0.071   |                |
| H22B  | 0.1444  | 0.9396  | 0.0499  | 0.071   |                |
| H22C  | 0.2880  | 1.0158  | 0.0454  | 0.071   |                |
| C23   | 0.4809  | 0.9309  | 0.2357  | 0.0286  |                |
| H23   | 0.5350  | 0.9523  | 0.1826  | 0.034   |                |
| N23A  | 0.5377  | 0.8821  | 0.3465  | 0.0228  | 0.855 (17)     |
| C23A  | 0.5377  | 0.8821  | 0.3465  | 0.0228  | 0.145 (17)     |
| C24   | 0.6857  | 0.8517  | 0.4121  | 0.0324  |                |
| H24   | 0.7636  | 0.8647  | 0.3785  | 0.039   |                |

*Acta Cryst. (2022). E78, 359-364*
### Atomic displacement parameters (Å²)

| Atom | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|------|-------|-------|-------|-------|-------|-------|
| C11  | 0.0214 (9) | 0.0258 (10) | 0.0284 (10) | 0.0043 (7) | 0.0106 (8) | 0.0048 (8) |
| N12  | 0.0192 (8) | 0.0252 (8) | 0.0332 (10) | 0.0036 (6) | 0.0124 (7) | 0.0046 (7) |
| C12  | 0.0237 (10) | 0.0383 (13) | 0.0512 (16) | 0.0028 (9) | 0.0209 (11) | 0.0092 (11) |
| C13  | 0.0195 (9) | 0.0253 (10) | 0.0338 (11) | 0.0055 (7) | 0.0091 (8) | 0.0063 (8) |
| N13A | 0.0191 (8) | 0.0209 (8) | 0.0302 (9) | 0.0031 (6) | 0.0102 (7) | 0.0030 (7) |
| C13A | 0.0191 (8) | 0.0209 (8) | 0.0302 (9) | 0.0031 (6) | 0.0102 (7) | 0.0030 (7) |
| C14  | 0.0308 (11) | 0.0270 (11) | 0.0370 (12) | 0.0038 (8) | 0.0162 (10) | 0.0077 (9) |
| C15  | 0.0304 (12) | 0.0281 (11) | 0.0472 (15) | 0.0001 (9) | 0.0224 (11) | 0.0042 (10) |
| C16  | 0.0203 (9) | 0.0283 (11) | 0.0483 (14) | 0.0022 (8) | 0.0161 (10) | -0.0006 (10) |
| C17  | 0.0186 (9) | 0.0262 (10) | 0.0330 (11) | 0.0045 (7) | 0.0076 (8) | -0.0008 (8) |
| C17A | 0.0193 (8) | 0.0194 (8) | 0.0263 (9) | 0.0037 (6) | 0.0085 (7) | -0.0003 (7) |
| C17B | 0.0193 (8) | 0.0194 (8) | 0.0263 (9) | 0.0037 (6) | 0.0085 (7) | -0.0003 (7) |
| C21  | 0.0229 (10) | 0.0273 (11) | 0.0381 (13) | -0.0006 (8) | 0.0120 (9) | -0.0079 (9) |
| N22  | 0.0312 (10) | 0.0267 (9) | 0.0270 (9) | 0.0090 (8) | 0.0039 (8) | -0.0032 (7) |
| C22  | 0.0502 (17) | 0.0425 (16) | 0.0310 (13) | 0.0197 (13) | -0.0042 (12) | -0.0023 (11) |
| N23  | 0.0346 (12) | 0.0255 (10) | 0.0258 (10) | 0.0061 (8) | 0.0135 (9) | 0.0002 (8) |
| N23A | 0.0224 (8) | 0.0213 (8) | 0.0246 (8) | 0.0021 (6) | 0.0109 (7) | -0.0006 (6) |
| N23B | 0.0224 (8) | 0.0213 (8) | 0.0246 (8) | 0.0021 (6) | 0.0109 (7) | -0.0006 (6) |
| C24  | 0.0242 (10) | 0.0300 (11) | 0.0367 (12) | 0.0039 (8) | 0.0096 (9) | -0.0058 (9) |
| C25  | 0.0422 (15) | 0.0280 (12) | 0.0367 (14) | 0.0103 (10) | -0.0029 (11) | -0.0034 (10) |
| C26  | 0.067 (2) | 0.0246 (12) | 0.0316 (13) | 0.007 (12) | 0.0102 (13) | 0.0041 (10) |
| C27  | 0.0556 (17) | 0.0241 (11) | 0.0363 (13) | -0.0096 (10) | 0.0244 (13) | -0.0013 (9) |
| C27A | 0.0263 (10) | 0.0216 (9) | 0.0283 (10) | -0.0020 (7) | 0.0135 (8) | -0.0026 (7) |
| N27A | 0.0263 (10) | 0.0216 (9) | 0.0283 (10) | -0.0020 (7) | 0.0135 (8) | -0.0026 (7) |
| Zn1  | 0.01984 (12) | 0.02715 (13) | 0.02316 (13) | 0.00151 (9) | 0.00564 (9) | 0.00513 (9) |
| C11  | 0.0206 (2) | 0.0329 (3) | 0.0284 (2) | 0.00323 (18) | 0.00568 (19) | 0.0096 (2) |
| C12  | 0.01846 (15) | 0.02384 (12) | 0.03012 (12) | 0.00196 (10) | 0.01175 (9) | 0.01045 (8) |
| I2   | 0.01846 (15) | 0.02384 (12) | 0.03012 (12) | 0.00196 (10) | 0.01175 (9) | 0.01045 (8) |
|       | | | | | | |
|-------|---|---|---|---|---|---|
| Cl3   | 0.0298 (3) | 0.0181 (4) | 0.0504 (5) | 0.0077 (4) | 0.0154 (3) | 0.0078 (4) |
| I3    | 0.0298 (3) | 0.0181 (4) | 0.0504 (5) | 0.0077 (4) | 0.0154 (3) | 0.0078 (4) |
| Cl4   | 0.0276 (3) | 0.0452 (4) | 0.0222 (4) | -0.0028 (2) | 0.0058 (4) | -0.0034 (4) |
| I4    | 0.0276 (3) | 0.0452 (4) | 0.0222 (4) | -0.0028 (2) | 0.0058 (4) | -0.0034 (4) |

**Geometric parameters (Å, °)**

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| C11—N17A      | 1.363 (3)    | N22—C23       | 1.332 (3)    |
| C11—C17A      | 1.363 (3)    | N22—C22       | 1.465 (3)    |
| C11—N12       | 1.364 (3)    | C22—H22A      | 0.9800       |
| C11—H11       | 0.9500       | C22—H22B      | 0.9800       |
| N12—C13       | 1.338 (3)    | C22—H22C      | 0.9800       |
| N12—C12       | 1.462 (3)    | C23—C23A      | 1.338 (3)    |
| C12—H12A      | 0.9800       | C23—N23A      | 1.338 (3)    |
| C12—H12B      | 0.9800       | C23—H23       | 0.9500       |
| C12—H12C      | 0.9800       | N23A—C27A     | 1.400 (3)    |
| C13—C13A      | 1.341 (3)    | N23A—C24      | 1.401 (3)    |
| C13—N13A      | 1.341 (3)    | C23A—N27A     | 1.400 (3)    |
| C13—H13       | 0.9500       | C23A—C24      | 1.401 (3)    |
| N13A—C14      | 1.392 (3)    | C24—C25       | 1.348 (4)    |
| N13A—C17A     | 1.408 (3)    | C24—H24       | 0.9500       |
| C13A—C14      | 1.392 (3)    | C25—C26       | 1.406 (5)    |
| C13A—N17A     | 1.408 (3)    | C25—H25       | 0.9500       |
| C14—C15       | 1.345 (4)    | C26—C27       | 1.347 (5)    |
| C14—H14       | 0.9500       | C26—H26       | 0.9500       |
| C15—C16       | 1.432 (4)    | C27—N27A      | 1.422 (4)    |
| C15—H15       | 0.9500       | C27—C27A      | 1.422 (4)    |
| C16—C17       | 1.350 (4)    | C27—H27       | 0.9500       |
| C16—H16       | 0.9500       | Zn1—C13       | 2.2689 (10)  |
| C17—N17A      | 1.411 (3)    | Zn1—C14       | 2.2780 (11)  |
| C17—C17A      | 1.411 (3)    | Zn1—C11       | 2.2884 (6)   |
| C17—H17       | 0.9500       | Zn1—C12       | 2.346 (3)    |
| C21—N27A      | 1.365 (4)    | Zn1—I3        | 2.542 (4)    |
| C21—C27A      | 1.365 (4)    | Zn1—I4        | 2.568 (3)    |
| C21—N22       | 1.368 (4)    | Zn1—I2        | 2.5969 (4)   |
| C21—H21       | 0.9500       |               |              |

N17A—C11—N12  107.2 (2)  H22A—C22—H22C  109.5
C17A—C11—N12  107.2 (2)  H22B—C22—H22C  109.5
C17A—C11—H11  126.4      N22—C23—C23A  107.6 (2)
N12—C11—H11  126.4      N22—C23—N23A  107.6 (2)
C13—N12—C11  110.52 (19) N22—C23—H23  126.2
C13—N12—C12  125.2 (2)  N23A—C23—H23  126.2
C11—N12—C12  124.3 (2)  C23—N23A—C27A  109.2 (2)
N12—C12—H12A  109.5      C23—N23A—C24  129.8 (2)
N12—C12—H12B  109.5      C27A—N23A—C24  121.1 (2)
H12A—C12—H12B  109.5      C23—C23A—N27A  109.2 (2)
N12—C12—H12C  109.5      C23—C23A—C24  129.8 (2)
| Bond                  | Length (Å) | Bond                  | Length (Å) | Bond                  | Length (Å) |
|----------------------|------------|----------------------|------------|----------------------|------------|
| H12A—C12—H12C       | 109.5      | N27A—C23A—C24       | 121.1      |
| H12B—C12—H12C       | 109.5      | C25—C24—N23A        | 118.2      |
| N12—C13—C13A        | 107.4 (2)  | C25—C24—C23A        | 118.2      |
| N12—C13—N13A        | 107.4 (2)  | C25—C24—H24         | 120.9      |
| N12—C13—H13         | 126.3      | N23A—C24—H24        | 120.9      |
| N13A—C13—H13        | 126.3      | C24—C25—C26         | 121.6      |
| C13—N13A—C14        | 129.9 (2)  | C24—C25—H25         | 119.2      |
| C13—N13A—C17A       | 108.77 (19)| C26—C25—H25         | 119.2      |
| C14—N13A—C17A       | 121.32 (19)| C27—C26—C25         | 121.4      |
| C13—C13A—C14        | 129.9 (2)  | C27—C26—H26         | 119.3      |
| C13—C13A—N17A       | 108.77 (19)| C25—C26—H26         | 119.3      |
| C14—C13A—N17A       | 121.32 (19)| C26—C27—N27A        | 118.6      |
| C15—C14—N13A        | 118.6 (2)  | C26—C27—C27A        | 118.6      |
| C15—C14—C13A        | 118.6 (2)  | C26—C27—H27         | 120.7      |
| C15—C14—H14         | 120.7      | C27A—C27—H27        | 120.7      |
| N13A—C14—H14        | 120.7      | C21—C27A—N23A       | 105.9      |
| C14—C15—C16         | 120.9 (2)  | C21—C27A—C27        | 135.0      |
| C14—C15—H15         | 119.5      | N23A—C27A—C27       | 119.1      |
| C16—C15—H15         | 119.5      | C21—N27A—C23A       | 105.9      |
| C17—C16—C15         | 121.3 (2)  | C21—N27A—C27        | 135.0      |
| C17—C16—H16         | 119.4      | C23A—N27A—C27       | 119.1      |
| C15—C16—H16         | 119.4      | C13—Zn1—C14         | 112.60 (5) |
| C16—C17—N17A        | 118.5 (2)  | C13—Zn1—C11         | 108.40 (4) |
| C16—C17—C17A        | 118.5 (2)  | C14—Zn1—C11         | 107.71 (4) |
| C16—C17—H17         | 120.7      | C13—Zn1—C12         | 110.84 (13)|
| C17A—C17—H17        | 120.7      | C14—Zn1—C12         | 106.83 (14)|
| C11—C17A—N13A       | 106.19 (18)| C11—Zn1—C12         | 110.41 (12)|
| C11—C17A—C17        | 134.5 (2)  | C13—Zn1—I3          | 3.2 (2)    |
| N13A—C17A—C17       | 119.4 (2)  | C14—Zn1—I3          | 115.8 (2)  |
| C11—N17A—C13A       | 106.19 (18)| C11—Zn1—I3          | 106.36 (19)|
| C11—N17A—C17        | 134.5 (2)  | C12—Zn1—I3          | 109.7 (2)  |
| C13A—N17A—C17       | 119.4 (2)  | C13—Zn1—I4          | 107.23 (14)|
| N27A—C21—N22        | 107.2 (2)  | C14—Zn1—I4          | 5.44 (15)  |
| C27A—C21—N22        | 107.2 (2)  | C11—Zn1—I4          | 109.51 (13)|
| C27A—C21—H21        | 126.4      | C13—Zn1—I4          | 110.37 (19)|
| N22—C21—H21         | 126.4      | I3—Zn1—I4           | 110.4 (2)  |
| C23—N22—C21         | 110.1 (2)  | C13—Zn1—I2          | 109.83 (4) |
| C23—N22—C22         | 124.1 (3)  | C14—Zn1—I2          | 106.78 (4) |
| C21—N22—C22         | 125.7 (3)  | C11—Zn1—I2          | 111.54 (2) |
| N22—C22—H22A        | 109.5      | C12—Zn1—I2          | 1.24 (13)  |
| N22—C22—H22B        | 109.5      | I3—Zn1—I2           | 108.8 (2)  |
| H22A—C22—H22B       | 109.5      | I4—Zn1—I2           | 110.22 (13)|
| N22—C22—H22C        | 109.5      |                      |            |

N17A—C11—N12—C13    0.4 (3)  N27A—C21—N22—C23    0.0 (3)
C11—N12—C13—C13A −0.6 (3) C21—N22—C23—C23A 0.0 (3)
C12—N12—C13—C13A −179.8 (2) C22—N22—C23—C23A 177.8 (2)
C11—N12—C13—N13A −0.6 (3) C21—N22—N23A—C27A 0.0 (3)
C12—N12—C13—N13A −179.8 (2) C22—C23—N23A—C27A 0.1 (3)
N12—C13—N13A—C14 −0.6 (3) C22—C23—C23A—N27A 0.1 (3)
N12—C13—C13A—C14 −179.8 (2) C22—C23—C23A—C24 −179.5 (2)
N12—C13—C13A—N17A 0.4 (3) C22—C23—C23A—C24 −179.5 (2)
C13—N13A—C14—C15 177.2 (2) C23—N23A—C24—C25 179.6 (2)
C17A—N13A—C14—C15 −0.5 (3) C27A—N23A—C24—C25 0.2 (3)
C13—C13A—C14—C15 −177.2 (2) C23—C23A—C24—C25 179.6 (2)
N17A—C13A—C14—C15 0.4 (3) C27A—C23A—C24—C25 0.2 (3)
N13A—C14—C15—C16 1.6 (4) N23A—C24—C25—C26 −0.8 (4)
C13A—C14—C15—C16 1.6 (4) N23A—C24—C25—C26 −0.8 (4)
C14—C15—C16—C17 1.0 (4) C24—C25—C26—C27 0.8 (4)
C15—C16—C17—N17A −0.8 (4) C25—C26—C27—N27A −0.1 (4)
N15—C16—C17—N17A −0.8 (4) C25—C26—C27—N27A −0.1 (4)
C11—C17—N17A—C13A −0.2 (2) C21—C27—N27A—C23A 0.1 (2)
N12—C11—N17A—C13A −0.1 (2) C22—C27—N27A—C23A 0.1 (2)
C13—N13A—C17A—C11 −0.2 (2) C23—N23A—C27A—C21 −0.1 (2)
C14—N13A—C17A—C11 177.9 (2) C24—N23A—C27A—C21 179.5 (2)
C13—N13A—C17A—C17 −179.4 (2) C23—N23A—C27A—C27 −179.1 (2)
C14—N13A—C17A—C17 −1.3 (3) C24—N23A—C27A—C27 0.5 (3)
C16—C17—C17A—C11 −177.1 (2) C26—C27—C27A—C21 −179.1 (3)
C16—C17—C17A—N13A 1.9 (3) C26—C27—C27A—C21 −179.1 (3)
N12—C11—N17A—C13A −0.1 (2) C22—C27—C27A—N27A 0.5 (3)
N12—C11—N17A—C17 178.9 (2) C22—C27—C27A—N27A 0.5 (3)
C13—C13A—N17A—C11 −0.2 (2) C23—C27A—N27A—C12 −0.1 (2)
C14—C13A—N17A—C11 177.9 (2) C24—C27A—N27A—C12 179.5 (2)
C13—C13A—N17A—C17 −179.4 (2) C23—C27A—N27A—C27 −179.1 (2)
C14—C13A—N17A—C17 −1.3 (3) C24—C27A—N27A—C27 0.5 (3)
C16—C17—N17A—C11 −177.1 (2) C26—C27—N27A—C21 −179.1 (3)
C16—C17—N17A—C13A 1.9 (3) C26—C27—N27A—C21 −179.1 (3)

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A   | D—H···A |
|-------------|------|-------|---------|---------|
| C13—H13···I4i | 0.95 | 2.88  | 3.349 (5) | 112 |
| C12—H12B···Cl4i | 0.98 | 2.78  | 3.562 (3) | 137 |
| C12—H12C···C13ii | 0.98 | 2.80  | 3.698 (3) | 153 |
| C11—H11···C11iii | 0.95 | 2.72  | 3.484 (2) | 138 |
| C22—H22A···I2ii | 0.98 | 3.06  | 3.946 (3) | 151 |
| C22—H22C···I3iii | 0.98 | 3.00  | 3.562 (9) | 117 |
| C23—H23···C11ii | 0.95 | 2.83  | 3.486 (3) | 127 |
| C24—H24···C13iii | 0.95 | 2.71  | 3.579 (3) | 152 |
| C27—H27···C14iv | 0.95 | 2.75  | 3.624 (3) | 153 |

Symmetry codes: (i) −x+2, −y+1, −z+1; (ii) x, y+1, z; (iii) −x+1, −y+1, −z; (iv) −x+1, −y+1, −z+1.
Bis(2-methylimidazo[1,5-a]pyridinium) dibromodichloridozincate(II) (II)

Crystal data

\[(\text{C}_8\text{H}_9\text{N}_2)_2[\text{CdBr}_2.42\text{Cl}_{1.58}]\]

\[M_r = 628.14\]

Triclinic, \(P\)

\[a = 9.5172 (5) \, \text{Å}\]

\[b = 10.8293 (6) \, \text{Å}\]

\[c = 10.9697 (6) \, \text{Å}\]

\[\alpha = 99.620 (5)°\]

\[\beta = 110.413 (5)°\]

\[\gamma = 90.827 (5)°\]

\[V = 1041.45 (10) \, \text{Å}^3\]

\[Z = 2\]

\[\text{F}(000) = 603\]

\[D_r = 2.003 \, \text{Mg m}^{-3}\]

\[\text{Mo K}\alpha\, \text{radiation, } \lambda = 0.71073 \, \text{Å}\]

Cell parameters from 6082 reflections

\[\theta = 2.5–31.9°\]

\[\mu = 5.90 \, \text{mm}^{-1}\]

\[\text{T} = 100 \, \text{K}\]

Data collection

Oxford Diffraction Gemini diffractometer

Graphite monochromator

Detector resolution: 10.4738 pixels mm\(^{-1}\)

\[\omega\] scans

Absorption correction: analytical

CrysAlis Pro (Rigaku OD, 2016)

\[T_{\text{min}} = 0.206, T_{\text{max}} = 0.53\]

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\[R[F^2 > 2\sigma(F^2)] = 0.036\]

\[wR(F^2) = 0.068\]

\[S = 1.04\]

6879 reflections

246 parameters

8 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 0.3916P]\]

\[P = (F_o^2 + 2F_c^2)/3\]

\[(\Delta/\sigma)_{\text{max}} = 0.001\]

\[\Delta\rho_{\text{max}} = 0.89 \, \text{e Å}^{-3}\]

\[\Delta\rho_{\text{min}} = -0.77 \, \text{e Å}^{-3}\]

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. The halide atom sites were modelled as being part Br and part Cl with site occupancies refined to 0.417 (2), 0.857 (2), 0.558 (2) and 0.590 (2) for the Br occupancy for sites 1-4 with the Cl occupancies being the complements. Cd-X bond lengths of the disordered atoms were restrained to ideal values. The cations were modelled as being rotationally disordered by 180 degrees. The site occupancies refined to 0.73 (2) and its complement for cation 1 and 0.75 (2) and its complement for cation 2.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))

|      | \(x\)     | \(y\)     | \(z\)     | \(U_{iso}/U_{eq}\) | Occ. (<1) |
|------|-----------|-----------|-----------|---------------------|-----------|
| C11  | 0.6551 (3) | 0.6498 (2) | 0.1036 (3) | 0.0215 (6)          |           |
| H11  | 0.643060  | 0.698431  | 0.036699  | 0.026*              |           |
| N12  | 0.7851 (3) | 0.6065 (2) | 0.1763 (2) | 0.0203 (5)          |           |
| C12  | 0.9297 (3) | 0.6271 (3) | 0.1610 (3) | 0.0269 (7)          |           |
| Atom  | X        | Y        | Z        | Temperature (Å²) |
|-------|----------|----------|----------|------------------|
| H12A  | 0.988955 | 0.697944 | 0.228531 | 0.040            |
| H12B  | 0.912731 | 0.645988 | 0.072888 | 0.040            |
| H12C  | 0.984506 | 0.551360 | 0.171451 | 0.040            |
| C13   | 0.7613 (3)| 0.5408 (2)| 0.2620 (3)| 0.0208 (6)       |
| H13   | 0.834623 | 0.500983 | 0.323175 | 0.025            |
| N13A  | 0.6145 (3)| 0.5421 (2)| 0.2452 (3)| 0.0199 (6)       |
| C14   | 0.5319 (4)| 0.4908 (3)| 0.3114 (3)| 0.0274 (7)       |
| H14   | 0.579079 | 0.444386 | 0.378932 | 0.033            |
| C15   | 0.3853 (4)| 0.5089 (3)| 0.2773 (4)| 0.0329 (8)       |
| H15   | 0.328458 | 0.476488 | 0.322639 | 0.039            |
| C16   | 0.3130 (4)| 0.5764 (3)| 0.1734 (4)| 0.0313 (7)       |
| H16   | 0.208509 | 0.586460 | 0.150273 | 0.038            |
| C17   | 0.3887 (3)| 0.6259 (2)| 0.1076 (3)| 0.0243 (6)       |
| H17   | 0.339129 | 0.669834 | 0.038431 | 0.029            |
| C17A  | 0.5446 (3)| 0.6103 (2)| 0.1446 (3)| 0.0197 (6)       |
| N17A  | 0.5446 (3)| 0.6103 (2)| 0.1446 (3)| 0.0197 (6)       |
| C21   | 0.3022 (3)| 0.8993 (2)| 0.3242 (3)| 0.0221 (6)       |
| H21   | 0.207038 | 0.901456 | 0.334175 | 0.027            |
| N22   | 0.3367 (3)| 0.9351 (2)| 0.2233 (2)| 0.0219 (5)       |
| C22   | 0.2316 (4)| 0.9859 (3)| 0.1121 (3)| 0.0309 (7)       |
| H22A  | 0.285214 | 1.008631 | 0.056212 | 0.046            |
| H22B  | 0.190771 | 1.060694 | 0.146702 | 0.046            |
| H22C  | 0.149190 | 0.922204 | 0.059430 | 0.046            |
| C23   | 0.4808 (4)| 0.9189 (2)| 0.2403 (3)| 0.0225 (6)       |
| H23   | 0.531495 | 0.936507 | 0.183524 | 0.027            |
| N23A  | 0.5413 (3)| 0.8728 (2)| 0.3535 (2)| 0.0181 (5)       |
| C23A  | 0.5413 (3)| 0.8728 (2)| 0.3535 (2)| 0.0181 (5)       |
| C24   | 0.6873 (3)| 0.8389 (3)| 0.4152 (3)| 0.0250 (6)       |
| H24   | 0.762633 | 0.847636 | 0.378149 | 0.030            |
| C25   | 0.7187 (4)| 0.7935 (3)| 0.5287 (3)| 0.0285 (7)       |
| H25   | 0.816635 | 0.768429 | 0.570170 | 0.034            |
| C26   | 0.6081 (4)| 0.7824 (3)| 0.5877 (3)| 0.0285 (7)       |
| H26   | 0.634114 | 0.752055 | 0.668515 | 0.034            |
| C27   | 0.4670 (4)| 0.8146 (2)| 0.5297 (3)| 0.0252 (7)       |
| H27   | 0.393603 | 0.807294 | 0.569120 | 0.030            |
| C27A  | 0.4298 (3)| 0.8598 (2)| 0.4078 (3)| 0.0211 (6)       |
| N27A  | 0.4298 (3)| 0.8598 (2)| 0.4078 (3)| 0.0211 (6)       |
| Cd1   | 0.84620 (2)| 0.18609 (2)| 0.25086 (2)| 0.01928 (6)     |
| Br1   | 0.5610 (3)| 0.1881 (11)| 0.1247 (10)| 0.0222 (4)       |
| Cl1   | 0.5727 (5)| 0.1844 (19)| 0.1340 (18)| 0.0222 (4)       |
| Br2   | 1.0021 (2)| 0.2985 (2)| 0.1431 (2)| 0.02319 (16)    |
| Cl2   | 1.003 (3)| 0.291 (3)| 0.155 (3)| 0.02319 (16)    |
| Br3   | 0.9014 (7)| 0.04313 (18)| 0.2368 (6)| 0.0262 (2)       |
| Cl3   | 0.902 (2)| −0.0282 (6)| 0.2367 (19)| 0.0262 (2)       |
| Br4   | 0.8962 (4)| 0.31677 (16)| 0.48575 (14)| 0.0245 (3)     |
| Cl4   | 0.8977 (14)| 0.2952 (7)| 0.4831 (5)| 0.0245 (3)       |
Atomic displacement parameters (Å²)

|     | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|-----|------|------|------|------|------|------|
| C11 | 0.0217 (16) | 0.0175 (13) | 0.0258 (15) | 0.0023 (10) | 0.0095 (13) | 0.0031 (11) |
| N12 | 0.0165 (12) | 0.0187 (11) | 0.0269 (13) | 0.0025 (9) | 0.0101 (11) | 0.0026 (9) |
| C1  | 0.0190 (16) | 0.0296 (16) | 0.0397 (18) | 0.0051 (12) | 0.0179 (14) | 0.0103 (13) |
| C13 | 0.0176 (15) | 0.0177 (13) | 0.0269 (15) | 0.0012 (10) | 0.0082 (12) | 0.0030 (10) |
| N13A| 0.0163 (13) | 0.0165 (12) | 0.0273 (14) | 0.0012 (9) | 0.0098 (11) | 0.0011 (9) |
| C13A| 0.0163 (13) | 0.0165 (12) | 0.0273 (14) | 0.0012 (9) | 0.0098 (11) | 0.0011 (9) |
| C14 | 0.0330 (19) | 0.0191 (14) | 0.0350 (17) | 0.0005 (12) | 0.0183 (15) | 0.0048 (12) |
| C15 | 0.035 (2) | 0.0243 (15) | 0.048 (2) | −0.0025 (13) | 0.0285 (18) | 0.0015 (14) |
| C16 | 0.0151 (15) | 0.0263 (15) | 0.050 (2) | −0.0026 (11) | 0.0148 (15) | −0.0063 (14) |
| C17 | 0.0172 (15) | 0.0210 (14) | 0.0313 (16) | 0.0025 (11) | 0.0077 (13) | −0.0027 (11) |
| C17A| 0.0176 (14) | 0.0143 (12) | 0.0251 (14) | 0.0008 (9) | 0.0075 (12) | −0.0020 (10) |
| N17A| 0.0176 (14) | 0.0143 (12) | 0.0251 (14) | 0.0008 (9) | 0.0075 (12) | −0.0020 (10) |
| C21 | 0.0206 (15) | 0.0199 (13) | 0.0246 (15) | 0.0023 (11) | 0.0090 (13) | −0.0012 (11) |
| N22 | 0.0241 (14) | 0.0179 (11) | 0.0205 (12) | 0.0026 (9) | 0.0054 (11) | 0.0007 (9) |
| C22 | 0.0335 (19) | 0.0267 (16) | 0.0252 (16) | 0.0060 (13) | 0.0020 (15) | 0.0037 (12) |
| C23 | 0.0291 (17) | 0.0176 (13) | 0.0218 (14) | 0.0028 (11) | 0.0114 (13) | 0.0013 (10) |
| N23A| 0.0214 (14) | 0.0159 (11) | 0.0189 (12) | 0.0026 (9) | 0.0104 (11) | 0.0012 (9) |
| C23A| 0.0214 (14) | 0.0159 (11) | 0.0189 (12) | 0.0026 (9) | 0.0104 (11) | 0.0012 (9) |
| C24 | 0.0182 (15) | 0.0247 (15) | 0.0331 (17) | 0.0007 (11) | 0.0139 (14) | −0.0027 (12) |
| C25 | 0.0250 (17) | 0.0191 (14) | 0.0332 (17) | 0.0028 (11) | 0.0023 (14) | 0.0000 (12) |
| C26 | 0.038 (2) | 0.0200 (14) | 0.0233 (15) | −0.0037 (13) | 0.0059 (14) | 0.0050 (11) |
| C27 | 0.0344 (19) | 0.0206 (14) | 0.0241 (15) | −0.0060 (12) | 0.0171 (14) | −0.0004 (11) |
| C27A| 0.0240 (15) | 0.0159 (13) | 0.0251 (14) | −0.0011 (10) | 0.0137 (12) | −0.0025 (10) |
| N27A| 0.0240 (15) | 0.0159 (13) | 0.0251 (14) | −0.0011 (10) | 0.0137 (12) | −0.0025 (10) |
| Cd1 | 0.01779 (11) | 0.02089 (11) | 0.01967 (10) | 0.00058 (7) | 0.00668 (8) | 0.00518 (7) |
| Br1 | 0.0163 (4) | 0.0287 (6) | 0.0213 (13) | 0.0048 (8) | 0.0034 (6) | 0.0104 (7) |
| Cl1 | 0.0163 (4) | 0.0287 (6) | 0.0213 (13) | 0.0048 (8) | 0.0034 (6) | 0.0104 (7) |
| Br2 | 0.02510 (19) | 0.0221 (4) | 0.0273 (5) | 0.00083 (18) | 0.0134 (3) | 0.0089 (2) |
| Cl2 | 0.02510 (19) | 0.0221 (4) | 0.0273 (5) | 0.00083 (18) | 0.0134 (3) | 0.0089 (2) |
| Br3 | 0.0274 (3) | 0.0170 (6) | 0.0415 (3) | 0.0068 (8) | 0.0173 (2) | 0.0138 (8) |
| Cl3 | 0.0274 (3) | 0.0170 (6) | 0.0415 (3) | 0.0068 (8) | 0.0173 (2) | 0.0138 (8) |
| Br4 | 0.0239 (2) | 0.0248 (8) | 0.0214 (2) | −0.0037 (6) | 0.00643 (18) | −0.0006 (3) |
| Cl4 | 0.0239 (2) | 0.0248 (8) | 0.0214 (2) | −0.0037 (6) | 0.00643 (18) | −0.0006 (3) |

Geometric parameters (Å, °)

|     | C11—N12 | 1.356 (4) | N22—C23 | 1.337 (4) |
|-----|---------|----------|---------|----------|
| C11 | 1.368 (4) | C22—H22A | 0.9800 |
| C11 | 1.368 (4) | C22—H22B | 0.9800 |
| N12 | 0.9500 | C22—H22C | 0.9800 |
| C12 | 1.345 (4) | C23—C23A | 1.357 (4) |
| N12 | 1.462 (3) | C23—C23B | 0.9800 |
| C12 | 0.9800 | C23—H23 | 0.9500 |
| C12 | 0.9800 | N23A—C24 | 1.402 (4) |

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| Bond          | Length (Å) | Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|--------------|------------|
| C13—C13A     | 1.345 (4)  | N23A—C27A    | 1.402 (3)  |
| C13—N13A     | 1.345 (4)  | C23A—C24     | 1.402 (4)  |
| C13—H13      | 0.9500     | C23A—N27A    | 1.402 (3)  |
| N13A—C14     | 1.404 (4)  | C24—C25      | 1.353 (4)  |
| N13A—C17A    | 1.408 (4)  | C24—H24      | 0.9500     |
| C13A—C14     | 1.404 (4)  | C25—C26      | 1.427 (4)  |
| C13A—N17A    | 1.408 (4)  | C25—H25      | 0.9500     |
| C14—C15      | 1.339 (4)  | C26—C27      | 1.350 (4)  |
| C14—H14      | 0.9500     | C26—H26      | 0.9500     |
| C15—C16      | 1.433 (5)  | C27—N27A     | 1.431 (4)  |
| C15—H15      | 0.9500     | C27—C27A     | 1.431 (4)  |
| C16—C17      | 1.344 (4)  | C27—H27      | 0.9500     |
| C16—H16      | 0.9500     | Cd1—Cl3      | 2.380 (4)  |
| C17—N17A     | 1.415 (4)  | Cd1—Cl2      | 2.460 (5)  |
| C17—C17A     | 1.415 (4)  | Cd1—Cl1      | 2.467 (3)  |
| C17—H17      | 0.9500     | Cd1—Cl4      | 2.497 (4)  |
| C21—N27A     | 1.366 (4)  | Cd1—Br3      | 2.535 (12) |
| C21—C27A     | 1.366 (4)  | Cd1—Br1      | 2.5834 (17)|
| C21—N22      | 1.369 (4)  | C21—C27A     | 1.366 (4)  |
| C21—H21      | 0.9500     | C21—N27A     | 1.369 (4)  |

N12—C11—N17A  | 107.3 (2)  | N22—C23—N23A | 107.3 (2)  |
N12—C11—C17A  | 107.3 (2)  | N22—C23—H23  | 126.3      |
N12—C11—H11   | 126.3      | N23A—C23—H23 | 126.3      |
C17A—C11—H11  | 126.3      | C23—N23A—C24 | 130.4 (3)  |
C13—N12—C11   | 110.5 (2)  | C23—N23A—C27A| 108.7 (3)  |
C13—N12—C12   | 125.2 (3)  | C24—N23A—C27A| 120.9 (2)  |
C11—N12—C12   | 124.3 (2)  | C23—C23A—C24 | 130.4 (3)  |
N12—C12—H12A  | 109.5      | C23—C23A—N23A| 108.7 (3)  |
N12—C12—H12B  | 109.5      | C24—C23A—N27A| 120.9 (2)  |
H12A—C12—H12B | 109.5      | C25—C24—N23A | 118.6 (3)  |
N12—C12—H12C  | 109.5      | C25—C24—C23A | 118.6 (3)  |
H12A—C12—H12C | 109.5      | C25—C24—H24  | 120.7      |
H12B—C12—H12C | 109.5      | N23A—C24—H24 | 120.7      |
C13A—C13—N12  | 107.4 (3)  | C24—C25—C26  | 121.6 (3)  |
N13A—C13—N12  | 107.4 (3)  | C24—C25—H25  | 119.2      |
N13A—C13—H13  | 126.3      | C26—C25—H25  | 119.2      |
N12—C13—H13   | 126.3      | C27—C26—C25  | 120.6 (3)  |
C13—N13A—C14  | 130.7 (3)  | C27—C26—H26  | 119.7      |
C13—N13A—C17A | 108.6 (2)  | C25—C26—H26  | 119.7      |
C14—N13A—C17A | 120.8 (2)  | C26—C27—N23A | 118.9 (3)  |
C13—C13A—C14  | 130.7 (3)  | C26—C27—C27A | 118.9 (3)  |
C13—C13A—N17A | 108.6 (2)  | C26—C27—H27  | 120.5      |
C14—C13A—N17A | 120.8 (2)  | C27A—C27—H27 | 120.5      |
C15—C14—N13A  | 118.6 (3)  | C21—C27A—N23A| 106.2 (2)  |
C15—C14—C13A  | 118.6 (3)  | C21—C27A—C27 | 134.4 (3)  |
C15—C14—H14   | 120.7      | N23A—C27A—C27 | 119.4 (3)  |
N13A—C14—H14  | 120.7      | C21—N27A—C23A| 106.2 (2)  |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|----------|----------------------|----------|
| C14—C15—C16         | 120.8 (3) | C21—N27A—C27         | 134.4 (3) |
| C14—C15—H15         | 119.6    | C23A—N27A—C27        | 119.4 (3) |
| C16—C15—H15         | 119.6    | C13—Cd1—C12          | 107.3 (10) |
| C17—C16—C15         | 122.0 (3) | C13—Cd1—Cl1          | 106.1 (7)  |
| C17—C16—H16         | 119.0    | C12—Cd1—Cl1          | 114.9 (9)  |
| C15—C16—H16         | 119.0    | C13—Cd1—Cl4          | 112.7 (5)  |
| C16—C17—N17A        | 117.9 (3) | C12—Cd1—Cl4          | 109.6 (9)  |
| C16—C17—C17A        | 117.9 (3) | C11—Cd1—Cl4          | 106.3 (6)  |
| C16—C17—H17         | 121.1    | C13—Cd1—Br3          | 1.0 (6)    |
| C17A—C17—H17        | 121.1    | C12—Cd1—Br3          | 108.4 (9)  |
| C11—C17A—N13A       | 106.3 (2) | C11—Cd1—Br3          | 105.3 (5)  |
| C11—C17A—C17        | 133.9 (3) | C14—Cd1—Br3          | 112.4 (2)  |
| N13A—C17A—C17       | 119.9 (2) | C13—Cd1—Br1          | 107.0 (5)  |
| C11—N17A—C13A       | 106.3 (2) | C12—Cd1—Br1          | 113.4 (8)  |
| C11—N17A—C17        | 133.9 (3) | C11—Cd1—Br1          | 1.5 (7)    |
| C13A—N17A—C17       | 119.9 (2) | C14—Cd1—Br1          | 106.9 (4)  |
| N27A—C21—N22        | 107.5 (3) | Br3—Cd1—Br1          | 106.2 (3)  |
| C27A—C21—N22        | 107.5 (3) | C13—Cd1—Br2          | 108.3 (5)  |
| C27A—C21—H21        | 126.2    | C12—Cd1—Br2          | 2.1 (8)    |
| N22—C21—H21         | 126.2    | C11—Cd1—Br2          | 112.8 (5)  |
| C23—N22—C21         | 110.2 (2) | C14—Cd1—Br2          | 110.6 (2)  |
| C23—N22—C22         | 124.3 (3) | Br3—Cd1—Br2          | 109.34 (14)|
| C21—N22—C22         | 125.5 (3) | Br1—Cd1—Br2          | 111.3 (3)  |
| N22—C22—H22A        | 109.5    | C13—Cd1—Br4          | 117.3 (5)  |
| N22—C22—H22B        | 109.5    | C12—Cd1—Br4          | 106.6 (9)  |
| H22A—C22—H22B       | 109.5    | C11—Cd1—Br4          | 104.9 (5)  |
| N22—C22—H22C        | 109.5    | C14—Cd1—Br4          | 4.6 (2)    |
| H22A—C22—H22C       | 109.5    | Br3—Cd1—Br4          | 117.00 (15)|
| H22B—C22—H22C       | 109.5    | Br1—Cd1—Br4          | 105.4 (3)  |
| N22—C23—C23A        | 107.3 (2) | Br2—Cd1—Br4          | 107.57 (8) |

N17A—C11—N12—C13    0.0 (3)  N27A—C21—N22—C23    0.3 (3)  
C17A—C11—N12—C13    0.0 (3)  C27A—C21—N22—C23    0.3 (3)  
N17A—C11—N12—C12    179.1 (2) | N27A—C21—N22—C22    −179.0 (2) |
C17A—C11—N12—C12    179.1 (2) | C27A—C21—N22—C22    −179.0 (2) |
C11—N12—C13—C13A    −0.3 (3) | C21—N22—C23—C23A    −0.3 (3)  
C12—N12—C13—C13A    −0.3 (3) | C22—N22—C23—C23A    179.0 (2) |
C11—N12—C13—N13A    −0.3 (3) | C21—N22—C23—N23A    −0.3 (3)  
C12—N12—C13—N13A    −0.3 (3) | C22—N22—C23—N23A    179.0 (2) |
N12—C13—N13A—C14    −178.2 (3) | N22—C23—N23A—C24    179.5 (2) |
N12—C13—N13A—C17A   0.4 (3)  | N22—C23—N23A—C27A    0.2 (3)  
N12—C13—C13A—C14    −178.2 (3) | N22—C23—C23A—C24    179.5 (2) |
N12—C13—C13A—N17A   0.4 (3)  | N22—C23—C23A—N27A    0.2 (3)  
C13—N13A—C14—C15    178.1 (3) | C23—N23A—C24—C25    −179.4 (3) |
C17A—N13A—C14—C15   −0.4 (4) | C27A—N23A—C24—C25    −0.1 (4)  
C13—C13A—C14—C15    178.1 (3) | C23—C23A—C24—C25    −179.4 (3) |
N17A—C13A—C14—C15   −0.4 (4) | N27A—C23A—C24—C25    −0.1 (4)  
N13A—C14—C15—C16    1.5 (4)  | N23A—C24—C25—C26    −1.5 (4)  

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C13A—C14—C15—C16  1.5 (4)  C23A—C24—C25—C26  −1.5 (4)
C14—C15—C16—C17  −1.1 (5)  C24—C25—C26—C27  1.5 (4)
C15—C16—C17—N17A  −0.5 (4)  C25—C26—C27—N27A  0.1 (4)
C15—C16—C17—C17A  −0.5 (4)  C25—C26—C27—C27A  0.1 (4)
N12—C11—C17A—N13A  0.2 (3)  N22—C21—C27A—N23A  −0.2 (3)
N12—C11—C17A—C17  179.7 (3)  N22—C21—C27A—C27  178.5 (3)
C13—N13A—C17A—N13A  −0.4 (3)  C23—N23A—C27A—C21  0.0 (3)
C13—N13A—C17A—C17  178.3 (2)  C23—N23A—C27A—C27  −179.4 (2)
N12—C11—C17A—C11  −0.4 (3)  N22—C21—C27A—C27  178.5 (3)
N12—C11—C17A—C17  179.7 (3)  N22—C21—C27A—C27  178.5 (3)
C13—C13A—N17A—C11  −0.4 (3)  C23—C23A—N27A—C21  0.0 (3)
C13—C13A—N17A—C17  178.3 (2)  C23—C23A—N27A—C27  −179.4 (2)
C13—C13A—N17A—C13A  −1.2 (4)  C23—C23A—N27A—C27  1.7 (4)
C14—C13A—N17A—C11  −177.8 (3)  C24—C24A—N27A—C21  179.8 (3)
C14—C13A—N17A—C17  178.3 (3)  C24—C24A—N27A—C27  −178.9 (2)
C14—C13A—N17A—C13A  1.6 (4)  C24—C24A—N27A—C27  1.7 (4)

Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|---------|------|-------|-------|--------|
| C11—H11···Br1i | 0.95 | 2.61  | 3.401 (9) | 141 |
| C12—H12···Br2ii | 0.98 | 2.90  | 3.820 (3) | 156 |
| C12—H12···Br2  | 0.98 | 2.72  | 3.621 (4) | 153 |
| C13—H13···Br4  | 0.95 | 2.83  | 3.666 (4) | 148 |
| C13—H13···Br4iii | 0.95 | 3.09  | 3.577 (4) | 113 |
| C17—H17···Br1i | 0.95 | 2.92  | 3.649 (12) | 134 |
| C21—H21···Br3vi | 0.95 | 2.84  | 3.685 (6) | 149 |
| C23—H23···Br1i | 0.95 | 2.93  | 3.541 (12) | 123 |
| C24—H24···Br3i | 0.95 | 2.75  | 3.627 (6) | 155 |
| C27—H27···Br4vi | 0.95 | 2.87  | 3.657 (4) | 141 |

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

Bis(2-methylimidazo[1,5-alpyridinium) trichloridooxidozincate(II) (III)

Crystal data

(C8H9N2)2[CdCl3.90I0.10]  Z = 2
Mf = 529.69  F(000) = 523
Triclinic, P1  Dp = 1.745 Mg m−3
a = 9.4304 (3) Å  Cu Kα radiation, λ = 1.54178 Å
b = 10.7968 (3) Å  Cell parameters from 10758 reflections
C = 10.7565 (3) Å  θ = 4.2–67.2°
a = 99.209 (3)°  μ = 14.69 mm−1
β = 110.746 (3)°  T = 100 K
γ = 90.837 (2)°  Needle, colourless
V = 1007.97 (5) Å3  0.25 × 0.08 × 0.04 mm
Data collection

Oxford Diffraction Gemini diffractometer
Radiation source: sealed X-ray tube, Enhance Ultra (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.4738 pixels mm\(^{-1}\)
\(\omega\) scans
Absorption correction: analytical
CrysAlis Pro (Rigaku OD, 2016)

\[ T_{\text{min}} = 0.052, \quad T_{\text{max}} = 0.522 \]
18506 measured reflections
3581 independent reflections
3309 reflections with \( I > 2\sigma(I) \)

\[ \theta_{\text{max}} = 67.3^\circ, \quad \theta_{\text{min}} = 4.2^\circ \]
\( h = -11 \rightarrow 11 \)
\( k = -12 \rightarrow 12 \)
\( l = -12 \rightarrow 12 \)

Refinement

Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.027 \)
\( wR(F^2) = 0.068 \)
\( S = 1.06 \)
3581 reflections
234 parameters
2 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

\[ w = 1/[\sigma(Fo^2) + (0.0384P)^2 + 0.6373P] \]
where \( P = (Fo^2 + 2Fc^2)/3 \)
\( (\Delta/\sigma)_{\text{max}} < 0.001 \)
\( \Delta \rho_{\text{max}} = 0.79 e \text{Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.46 e \text{Å}^{-3} \)

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. The halogen site 2 was modelled as being part Cl and part I, with Cl site occupancies refined to 0.9008 (15) with the I site occupancies being its complement. Cd-X bond lengths of the disordered atoms were restrained to ideal values. The cations were modelled as being rotationally disordered by 180 degrees. The site occupancies refined to 0.72 (3) and its complement for cation 1 and 0.81 (3) and its complement for cation 2.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))

|   | x       | y       | z       | U\(_{eq}\) | Occ. (<1) |
|---|---------|---------|---------|-----------|-----------|
| C11 | 0.6607 (3) | 0.6542 (3) | 0.1045 (3) | 0.0263 (6) |
| H11 | 0.649443 | 0.704261 | 0.037015 | 0.032* |
| N12 | 0.7924 (3) | 0.6108 (2) | 0.1810 (2) | 0.0254 (5) |
| C12 | 0.9396 (3) | 0.6325 (3) | 0.1681 (3) | 0.0326 (7) |
| H12A | 1.010714 | 0.681187 | 0.252843 | 0.049* |
| H12B | 0.926939 | 0.679406 | 0.094506 | 0.049* |
| H12C | 0.979688 | 0.551513 | 0.148316 | 0.049* |
| C13 | 0.7667 (3) | 0.5435 (3) | 0.2662 (3) | 0.0279 (6) |
| H13 | 0.840247 | 0.503253 | 0.329448 | 0.034* |
| N13A | 0.6172 (3) | 0.5435 (2) | 0.2456 (3) | 0.0273 (7) | 0.72 (3) |
| C13A | 0.6172 (3) | 0.5435 (2) | 0.2456 (3) | 0.0273 (7) | 0.28 (3) |
| C14 | 0.5312 (4) | 0.4912 (3) | 0.3101 (3) | 0.0371 (7) |
| H14 | 0.577624 | 0.444977 | 0.380184 | 0.045* |
| C15 | 0.3812 (4) | 0.5080 (3) | 0.2705 (4) | 0.0409 (8) |
| H15 | 0.321888 | 0.473974 | 0.314089 | 0.049* |
| C16 | 0.3102 (4) | 0.5760 (3) | 0.1644 (4) | 0.0367 (7) |
| H16 | 0.204106 | 0.585364 | 0.137727 | 0.044* |
### Atomic displacement parameters (Å²)

|    | \(U^{11}\)   | \(U^{22}\)   | \(U^{33}\)   | \(U^{12}\)   | \(U^{13}\)   | \(U^{23}\)   |
|----|---------------|---------------|---------------|---------------|---------------|---------------|
| C11| 0.0271 (14)   | 0.0234 (14)   | 0.0276 (15)   | 0.0046 (12)   | 0.0096 (11)   | 0.0023 (11)   |
| N12| 0.0249 (12)   | 0.0222 (12)   | 0.0287 (12)   | 0.0027 (10)   | 0.0110 (10)   | 0.0002 (10)   |
| C12| 0.0286 (15)   | 0.0320 (16)   | 0.0397 (17)   | 0.0046 (13)   | 0.0163 (13)   | 0.0038 (13)   |
| C13| 0.0292 (15)   | 0.0238 (14)   | 0.0282 (15)   | 0.0034 (12)   | 0.0083 (12)   | 0.0022 (11)   |
| N13A| 0.0297 (14)  | 0.0203 (13)   | 0.0311 (14)   | 0.0020 (10)   | 0.0122 (11)   | −0.0002 (10)  |
| C13A| 0.0297 (14)  | 0.0203 (13)   | 0.0311 (14)   | 0.0020 (10)   | 0.0122 (11)   | −0.0002 (10)  |
| C14| 0.0490 (19)   | 0.0291 (16)   | 0.0414 (18)   | 0.0038 (14)   | 0.0249 (15)   | 0.0095 (14)   |
| C15| 0.046 (2)     | 0.0317 (17)   | 0.054 (2)     | −0.0027 (15)  | 0.0321 (17)   | 0.0006 (15)   |
| C16| 0.0281 (15)   | 0.0305 (16)   | 0.050 (2)     | −0.0005 (13)  | 0.0182 (14)   | −0.0065 (14)  |
| C17| 0.0281 (15)   | 0.0262 (15)   | 0.0329 (16)   | 0.0052 (12)   | 0.0102 (12)   | −0.0040 (12)  |
| C17A| 0.0272 (14)  | 0.0210 (14)   | 0.0284 (15)   | 0.0040 (11)   | 0.0096 (11)   | −0.0012 (11)  |
| N17A| 0.0272 (14)  | 0.0210 (14)   | 0.0284 (15)   | 0.0040 (11)   | 0.0096 (11)   | −0.0012 (11)  |
| C21| 0.0288 (15)   | 0.0248 (15)   | 0.0349 (16)   | 0.0042 (12)   | 0.0133 (12)   | −0.0035 (12)  |

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N22 0.0377 (14) 0.0227 (12) 0.0269 (13) 0.0037 (11) 0.0085 (11) −0.0015 (10)
C22 0.0459 (19) 0.0349 (18) 0.0314 (17) 0.0067 (15) 0.0033 (14) 0.0014 (14)
C23 0.0398 (17) 0.0233 (15) 0.0285 (15) 0.0008 (13) 0.0159 (13) −0.0010 (12)
N23A 0.0334 (14) 0.0203 (12) 0.0285 (13) 0.0000 (10) 0.0156 (11) −0.0031 (10)
C23A 0.0334 (14) 0.0203 (12) 0.0285 (13) 0.0000 (10) 0.0156 (11) −0.0031 (10)
C24 0.0269 (15) 0.0257 (15) 0.0430 (18) −0.0015 (12) 0.0172 (13) −0.0080 (13)
C25 0.0332 (16) 0.0261 (16) 0.0409 (18) 0.0056 (13) 0.0058 (14) −0.0027 (13)
C26 0.049 (2) 0.0265 (16) 0.0296 (16) −0.0022 (14) 0.0083 (14) 0.0009 (13)
C27 0.0436 (18) 0.0245 (15) 0.0306 (16) −0.0064 (13) 0.0192 (14) −0.0029 (12)
C27A 0.0297 (15) 0.0222 (14) 0.0291 (15) −0.0010 (11) 0.0147 (12) −0.0038 (11)
N27A 0.0297 (15) 0.0222 (14) 0.0291 (15) −0.0010 (11) 0.0147 (12) −0.0038 (11)
Cd1 0.02659 (12) 0.02715 (13) 0.02568 (12) 0.00296 (8) 0.00879 (8) 0.00419 (8)
C11 0.0268 (3) 0.0371 (4) 0.0308 (4) 0.0035 (3) 0.0079 (3) 0.0094 (3)
C12 0.0328 (10) 0.0261 (7) 0.0321 (7) 0.0008 (6) 0.0181 (5) 0.0086 (4)
I2 0.0328 (10) 0.0261 (7) 0.0321 (7) 0.0008 (6) 0.0181 (5) 0.0086 (4)
C13 0.0409 (4) 0.0297 (4) 0.0459 (4) 0.0095 (3) 0.0204 (3) 0.0128 (3)
C14 0.0351 (4) 0.0413 (4) 0.0278 (4) −0.0015 (3) 0.0094 (3) 0.0000 (3)

Geometric parameters (Å, º)

| Bond/Distance | Value1 | Value2 | Value3 | Value4 | Value5 | Value6 |
|---------------|--------|--------|--------|--------|--------|--------|
| C11—N12       | 1.362  |        |        |        |        |        |
| C11—N17A      | 1.363  |        |        |        |        |        |
| C11—C17A      | 1.363  |        |        |        |        |        |
| C11—H11       | 0.9500 |        |        |        |        |        |
| N12—C13       | 1.338  |        |        |        |        |        |
| N12—C12       | 1.462  |        |        |        |        |        |
| C12—H12A      | 0.9800 |        |        |        |        |        |
| C12—H12B      | 0.9800 |        |        |        |        |        |
| C12—H12C      | 0.9800 |        |        |        |        |        |
| C13—C13A      | 1.347  |        |        |        |        |        |
| C13—N13A      | 1.347  |        |        |        |        |        |
| C13—H13       | 0.9500 |        |        |        |        |        |
| N13A—C17A     | 1.402  |        |        |        |        |        |
| N13A—C14      | 1.402  |        |        |        |        |        |
| C13A—N17A     | 1.402  |        |        |        |        |        |
| C13A—C14      | 1.402  |        |        |        |        |        |
| C14—C15       | 1.350  |        |        |        |        |        |
| C14—H14       | 0.9500 |        |        |        |        |        |
| C15—C16       | 1.425  |        |        |        |        |        |
| C15—H15       | 0.9500 |        |        |        |        |        |
| C16—C17       | 1.348  |        |        |        |        |        |
| C16—H16       | 0.9500 |        |        |        |        |        |
| C17—N17A      | 1.413  |        |        |        |        |        |
| C17—C17A      | 1.413  |        |        |        |        |        |
| C17—H17       | 0.9500 |        |        |        |        |        |
| C21—N27A      | 1.360  |        |        |        |        |        |
| C21—C27A      | 1.360  |        |        |        |        |        |
| C21—N22       | 1.364  |        |        |        |        |        |
N12—C11—N17A 107.1 (3) C23—N22—C22 124.4 (3)
N12—C11—C17A 107.1 (3) C21—N22—C22 125.1 (3)
N12—C11—H11 126.4 N22—C22—H22A 109.5
C17A—C11—H11 126.4 N22—C22—H22B 109.5
C13—N12—C11 110.5 (2) H22A—C22—H22B 109.5
C13—N12—C12 125.3 (3) N22—C22—H22C 109.5
C11—N12—C12 124.2 (2) H22A—C22—H22C 109.5
N12—C12—H12A 109.5 H22B—C22—H22C 109.5
N12—C12—H12B 109.5 N22—C23—C23A 107.4 (3)
H12A—C12—H12B 109.5 N22—C23—N23A 107.4 (3)
N12—C12—H12C 109.5 N22—C23—H23 126.3
H12A—C12—H12C 109.5 C23—N23A—C24 130.1 (3)
N12—C13—C13A 107.3 (3) C23—N23A—C27A 108.4 (3)
N12—C13—N13A 107.3 (3) C24—N23A—C27A 121.5 (3)
N12—C13—H13 126.3 C23—C23A—C24 130.1 (3)
N13A—C13—H13 126.3 C23—C23A—N27A 108.4 (3)
C13—N13A—C17A 108.5 (2) C24—C23A—N27A 121.5 (3)
C13—N13A—C14 131.1 (3) C25—C24—N23A 118.1 (3)
C17A—N13A—C14 120.4 (3) C25—C24—C23A 118.1 (3)
C13—C13A—N17A 108.5 (2) C25—C24—H24 120.9
C13—C13A—C14 131.1 (3) N23A—C24—C25 120.9
N13A—C14—H14 120.7 N23A—C24—H25 121.3 (3)
C14—C15—C16 121.1 (3) N26—C24—C25 119.3
C14—C15—H15 119.5 N26—C24—H25 119.3
C16—C15—H15 119.5 C27—C26—C25 121.2 (3)
C17—C16—C15 121.4 (3) C27—C26—H26 119.4
C17—C16—H16 119.3 C27—C26—H27 120.5
C15—C16—H16 119.3 C27A—C27—H27 120.5
C16—C17—N17A 118.2 (3) C21—C27A—N23A 106.9 (3)
C16—C17—C17A 118.2 (3) C21—C27A—C27 134.1 (3)
C16—C17—H17 120.9 N23A—C27A—C27 119.0 (3)
C17A—C17—H17 120.9 C21—C27A—C23A 106.9 (3)
C11—C17A—N13A 106.5 (2) C21—N27A—C27 134.1 (3)
C11—C17A—C17 133.2 (3) C23A—N27A—C27 119.0 (3)
N13A—C17A—C17 120.3 (3) C13—Cd1—C12 109.94 (9)
C11—N17A—C13A 106.5 (2) C13—Cd1—C14 116.91 (3)
C11—N17A—C17 133.2 (3) C12—Cd1—C14 106.67 (9)
C13A—N17A—C17 120.3 (3) C13—Cd1—C11 105.93 (3)
N27A—C21—N22 106.9 (3) C12—Cd1—C11 112.21 (9)
C27A—C21—N22 106.9 (3) C14—Cd1—C11 105.20 (3)
C27A—C21—H21 126.6 C13—Cd1—I2 109.2 (2)
N22—C21—H21 126.6 C12—Cd1—I2 0.9 (3)
C14—Cd1—I2 106.7 (2)
### Hydrogen-bond geometry (Å, °)

| D—H···A          | D—H   | H···A  | D···A    | D—H···A |
|------------------|-------|-------|----------|---------|
| C13—H13···Cl4    | 0.95  | 2.77  | 3.597 (3) | 146     |
| C12—H124···Cl4i  | 0.98  | 2.71  | 3.520 (3) | 141     |
| C12—H12C···Cl2   | 0.98  | 2.76  | 3.652 (5) | 152     |
| C11—H11···C11i   | 0.95  | 2.64  | 3.412 (3) | 139     |
| C17—H17···C11i   | 0.95  | 2.81  | 3.560 (3) | 137     |
|          |   d   |  R   |    E   |  θ  |
|----------|-------|------|--------|-----|
| C21—H21···Cl3<sup>iii</sup> | 0.95  | 2.78 | 3.623 (3) | 148 |
| C23—H23···Cl1<sup>iv</sup>   | 0.95  | 2.83 | 3.447 (3) | 123 |
| C24—H24···Cl3<sup>iv</sup>   | 0.95  | 2.68 | 3.568 (3) | 155 |
| C27—H27···Cl4<sup>v</sup>    | 0.95  | 2.79 | 3.605 (3) | 144 |

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