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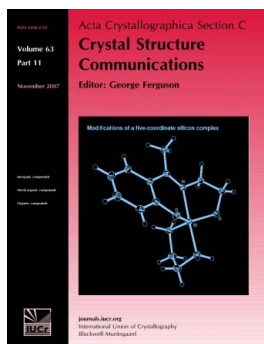
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Ionothermal synthesis and crystal structure of a new organic–inorganic hybrid compound: *catena*-poly[bis(1-ethyl-3-methylimidazolium) [hepta- μ -bromido-pentacuprate(I)]]

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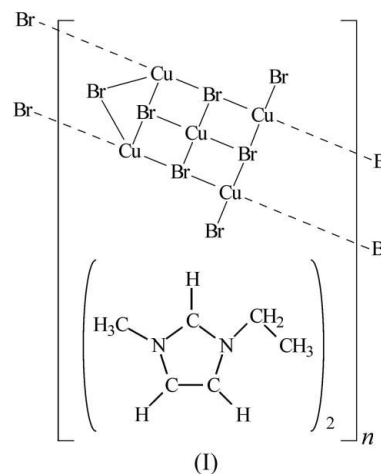
A new organic–inorganic hybrid compound, *catena*-poly[bis(1-ethyl-3-methylimidazolium) [μ_5 -bromido-tri- μ_3 -bromido-tri- μ_2 -bromido-pentacuprate(I)]]], $\{(\text{C}_6\text{H}_{11}\text{N}_2)_2[\text{Cu}_5\text{Br}_7]\}_n$, has been obtained under ionothermal conditions from a reaction mixture containing $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, As_2O_5 , 1-ethyl-3-methylimidazolium bromide and distilled water. The crystal structure consists of complex $[\text{Cu}_5\text{Br}_7]^{2-}$ anions arranged in sinusoidal $\{[\text{Cu}_5\text{Br}_7]^{2-}\}_n$ chains running along the *a* axis, which are surrounded by 1-ethyl-3-methylimidazolium cations. Three of the five unique Br atoms and one of the three Cu^{I} atoms occupy special positions with half-occupancy (a mirror plane perpendicular to the *b* axis, site symmetry *m*). The Cu^{I} ions are in a distorted tetrahedral coordination environment, with four Br atoms at distances ranging from 2.3667 (10) to 2.6197 (13) Å, and an outlier at 3.0283 (12) Å, exceptionally elongated and with a small contribution to the bond-valence sum of only 6.7%. Short C—H...Br contacts build up a three-dimensional network. The Cu...Cu distances within the chain range from 2.8390 (12) to 3.0805 (17) Å, indicating the existence of weak $\text{Cu}^{\text{I}} \cdots \text{Cu}^{\text{I}}$ cuprophilic interactions.

Keywords: crystal structure; organic–inorganic hybrid compound; copper(I) bromide; ionothermal synthesis; 1-ethyl-3-methylimidazolium bromide; Cu...Cu interactions.

1. Introduction

The increasing attention paid to organic–inorganic hybrid materials originates from their fascinating magnetic, electrical, optical and porous properties, as well as from the variety and diversity of their structures and topologies (Zhang & Xiong,

2012; Zhou *et al.*, 2012). Among hybrid compounds reported so far, copper(I) halides with different organic templates have been widely investigated due to their rich photoluminescent properties and intriguing topologies (Graham *et al.*, 2000; Wang *et al.*, 2002; Peng *et al.*, 2010; Xin *et al.*, 2013; Liu *et al.*, 2014). Copper(I) tends to form a variety of coordination compounds with halides, ranging from zero-dimensional complexes to three-dimensional frameworks (Subramanian & Hoffmann, 1992; Peng *et al.*, 2010; Gao *et al.*, 2010; Liu *et al.*, 2014). The introduction of organic molecules in the synthesis of polynuclear copper(I) halides is the most extensively and effectively employed strategy to modulate copper(I) halide structures (Xin *et al.*, 2013). Only a few reports of the solid-state structures of imidazolium salts containing transition metals and halide anions have been published (Zeller *et al.*, 2005; Chen *et al.*, 2011; Ji *et al.*, 2011; Hu *et al.*, 2011; Shao & Yu, 2014). They all show short contacts between the halide atoms of the cuprate(I) anion and the H atoms of the 1-ethyl-3-methylimidazolium (emim) cation.



Although the title compound, *catena*-poly[bis(1-ethyl-3-methylimidazolium) [μ_5 -bromido-tri- μ_3 -bromido-tri- μ_2 -bromido-pentacuprate(I)]]], $\{(\text{emim})_2[\text{Cu}_5\text{Br}_7]\}_n$, (I), was obtained unintentionally, it fits perfectly into our research concerning the iono- and hydrothermal synthesis, crystallography and properties of organic–inorganic hybrid compounds (Karanović *et al.*, 2011). We report here the details of the ionothermal synthesis and structural characterization of this new organically templated copper(I) bromide.

2. Experimental

2.1. Synthesis and crystallization

While working on the preparation of inorganic arsenites and arsenates using ionic liquids as a medium, the title compound was obtained by reaction of 2.00 g of an equimolar mixture of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Fluka), $\text{Cu}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (Alfa Products) and As_2O_5 (AlfaAesar) in a Teflon vessel ($V \sim 8 \text{ cm}^3$) with a 4:1 mixture of emim bromide and distilled water as the medium. The Teflon vessel was enclosed in a stainless steel autoclave and heated for 4 h under autogenous pressure to 493 K, held at this temperature for 72 h, and

Table 1

Experimental details.

Crystal data	
Chemical formula	(C ₆ H ₁₁ N ₂) ₂ [Cu ₅ Br ₇]
<i>M</i> _r	1099.41
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.736 (3), 20.481 (4), 10.038 (2)
<i>V</i> (Å ³)	2618.3 (9)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ^{−1})	14.69
Crystal size (mm)	0.08 × 0.05 × 0.03
Data collection	
Diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan (Otwinowski <i>et al.</i> , 2003)
<i>T</i> _{min} , <i>T</i> _{max}	0.418, 0.644
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	45708, 3085, 2307
<i>R</i> _{int}	0.055
(sin θ/λ) _{max} (Å ^{−1})	0.649
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.069, 1.02
No. of reflections	3085
No. of parameters	133
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ^{−3})	1.48, −1.18

Computer programs: *COLLECT* (Nonius, 2002), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO-SMN* (Otwinowski *et al.*, 2003), *SIR97* (Altomare *et al.*, 1999), *SHELXL97* (Sheldrick, 2008), *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006), *ATOMS* (Dowty, 2000) and *pubCIF* (Westrip, 2010).

cooled to room temperature over a period of 72 h. Colourless prismatic crystals of (emim)₂[Cu₅Br₇] (yield 20%) were obtained together with blue prismatic crystals of BaCuAs₂O₇ (yield 80%) (Chen & Wang, 1996). The crystals were washed with ethanol and dried in air.

2.2. Refinement

A complete sphere of reciprocal space (*φ* and *ω* scans) was measured during data collection at room temperature. Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms attached to C atoms were located in geometrically calculated positions and refined using the riding model, with C–H = 0.96 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms, C–H = 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for methylene H atoms, and C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for imidazolium ring H atoms.

3. Results and discussion

The co-existence of (emim)₂[Cu₅Br₇] and BaCuAs₂O₇ as the reaction products showed that a partial reduction of Cu^{II} to Cu^I occurred during the synthesis. At first sight, this seems surprising, but reduction of Cu^{II} or oxidation of Cu^I in the course of hydrothermal reactions has already been observed. For example, in the preparation of Cu complexes with ethylenediamine, Hammond *et al.* (2001) started with CuBr or a CuBr/CuBr₂ mixture, and in both cases mixed-valence complexes were obtained. Liu *et al.* (2014) also prepared mixed-valence Cu^{I,II} or pure Cu^I complexes using CuBr₂ as a reactant in the presence of isonicotinic acid. All the mentioned

compounds belong to the group of bromidocuprates(I). In our case, the reduction can be explained by the high reaction temperature of 493 K. According to Chambreau *et al.* (2012), decomposition of emimBr should occur at 585 K, but the process starts slowly at 473 K with CH₃Br and C₂H₅Br as the main products. Very likely these organic bromides act as *in situ* reducing agents. Chemically and thermodynamically, the appearance of (emim)₂[Cu₅Br₇] demonstrates a high stability

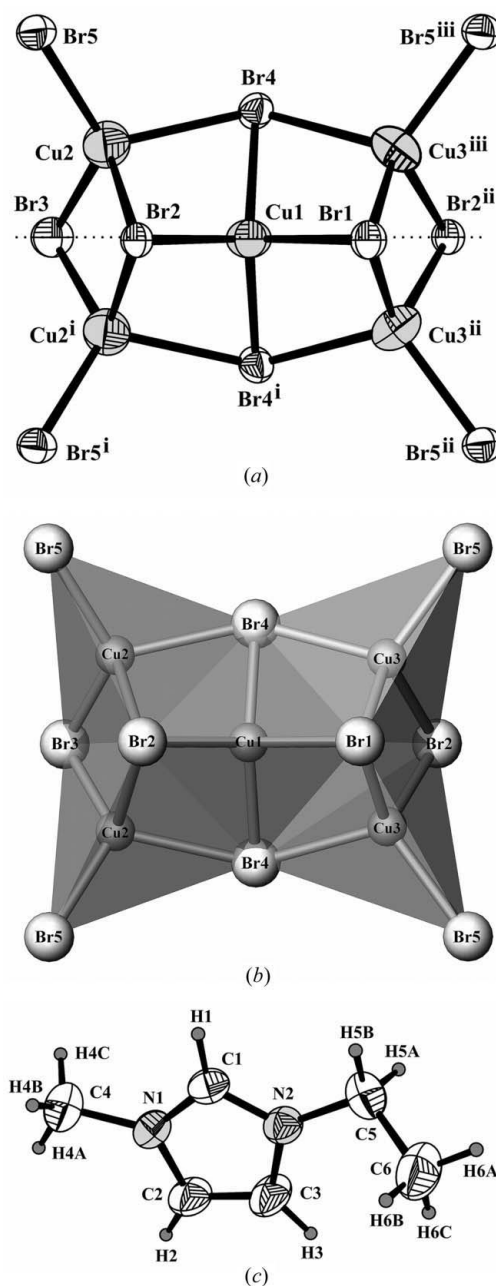


Figure 1

(a) A view of the pentanuclear [Cu₅Br₇]^{2−} anion, (b) a polyhedral view of the same unit (generic atom labels without symmetry codes have been used) and (c) a displacement ellipsoid plot (50% probability level) of the emim cation showing the atomic numbering scheme. The dotted line in (a) indicates the position of the mirror plane and connects atoms in special positions. [Symmetry codes: (i) *x*, −*y* + $\frac{1}{2}$, *z*; (ii) *x* + $\frac{1}{2}$, −*y* + $\frac{1}{2}$, −*z* + $\frac{1}{2}$; (iii) *x* + $\frac{1}{2}$, *y*, −*z* + $\frac{1}{2}$.]

of bromidocuprates(I) if Cu^{I} and Br^- ions are found in the same reaction mixture.

In the asymmetric unit of $(\text{emim})_2[\text{Cu}_5\text{Br}_7]$, there are three crystallographically distinct Cu^{I} atoms, five crystallographically unique Br atoms and two emim cations. The structure is based on pentanuclear structural units, where five Cu^{I} atoms (one Cu1 in a special position with half-occupancy, two Cu2 and two Cu3) are tetrahedrally coordinated, sharing tetrahedron edges (Fig. 1).

Similar to Cu1, three of the five unique Br atoms (Br1, Br2 and Br3) also occupy special positions with half-occupancy and all are located on the mirror plane perpendicular to the b axis (site symmetry m). The pentanuclear structural units are further joined in the sinusoidal $[\text{Cu}_5\text{Br}_7]^{2-}$ chains running parallel to the crystallographic a axis. These chains can be interpreted as the polymerization product of the $[\text{Cu}_5\text{Br}_7]^{2-}$ unit, where Br atoms are located at the vertices of a very distorted pentagonal bipyramid, forming a cage containing Cu^{I} ions in tetrahedral holes (Fig. 2).

The $[\text{Cu}_5\text{Br}_7]^{2-}$ chains show structural similarities to the three-dimensional $[\text{Cu}_5\text{Br}_7]^{2-}$ framework of $(\text{C}_5\text{H}_5\text{NH}_2)_2[\text{Cu}_5\text{Br}_7]$ (Chan *et al.*, 1978) and the $[\text{Cu}_5\text{Br}_7]^{2-}$ anions found in $[(\text{NCH}_3)(\text{C}_4\text{H}_9)_3]_2[\text{Cu}_5\text{Br}_7]$ (Andersson & Jagner, 1988), as well as to the sinusoidal $[\text{Cu}_5\text{Br}_7]^{2-}$ chain found in $[\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2][\text{Cu}_5\text{Br}_7]$ (Hammond *et al.*, 2001). In the $[\text{Cu}_5\text{Br}_7]^{2-}$ chains found in $[\text{Cu}(\text{en})_2][\text{Cu}_5\text{Br}_7]$ (Hammond *et al.*, 2001) and in the three-dimensional $[\text{Cu}_5\text{Br}_7]^{2-}$

Table 2

Selected geometric parameters (\AA , $^\circ$).

Cu1—Br4	2.4304 (8)	Cu3—Br5	2.3992 (9)
Cu1—Br4 ⁱ	2.4304 (8)	Cu3—Br1 ^{iv}	2.4692 (10)
Cu1—Br2	2.5089 (13)	Cu3—Br2	2.5958 (10)
Cu1—Br1	2.6197 (13)	Cu3—Br4 ^{iv}	2.6039 (10)
Cu1—Cu3 ⁱⁱ	2.8390 (12)	Cu3—Cu1 ^{iv}	2.8390 (12)
Cu1—Cu3 ⁱⁱⁱ	2.8390 (12)	Cu3—Cu3 ⁱ	2.9407 (17)
Cu1—Cu2 ⁱ	2.9243 (13)	N1—C1	1.314 (6)
Cu1—Cu2	2.9243 (13)	N1—C2	1.359 (6)
Cu2—Br3	2.3667 (10)	N1—C4	1.468 (6)
Cu2—Br5	2.4049 (10)	N2—C1	1.314 (6)
Cu2—Br4	2.5405 (10)	N2—C3	1.369 (6)
Cu2—Br2	3.0283 (12)	N2—C5	1.470 (6)
Cu2—Cu3	2.8659 (12)	C2—C3	1.344 (8)
Cu2—Cu2 ⁱ	3.0805 (17)	C5—C6	1.504 (8)
Br4—Cu1—Br4 ⁱ	118.15 (5)	Br5—Cu2—Br4	111.14 (4)
Br4—Cu1—Br2	112.52 (3)	Br3—Cu2—Br2	106.70 (4)
Br4 ⁱ —Cu1—Br2	112.52 (3)	Br5—Cu2—Br2	96.72 (3)
Br4—Cu1—Br1	107.61 (3)	Br4—Cu2—Br2	94.65 (3)
Br4 ⁱ —Cu1—Br1	107.61 (3)	Br5—Cu3—Br2	109.53 (4)
Br2—Cu1—Br1	95.75 (4)	Br5—Cu3—Br4 ^{iv}	111.73 (4)
Br3—Cu2—Br5	126.63 (4)	Br2—Cu3—Br4 ^{iv}	96.99 (4)
Br3—Cu2—Br4	113.80 (4)		

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

framework reported by Chan *et al.* (1978), the bipyramids were connected by additional face-sharing tetrahedra formed by Br atoms. Subramanian & Hoffmann (1992) examined the bonding between bridging Br and Cu atoms in planar and nonplanar model systems and found an extraordinary structural richness in these halidocuprates(I), consisting of molecular or polymeric $[\text{Cu}_x\text{Br}_y]^{n-}$ anions and various, often organic, counter-ions. The idealized polymeric $[\text{Cu}_5\text{Br}_7]^{2-}$ anion is constructed from two μ_5 -Br atoms at the apices of a

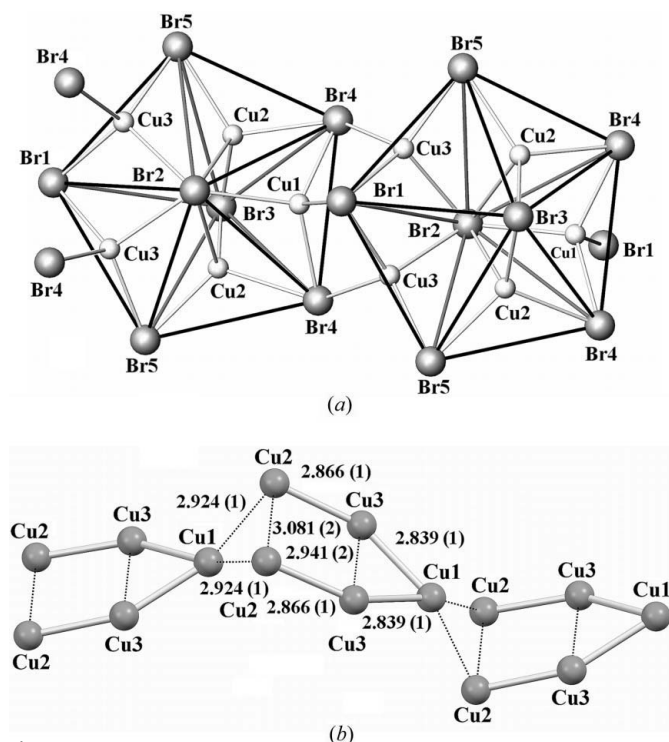


Figure 2

(a) The polymerization product of the $[\text{Cu}_5\text{Br}_7]^{2-}$ anion, with Br atoms at the vertices of a very distorted pentagonal bipyramid and Cu atoms in distorted tetrahedral positions. (b) A topological view of the $\text{Cu}\cdots\text{Cu}$ contacts. Thick lines show $\text{Cu}\cdots\text{Cu}$ distances shorter than 2.9 \AA , while dotted lines are used to represent longer distances. Generic atom labels without symmetry codes have been used.

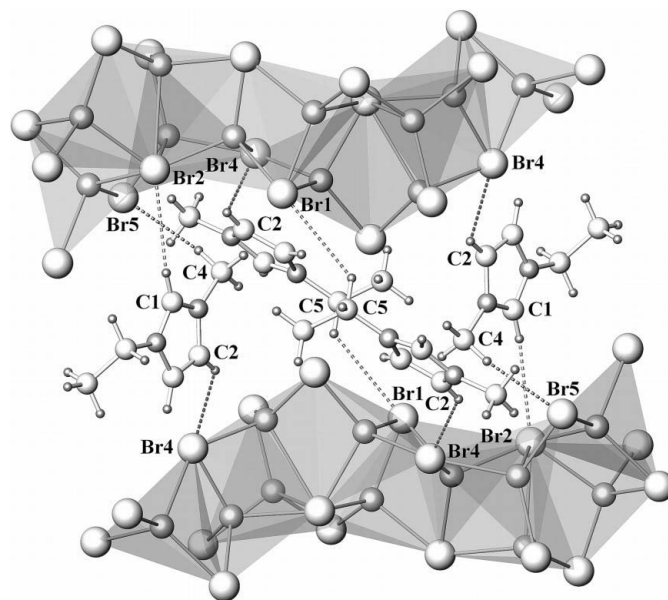


Figure 3

Polyhedral representation of the $[\text{Cu}_5\text{Br}_7]^{2-}$ sinusoidal chains, projected approximately onto the (021) plane, showing short contacts between Br atoms and emim cations. For the sake of clarity, only some of the contacts are shown and only C and Br atoms involved in these contacts are labelled. Generic atom labels without symmetry codes have been used.

Table 3

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots Br2 ^{iv}	0.93	2.97	3.803 (5)	150
C2—H2 \cdots Br4 ^v	0.93	2.84	3.534 (5)	133
C4—H4B \cdots Br5 ^{vi}	0.96	3.04	3.987 (6)	168
C5—H5A \cdots Br1 ^{vii}	0.97	3.11	3.774 (5)	127
C6—H6A \cdots Br3 ^{viii}	0.96	3.27	3.842 (6)	120

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

pentagonal bipyramid and the five μ_2 -Br atoms in the equatorial plane of the pentagon, with tetrahedral coordination around all five Cu atoms. They found that the Cu—Br distances increase from 2.227 to 2.421, 2.600 and 2.912 Å as the Br atoms go from terminal to bridging two, four and five Cu atoms, respectively.

Although in (emim)₂[Cu₅Br₇] all the Cu^I atoms are coordinated by four Br atoms in a distorted CuBr₄ tetrahedral arrangement, only one Br atom (Br2) is linked to all five Cu^I atoms (Fig. 2). Br3 is moved from another apex of the pentagonal bipyramid and consequently links to only two Cu^I atoms at distances of 2.3667 (10) Å, while another three Cu^I atoms are at distances longer than 4 Å. Cu1 is coordinated by three μ_3 -Br atoms (Br1 and two symmetry equivalents of Br4) and one μ_5 -Br atom (Br2). The coordination polyhedron of the Cu2 site is formed by two μ_2 -Br atoms (Br3 and Br5), one μ_3 -Br atom (Br4) and one μ_5 -Br atom (Br2). The geometry of the Cu3 site is completed by two μ_3 -Br atoms (Br1 and Br4), one μ_3 -Br atom (Br4) and one μ_5 -Br atom (Br2). The Cu—Br bond distances range from 2.3667 (10) to 2.6197 (13) Å, while the Br—Cu—Br angles vary from 94.65 (3) to 126.63 (4)° (Table 2). There is a very long Cu—Br outlier [Cu2—Br2 = 3.0283 (12) Å] whose contribution to the sum of the bond valences is only 6.7%. The described distortions convert ideal di- μ_5 -bromido-penta- μ_2 -bromido-pentacuprate(I) into deformed μ_5 -bromido-tri- μ_3 -bromido-tri- μ_2 -bromido-pentacuprate(I).

The $\{[Cu_5Br_7]^{2-}\}_n$ chains are crosslinked into a three-dimensional network by C—H \cdots Br (hydrogen-bond-like) interactions involving the emim cations (Fig. 3). They are established by imidazolium ring H atoms (H1 and H2), as well as by H atoms of the methylene (H5A) and a methyl (H4B) group (Table 3).

Bond-valence calculations (Wills, 2010; Brown, 1996) show that the Cu—Br bond lengths are consistent with the presence of Cu^I and Br⁻. The bond-valence sums for Cu^I are in the range 1.1–1.2 v.u. [1.155 (16) v.u. for Cu1, 1.083 (8) v.u. for Cu2 and 1.103 (10) v.u. for Cu3] and for Br are slightly undersaturated (Σv_{ij} in the range 0.73–0.84 v.u.), indicating that all the Br atoms act as hydrogen-bond acceptors.

Within the $\{[Cu_5Br_7]^{2-}\}_n$ chains there are weak Cu^I \cdots Cu^I interactions (Table 2), with Cu \cdots Cu distances close to or slightly longer than the sum of the van der Waals radii (2.80 Å; Bondi, 1964). Within the chain units, Cu^I atoms make perfectly

planar and slightly deformed pentagons, which are further connected in a zigzag manner (Fig. 3). Closed-shell contacts between two Cu⁺ ions (d^{10} configuration) are quite frequent, well documented and usually discussed in term of cuprophilicity. Thus, Dinda & Samuelson (2012) showed that Cu^I \cdots Cu^I interactions exist, but should be very weak, although involve some contribution of covalent bonding. In this way, Cu^I \cdots Cu^I interactions resemble features present in hydrogen bonds.

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supporting information

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Ionothermal synthesis and crystal structure of a new organic–inorganic hybrid compound: *catena*-poly[bis(1-ethyl-3-methylimidazolium) [hepta- μ -bromido-pentacuprate(I)]]

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Computing details

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 2012); molecular graphics: *Mercury* (Macrae *et al.*, 2006) and *ATOMS* (Dowty, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2010).

catena-Poly[bis(1-ethyl-3-methylimidazolium) [μ_5 -bromido-tri- μ_3 -bromido-tri- μ_2 -bromido-pentacuprate(I)]]

Crystal data

(C₆H₁₁N₂)₂[Cu₅Br₇]
 $M_r = 1099.41$
 Orthorhombic, *Pnma*
 $a = 12.736$ (3) Å
 $b = 20.481$ (4) Å
 $c = 10.038$ (2) Å
 $V = 2618.3$ (9) Å³
 $Z = 4$

$F(000) = 2048$
 $D_x = 2.789$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 $\mu = 14.69$ mm⁻¹
 $T = 293$ K
 Prism, colorless
 $0.08 \times 0.05 \times 0.03$ mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: Nonius KappaCCD
 ω and θ scans
 Absorption correction: multi-scan
 (Otwinowski *et al.*, 2003)
 $T_{\min} = 0.418$, $T_{\max} = 0.644$
 45708 measured reflections

3085 independent reflections
 2307 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -16 \rightarrow 15$
 $k = -26 \rightarrow 26$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.069$
 $S = 1.02$
 3085 reflections
 133 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 9.4671P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 1.48 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.18 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.82942 (8)	0.2500	0.26679 (10)	0.0514 (3)
Cu2	0.70539 (6)	0.17479 (4)	0.45799 (8)	0.0664 (2)
Cu3	0.50114 (6)	0.17821 (4)	0.33841 (9)	0.0655 (2)
Br1	0.89348 (5)	0.2500	0.01878 (7)	0.03839 (17)
Br2	0.63702 (5)	0.2500	0.21315 (7)	0.03377 (16)
Br3	0.70679 (6)	0.2500	0.63700 (7)	0.04681 (19)
Br4	0.88677 (4)	0.14820 (2)	0.36772 (5)	0.03742 (12)
Br5	0.58741 (4)	0.08417 (2)	0.42970 (5)	0.04333 (14)
N1	0.1721 (3)	0.4255 (2)	0.5215 (4)	0.0375 (9)
N2	0.0522 (3)	0.39696 (19)	0.6606 (4)	0.0381 (9)
C1	0.1105 (4)	0.3776 (2)	0.5599 (5)	0.0374 (11)
H1	0.1084	0.3363	0.5217	0.045*
C2	0.1533 (5)	0.4781 (3)	0.6006 (6)	0.0518 (14)
H2	0.1861	0.5186	0.5956	0.062*
C3	0.0782 (4)	0.4605 (3)	0.6875 (6)	0.0529 (15)
H3	0.0491	0.4866	0.7537	0.063*
C4	0.2476 (5)	0.4232 (3)	0.4112 (5)	0.0555 (15)
H4A	0.2827	0.4645	0.4039	0.083*
H4B	0.2112	0.4139	0.3296	0.083*
H4C	0.2983	0.3895	0.4279	0.083*
C5	−0.0265 (4)	0.3568 (3)	0.7296 (6)	0.0482 (13)
H5A	0.0024	0.3415	0.8134	0.058*
H5B	−0.0428	0.3189	0.6755	0.058*
C6	−0.1255 (4)	0.3946 (3)	0.7561 (7)	0.0652 (17)
H6A	−0.1752	0.3671	0.8008	0.098*
H6B	−0.1547	0.4093	0.6732	0.098*
H6C	−0.1097	0.4317	0.8112	0.098*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0529 (6)	0.0410 (5)	0.0602 (6)	0.000	−0.0027 (5)	0.000

Cu2	0.0635 (5)	0.0618 (5)	0.0739 (5)	−0.0127 (4)	0.0050 (4)	−0.0171 (4)
Cu3	0.0664 (5)	0.0577 (5)	0.0725 (5)	0.0162 (4)	0.0016 (4)	0.0098 (4)
Br1	0.0397 (4)	0.0418 (4)	0.0337 (4)	0.000	0.0018 (3)	0.000
Br2	0.0264 (3)	0.0341 (3)	0.0409 (4)	0.000	0.0006 (3)	0.000
Br3	0.0543 (5)	0.0449 (4)	0.0412 (4)	0.000	0.0002 (4)	0.000
Br4	0.0330 (2)	0.0374 (3)	0.0419 (3)	0.0012 (2)	0.0011 (2)	0.0088 (2)
Br5	0.0417 (3)	0.0343 (3)	0.0540 (3)	0.0001 (2)	0.0007 (2)	0.0038 (2)
N1	0.037 (2)	0.041 (2)	0.035 (2)	0.0030 (18)	0.0002 (17)	−0.0067 (19)
N2	0.041 (2)	0.035 (2)	0.038 (2)	−0.0013 (18)	0.0010 (18)	−0.0056 (18)
C1	0.040 (3)	0.032 (2)	0.039 (3)	0.001 (2)	−0.002 (2)	−0.007 (2)
C2	0.060 (4)	0.033 (3)	0.062 (4)	−0.006 (3)	0.014 (3)	−0.014 (3)
C3	0.062 (4)	0.039 (3)	0.058 (3)	−0.008 (3)	0.018 (3)	−0.023 (3)
C4	0.058 (4)	0.066 (4)	0.043 (3)	0.000 (3)	0.009 (3)	−0.006 (3)
C5	0.049 (3)	0.050 (3)	0.046 (3)	−0.009 (3)	0.003 (3)	0.006 (3)
C6	0.054 (4)	0.073 (4)	0.068 (4)	−0.010 (3)	0.017 (3)	−0.013 (4)

Geometric parameters (Å, °)

Cu1—Br4	2.4304 (8)	N1—C1	1.314 (6)
Cu1—Br4 ⁱ	2.4304 (8)	N1—C2	1.359 (6)
Cu1—Br2	2.5089 (13)	N1—C4	1.468 (6)
Cu1—Br1	2.6197 (13)	N2—C1	1.314 (6)
Cu1—Cu3 ⁱⁱ	2.8390 (12)	N2—C3	1.369 (6)
Cu1—Cu3 ⁱⁱⁱ	2.8390 (12)	N2—C5	1.470 (6)
Cu1—Cu2 ⁱ	2.9243 (13)	C1—Br4 ^v	3.482 (5)
Cu1—Cu2	2.9243 (13)	C1—H1	0.9300
Cu2—Br3	2.3667 (10)	C2—C3	1.344 (8)
Cu2—Br5	2.4049 (10)	C2—Br4 ^{vi}	3.534 (5)
Cu2—Br4	2.5405 (10)	C2—H2	0.9300
Cu2—Br2	3.0283 (12)	C3—Br4 ^{vi}	3.910 (5)
Cu2—Cu3	2.8659 (12)	C3—Br5 ^{vii}	3.952 (6)
Cu2—Cu2 ⁱ	3.0805 (17)	C3—H3	0.9300
Cu3—Br5	2.3992 (9)	C4—Br4 ^{viii}	3.622 (5)
Cu3—Br1 ^{iv}	2.4692 (10)	C4—Cu3 ⁱ	3.908 (6)
Cu3—Br2	2.5958 (10)	C4—Br5 ^{viii}	3.987 (6)
Cu3—Br4 ^{iv}	2.6039 (10)	C4—H4A	0.9600
Cu3—Cu1 ^{iv}	2.8390 (12)	C4—H4B	0.9600
Cu3—Cu3 ⁱ	2.9407 (17)	C4—H4C	0.9600
Br1—Cu3 ⁱⁱ	2.4692 (10)	C5—C6	1.504 (8)
Br1—Cu3 ⁱⁱⁱ	2.4692 (10)	C5—H5A	0.9700
Br2—Cu3 ⁱ	2.5958 (10)	C5—H5B	0.9700
Br2—Cu2 ⁱ	3.0283 (12)	C6—H6A	0.9600
Br3—Cu2 ⁱ	2.3667 (10)	C6—H6B	0.9600
Br4—Cu3 ⁱⁱⁱ	2.6039 (10)	C6—H6C	0.9600
Br4—Cu1—Br4 ⁱ	118.15 (5)	Br2—Cu3—Br4 ^{viii}	62.06 (2)
Br4—Cu1—Br2	112.52 (3)	Br4 ^{iv} —Cu3—Br4 ^{viii}	68.21 (2)
Br4 ⁱ —Cu1—Br2	112.52 (3)	Cu2 ⁱ —Cu3—Br4 ^{viii}	75.86 (2)

Br4—Cu1—Br1	107.61 (3)	Br3—Cu3—Br4 ^{viii}	104.99 (2)
Br4 ⁱ —Cu1—Br1	107.61 (3)	Br5—Cu3—Br2 ^{iv}	135.71 (3)
Br2—Cu1—Br1	95.75 (4)	Br2—Cu3—Br2 ^{iv}	114.24 (3)
Br4—Cu1—Br2 ⁱⁱⁱ	71.24 (3)	Br4 ^{iv} —Cu3—Br2 ^{iv}	57.09 (2)
Br4 ⁱ —Cu1—Br2 ⁱⁱⁱ	71.24 (3)	Br3—Cu3—Br2 ^{iv}	123.76 (2)
Br2—Cu1—Br2 ⁱⁱⁱ	170.55 (4)	Br4 ^{viii} —Cu3—Br2 ^{iv}	52.309 (11)
Br1—Cu1—Br2 ⁱⁱⁱ	74.80 (3)	C1—N1—C2	108.4 (4)
Cu3 ⁱⁱ —Cu1—Br2 ⁱⁱⁱ	41.39 (2)	C1—N1—C4	126.0 (4)
Cu3 ⁱⁱⁱ —Cu1—Br2 ⁱⁱⁱ	41.39 (2)	C2—N1—C4	125.6 (5)
Cu2 ⁱ —Cu1—Br2 ⁱⁱⁱ	120.38 (3)	C1—N2—C3	107.5 (4)
Cu2—Cu1—Br2 ⁱⁱⁱ	120.38 (3)	C1—N2—C5	125.3 (4)
Br3—Cu2—Br5	126.63 (4)	C3—N2—C5	127.1 (4)
Br3—Cu2—Br4	113.80 (4)	N1—C1—N2	109.7 (4)
Br5—Cu2—Br4	111.14 (4)	N1—C1—H1	125.1
Br3—Cu2—Br2	106.70 (4)	N2—C1—H1	125.1
Br5—Cu2—Br2	96.72 (3)	C3—C2—N1	106.9 (5)
Br4—Cu2—Br2	94.65 (3)	C3—C2—H2	126.5
Br3—Cu2—Br4 ⁱ	67.39 (3)	N1—C2—H2	126.5
Br5—Cu2—Br4 ⁱ	160.23 (4)	C2—C3—N2	107.4 (5)
Br4—Cu2—Br4 ⁱ	67.99 (3)	C2—C3—H3	126.3
Br2—Cu2—Br4 ⁱ	64.16 (2)	N2—C3—H3	126.3
Br5—Cu2—Br5 ⁱ	123.30 (3)	N1—C4—H4A	109.5
Br4—Cu2—Br5 ⁱ	116.72 (3)	N1—C4—H4B	109.5
Br2—Cu2—Br5 ⁱ	52.118 (17)	H4A—C4—H4B	109.5
Br1 ^{iv} —Cu2—Br5 ⁱ	52.230 (11)	N1—C4—H4C	109.5
Br4 ⁱ —Cu2—Br5 ⁱ	49.708 (16)	H4A—C4—H4C	109.5
Cu3 ⁱⁱⁱ —Cu2—Br5 ⁱ	100.380 (19)	H4B—C4—H4C	109.5
Br3—Cu2—Br4 ^{iv}	123.18 (3)	N2—C5—C6	111.5 (4)
Br5—Cu2—Br4 ^{iv}	50.37 (2)	N2—C5—H5A	109.3
Br4—Cu2—Br4 ^{iv}	117.35 (3)	C6—C5—H5A	109.3
Br4 ⁱ —Cu2—Br4 ^{iv}	111.37 (2)	N2—C5—H5B	109.3
Br5 ⁱ —Cu2—Br4 ^{iv}	80.783 (16)	C6—C5—H5B	109.3
Br5—Cu3—Br2	109.53 (4)	H5A—C5—H5B	108.0
Br5—Cu3—Br4 ^{iv}	111.73 (4)	C5—C6—H6A	109.5
Br2—Cu3—Br4 ^{iv}	96.99 (4)	C5—C6—H6B	109.5
Br5—Cu3—Br3	74.08 (3)	H6A—C6—H6B	109.5
Br2—Cu3—Br3	74.59 (3)	C5—C6—H6C	109.5
Br4 ^{iv} —Cu3—Br3	171.24 (3)	H6A—C6—H6C	109.5
Br5—Cu3—Br4 ^{viii}	171.10 (3)	H6B—C6—H6C	109.5

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
C1—H1 \cdots Br2 ^{iv}	0.93	2.97	3.803 (5)	150
C2—H2 \cdots Br4 ^{vi}	0.93	2.84	3.534 (5)	133
C4—H4B \cdots Br5 ^{viii}	0.96	3.04	3.987 (6)	168

C5—H5 <i>A</i> ⋯Br1 ^{ix}	0.97	3.11	3.774 (5)	127
C6—H6 <i>A</i> ⋯Br3 ^x	0.96	3.27	3.842 (6)	120

Symmetry codes: (iv) $x-1/2, y, -z+1/2$; (vi) $-x+1, y+1/2, -z+1$; (viii) $x-1/2, -y+1/2, -z+1/2$; (ix) $x-1, y, z+1$; (x) $x-1, y, z$.