

## Three-dimensional framework structures: isomorphous bis(2,6-diamino-3,5-dibromopyridinium) tetrabromidometallate(II) salts with Cd<sup>II</sup> and Mn<sup>II</sup>

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Received 9 May 2009

Accepted 20 July 2009

Online 25 July 2009

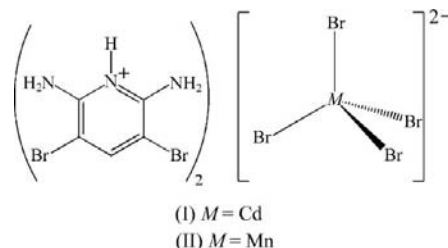
In the structural motifs of two isomorphous triclinic salts, (C<sub>5</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>3</sub>)<sub>2</sub>[MBr<sub>4</sub>] (*M* = Cd<sup>II</sup> and Mn<sup>II</sup>), each [MBr<sub>4</sub>]<sup>2−</sup> anion interacts with eight surrounding 2,6-diamino-3,5-dibromopyridinium cations through intermolecular C/N—H...Br and Br...Br interactions, leading to a three-dimensional framework structure. The cations show a minor degree of  $\pi$ – $\pi$  stacking, adding extra stability to the three-dimensional architecture.

### Comment

Intermolecular interactions are the essence of supramolecular chemistry (Desiraju, 1997), and the field of crystal supramolecularity seeks to understand intermolecular interactions by analysis of crystal packing. Dunitz's aphorism (Dunitz, 1991, 1996), 'the molecular crystal is the supramolecular entity par excellence', captures this view, and inspires research to extract this understanding.

Research in the field of organic–inorganic hybrid compounds is of great interest, because of their special magnetic (Cui *et al.*, 2000), electronic (Lacroix *et al.*, 1994) and optoelectronic properties (Chakravarthy & Guloy, 1997). The influence of the features of the organic cations on the packing interactions that govern the crystal organization is expected to affect the packing and thus the specific properties. In the light of previous research on hybrid compounds containing metal bromide anions with substituted pyridinium cations (Luque *et al.*, 2001; Haddad *et al.*, 2006; Al-Far & Ali, 2007*a,b*; Ali & Al-Far, 2007; Ali *et al.*, 2007, 2008), two isomorphous compounds containing the 2,6-diamino-3,5-dibromopyridinium cation (DadbpH) have been investigated, namely (DadbpH)<sub>2</sub>–[MBr<sub>4</sub>], with *M* = Cd for compound (I) and *M* = Mn for compound (II). These complexes were prepared from the reaction of 2,6-diaminopyridine with the corresponding

metal(II) salt in the presence of HBr and Br<sub>2</sub>. The introduction of amino groups at the 2- and 6-positions facilitates the electrophilic aromatic substitution of Br atoms at the 3- and 5-positions and increases the nucleophilicity at the ring N atom (Al-Far & Ali, 2007*b*). Therefore, protonation of the resulting 2,6-diamino-3,5-dibromopyridine takes place on the pyridine N atom rather than on the amino N atoms. The bromination and protonation of the pyridine ring were expected to create many important centres of interaction with the bromidometal anions, *e.g.* N—H...Br, ( $\pi$ )C—H...Br and possibly aryl–aryl ( $\pi$ ) stacking.



The [MBr<sub>4</sub>]<sup>2−</sup> anions in both (I) and (II) (Fig. 1) exhibit a slightly distorted tetrahedral arrangement around *M*, with *M*—Br bonds in the ranges 2.5678 (9)–2.5917 (11) and 2.4925 (10)–2.5073 (9) Å for *M* = Cd and Mn, respectively, giving mean values of 2.5821 (12) and 2.5011 (11) Å (Tables 1 and 3). The Br—*M*—Br angles have ranges of 101.99 (3)–114.59 (4) and 103.34 (4)–113.83 (4)° for *M* = Cd and Mn, respectively. These values are in accordance with the corresponding values in the literature (Al-Far & Ali, 2007*a*; Morawitz *et al.*, 2007). It is noteworthy that the Br—Mn—Br angles are narrower than for bis(dimethylammonium) tetrabromidomanganate(II) (Morawitz *et al.*, 2007), which might be due to the extensive packing interactions between the anion and surrounding cations in the present work compared with few interactions between the anion and cations (about four

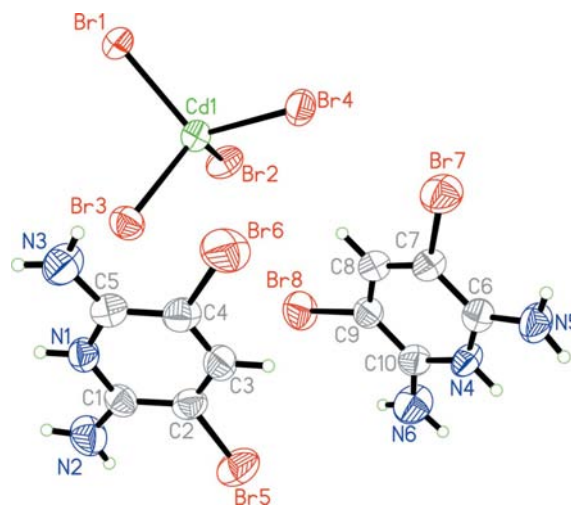
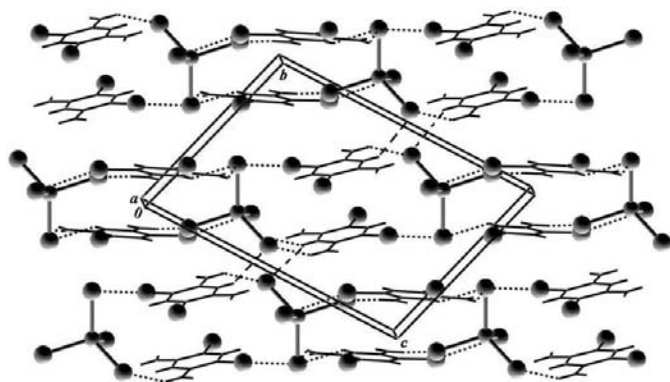


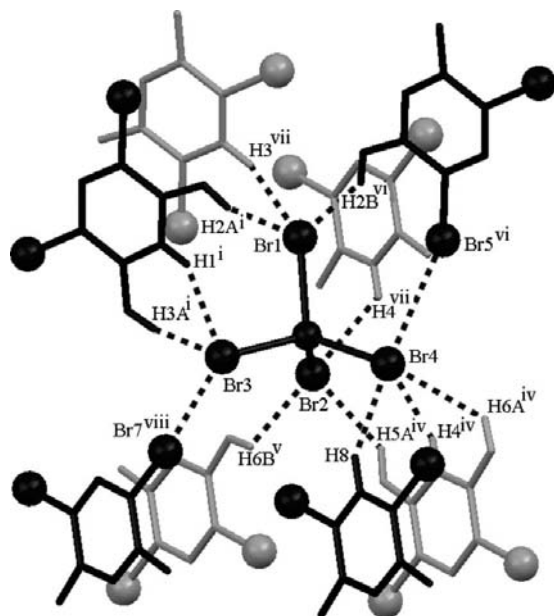
Figure 1

The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The isomorphous structure (II) is labelled in an analogous manner.



**Figure 2**

A representative packing diagram of the title isomorphous salts. Hydrogen bonds and Br...Br interactions are shown as dashed lines. Metals and Br atoms are shown as balls and all other atoms are shown as sticks.



**Figure 3**

Part of the cell contents of (I), showing some short amine/pyridine N—H...Br and Br...Br intermolecular interactions (dashed lines) for one  $[MBr_4]^{2-}$  anion. The isomorphous structure (II) is labelled in an analogous manner. [Symmetry codes: (i)  $-x, -y + 1, -z$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $-x, -y + 1, -z + 1$ ; (vi)  $1 + x, -1 + y, z$ ; (vii)  $x, y - 1, z$ ; (viii)  $-1 + x, y, z$ .]

short hydrogen-bonding interactions and no Br...Br interactions) in the much less crowded environment of the latter salt.

In the cations of (I) and (II), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The rings in the two independent cations are nearly planar, with the largest deviation from plane 1 (N1/C1–C5) being for atom Br5, which lies 0.081 (2) and 0.075 (3) Å out of this plane in (I) and (II), respectively. For plane 2 (N4/C6–C10), atom Br7 has the largest deviation, being 0.025 (3) and 0.050 (6) Å out of this plane in (I) and (II), respectively.

The crystal packing involves extensive cation–anion interactions. The packing diagram can be regarded as a three-

dimensional array of interacting cations and anions (Fig. 2) in which each anion interacts with eight surrounding cations (Fig. 3). Six of the cations interact *via* nine N—H...Br—M hydrogen-bonding interactions of types N—H...Br—M and H—N—H...Br—M, and two interactions of type C—H...Br (Fig. 3; Tables 2 and 4). Two of the cations interact with the anion *via* two C—Br...Br—M short contacts (see Table 5).

The cations also interact to some extent by offset face-to-face interactions, approximately along the (011) direction, adding extra structure stability. This is evident from their centroid (Cg) separation distances. In (I), the distance for cation I,  $Cg1 \cdots Cg1(-x, -y + 2, -z)$ , is 3.943 (3) Å, while for cation II,  $Cg1 \cdots Cg1(1 - x, 1 - y, 1 - z)$  is 3.760 (3) Å; the corresponding values for (II) are 3.922 (3) and 3.733 (3) Å. These separations are in accordance with those for calculated and experimentally observed stacked (offset face-to-face) interaction modes (Gould *et al.*, 1985; Hunter & Sanders, 1990; Hunter *et al.*, 1990; Hunter, 1994; Singh & Thornton, 1990). The stability of this type of structure is evident from the crystallization of these two isostructural compounds.

## Experimental

For the preparation of (I) and (II), 2,6-diaminopyridine (98%, 2 mmol) was dissolved in EtOH (95%, 25 ml) with heating and stirring. Another flask was prepared containing the corresponding metal salt, *viz.*  $CdBr_2$  or  $Mn(OAc)_2$  (1 mmol), dissolved in EtOH (95%, 10 ml). The two solutions were mixed together and acidified with HBr (48%, 2–3 ml).  $Br_2$  (liquid, 2–3 ml) was then added and the mixture heated (363 K) with stirring for 3 h. The solution was left to evaporate at room temperature, yielding colourless plate-shaped crystals [for (I)] or colourless crystal chips [for (II)] after 2 d. Some brown crystals were found in the vial used to prepare (II), and these proved to be  $[DadbpH]Br$ , one of two polymorphs of the compound (Haddad *et al.*, 2009).

## Compound (I)

### Crystal data

$(C_5H_6Br_2N_3)_2[CdBr_4]$   
 $M_r = 967.87$   
 Triclinic,  $P\bar{1}$   
 $a = 8.8759$  (18) Å  
 $b = 10.720$  (2) Å  
 $c = 14.137$  (3) Å  
 $\alpha = 73.07$  (3)°  
 $\beta = 86.87$  (3)°

$\gamma = 65.61$  (3)°  
 $V = 1168.7$  (5) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 14.62$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.25 \times 0.12 \times 0.04$  mm

### Data collection

Bruker SMART APEX  
 diffractometer  
 Absorption correction: empirical  
 (using intensity measurements)  
 (SADABS; Bruker, 2001)  
 $T_{min} = 0.114$ ,  $T_{max} = 0.557$

11259 measured reflections  
 4207 independent reflections  
 3281 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.037$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.082$   
 $S = 1.03$   
 4207 reflections

226 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{max} = 0.87$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.90$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (I).

Cd1—Br1	2.5896 (10)	Cd1—Br3	2.5791 (16)
Cd1—Br2	2.5917 (11)	Cd1—Br4	2.5678 (9)
Br1—Cd1—Br2	106.03 (3)	Br2—Cd1—Br3	113.34 (4)
Br1—Cd1—Br3	101.99 (3)	Br2—Cd1—Br4	107.05 (3)
Br1—Cd1—Br4	113.61 (4)	Br3—Cd1—Br4	114.59 (4)

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Br3 <sup>i</sup>	0.86	2.71	3.474 (4)	150
N2—H2A...Br1 <sup>i</sup>	0.86	2.83	3.400 (5)	125
N2—H2B...Br1 <sup>ii</sup>	0.86	2.70	3.411 (6)	141
N3—H3A...Br3 <sup>i</sup>	0.86	2.77	3.516 (5)	146
N4—H4...Br2 <sup>iii</sup>	0.86	2.82	3.446 (5)	131
N4—H4...Br4 <sup>iv</sup>	0.86	2.93	3.553 (4)	131
N5—H5A...Br2 <sup>iv</sup>	0.86	2.66	3.377 (5)	142
N6—H6A...Br4 <sup>iv</sup>	0.86	2.92	3.537 (6)	130
C8—H8...Br4	0.93	2.91	3.720 (5)	147
C3—H3...Br1 <sup>iii</sup>	0.93	2.86	3.693 (6)	150
N6—H6B...Br2 <sup>v</sup>	0.86	2.84	3.387 (6)	123

Symmetry codes: (i)  $-x, -y + 1, -z$ ; (ii)  $x - 1, y + 1, z$ ; (iii)  $x, y + 1, z$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $-x, -y + 1, -z + 1$ .**Compound (II)***Crystal data*

(C <sub>5</sub> H <sub>6</sub> Br <sub>2</sub> N <sub>3</sub> ) <sub>2</sub> [MnBr <sub>4</sub> ]	$\gamma = 66.159 (4)^\circ$
$M_r = 910.40$	$V = 1156.2 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.8776 (19) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.705 (2) \text{ \AA}$	$\mu = 14.40 \text{ mm}^{-1}$
$c = 13.962 (3) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 72.757 (4)^\circ$	$0.17 \times 0.12 \times 0.06 \text{ mm}$
$\beta = 86.692 (4)^\circ$	

*Data collection*

Bruker SMART APEX diffractometer	10998 measured reflections
Absorption correction: empirical (using intensity measurements) ( <i>SADABS</i> ; Bruker, 2001)	4154 independent reflections
$T_{\min} = 0.135, T_{\max} = 0.421$	3124 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.036$	226 parameters
$wR(F^2) = 0.089$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\max} = 0.85 \text{ e \AA}^{-3}$
4154 reflections	$\Delta\rho_{\min} = -0.61 \text{ e \AA}^{-3}$

H atoms were positioned geometrically, and constrained to refine with N—H = 0.86 Å (for NH and NH<sub>2</sub> groups) and C—H = 0.93 Å for aromatic H atoms, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

There are some 16 and 21 missing reflections (it is likely that the missing data were behind the beam stop), respectively, in the two reported structures as processed. Both samples were small crystals (thickness = 0.04 and 0.06 mm) and poorly diffracting. Redundant data were collected for both crystals but did not help. The size and the detector type contributed to the poor diffraction and poor detection issues despite long collection/exposure times (20 s).

**Table 3**

Selected geometric parameters (Å, °) for (II).

Mn1—Br1	2.5073 (10)	Mn1—Br3	2.4996 (11)
Mn1—Br2	2.5054 (11)	Mn1—Br4	2.4925 (11)
Br1—Mn1—Br2	106.57 (4)	Br2—Mn1—Br3	112.89 (4)
Br1—Mn1—Br3	103.34 (4)	Br2—Mn1—Br4	107.63 (4)
Br1—Mn1—Br4	112.39 (4)	Br3—Mn1—Br4	113.83 (4)

**Table 4**

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Br3 <sup>i</sup>	0.86	2.68	3.456 (4)	151
N2—H2A...Br1 <sup>i</sup>	0.86	2.79	3.389 (6)	128
N2—H2B...Br1 <sup>ii</sup>	0.86	2.71	3.433 (5)	143
N3—H3A...Br3 <sup>i</sup>	0.86	2.77	3.518 (5)	147
N4—H4...Br2 <sup>iii</sup>	0.86	2.90	3.485 (4)	127
N4—H4...Br4 <sup>iv</sup>	0.86	2.85	3.496 (4)	133
N5—H5A...Br2 <sup>iv</sup>	0.86	2.64	3.380 (5)	144
N6—H6A...Br4 <sup>iv</sup>	0.86	2.95	3.567 (6)	131
C8—H8...Br4	0.93	2.93	3.737 (5)	145
C3—H3...Br1 <sup>iii</sup>	0.93	2.87	3.701 (5)	149
N6—H6B...Br2 <sup>v</sup>	0.86	2.85	3.387 (5)	122

Symmetry codes: (i)  $-x, -y + 1, -z$ ; (ii)  $x - 1, y + 1, z$ ; (iii)  $x, y + 1, z$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $-x, -y + 1, -z + 1$ .**Table 5**

Comparative geometric parameters (Å, °) for halogen bonding in (I) and (II).

Contact/angle	(I)	(II)
Br5...Br4 <sup>ii</sup>	3.6133 (17)	3.6261 (10)
Br3...Br7 <sup>viii</sup>	3.5482 (16)	3.5544 (10)
C—Br5...Br4 <sup>ii</sup>	157	156
Br3...Br7 <sup>viii</sup> —C	175	175

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

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *XS* in *SHELXTL* (Version 6.10; Sheldrick, 2008); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

The University of Jordan, Al-Balqa'a Applied University and Al al-Bayt University are thanked for financial support. The authors also thank Dr Brendan Twamley for his help with the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3128). Services for accessing these data are described at the back of the journal.

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