

## Three isomorphous 2,6-dibromo-pyridinium tetrabromometallates: $(C_5H_4Br_2N)_2[MBr_4] \cdot 2H_2O$ ( $M = Cu, Cd$ and $Hg$ )

Rawhi H. Al-Far,<sup>a</sup> Salim F. Haddad<sup>b</sup> and Basem Fares Ali<sup>c\*</sup>

<sup>a</sup>Faculty of Information Technology and Science, Al-Balqa'a Applied University, Salt, Jordan, <sup>b</sup>Department of Chemistry, University of Jordan, Amman 11942, Jordan, and <sup>c</sup>Department of Chemistry, Al al-Bayt University, Mafraq 25113, Jordan  
Correspondence e-mail: bfali@aabu.edu.jo

Received 22 July 2009

Accepted 17 September 2009

Online 28 October 2009

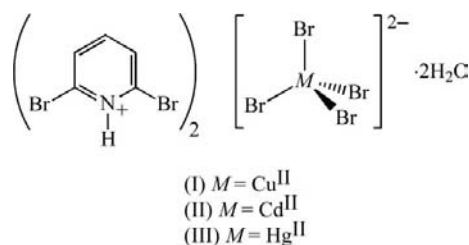
The structures of three isomorphous compounds, namely bis(2,6-dibromopyridinium) tetrabromidocuprate(II) dihydrate,  $(C_5H_4Br_2N)_2[CuBr_4] \cdot 2H_2O$ , bis(2,6-dibromopyridinium) tetrabromidocadmiate(II) dihydrate,  $(C_5H_4Br_2N)_2[CdBr_4] \cdot 2H_2O$ , and bis(2,6-dibromopyridinium) tetrabromidomercurate(II) dihydrate,  $(C_5H_4Br_2N)_2[HgBr_4] \cdot 2H_2O$ , show a crystal supramolecularity represented by  $M-Br \cdots H-O-H \cdots Br-M$  intermolecular interactions along with  $(\pi)N-H \cdots OH_2$  hydrogen-bonding interactions forming layers connected *via* aryl-aryl face-to-face stacking of cations, leading to a three-dimensional network. The anions have significantly distorted tetrahedral geometry and crystallographic  $C_2$  symmetry. The stability of this crystal lattice is evidenced by the crystallization of a whole series of isomorphous compounds.

### Comment

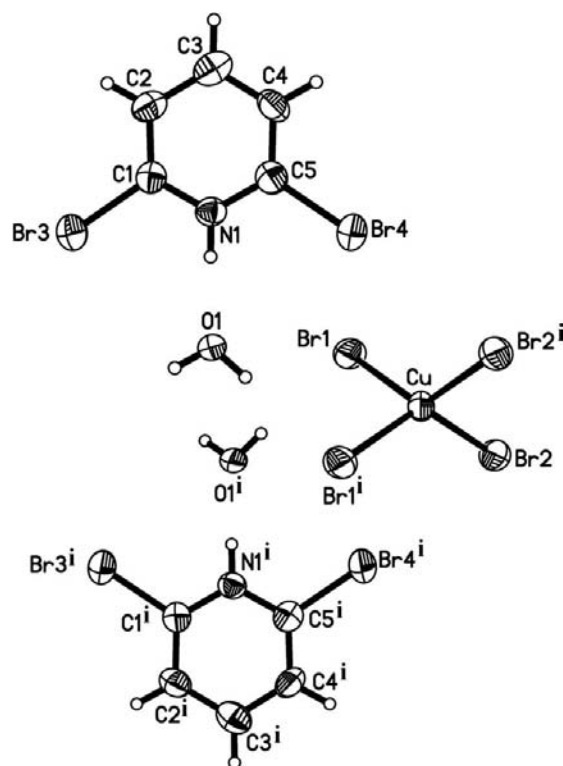
Noncovalent interactions play an important role in the organization of structural units in both natural and artificial systems (Desiraju, 1997). The consequences of such interactions may affect the properties of many materials found and utilized in areas such as biology (Hunter, 1994; Desiraju & Steiner, 1999), crystal engineering (Allen *et al.*, 1997; Dolling *et al.*, 2001) and materials science (Panunto *et al.*, 1987; Robinson *et al.*, 2000).

Organic-inorganic hybrid compounds are of great interest to researchers because of their special magnetic (Cui *et al.*, 2000), electronic (Lacroix *et al.*, 1994) and optoelectronic properties (Chakravarthy & Guloy, 1997). It is expected that the packing interactions that govern the crystal organization will be influenced by the features of the organic cations, which in turn will affect specific properties of solids. On the other hand, the results of a series of structure analyses and theoretical calculations (Awwadi *et al.*, 2007, and references therein)

show the significance of linear  $C-Br \cdots Br$  synthons in influencing the structures of crystalline materials, suggesting their use as potential building blocks in crystal engineering *via* supramolecular synthesis. This inspired our interest in the role of the  $C-Br \cdots Br-M$  synthon in the control of the packing of different metal halide anions such as  $[MBr_4]^{2-}$  in crystalline lattices. In continuation of previous work (Luque *et al.*, 2001; Haddad *et al.*, 2006; Al-Far & Ali, 2007*a,b*; Ali & Al-Far, 2007) on complexes containing cationic pyridine derivatives with bromidometal anions, herein we describe the crystallization of three isomorphous compounds containing the 2,6-dibromopyridinium cation (denoted 2,6-dbpH), namely bis(2,6-dibromopyridinium) tetrabromidocuprate(II) dihydrate, (I), bis(2,6-dibromopyridinium) tetrabromidocadmiate(II) dihydrate, (II), and bis(2,6-dibromopyridinium) tetrabromidomercurate(II) dihydrate, (III), along with their crystal packing



and crystal supramolecularity analyses. Comparison of packing forces as related to metal halide distortions,  $[MBr_4]^{2-}$  ( $M = Cu^{II}$ ,  $Cd^{II}$  and  $Hg^{II}$ ), with different electronic config-



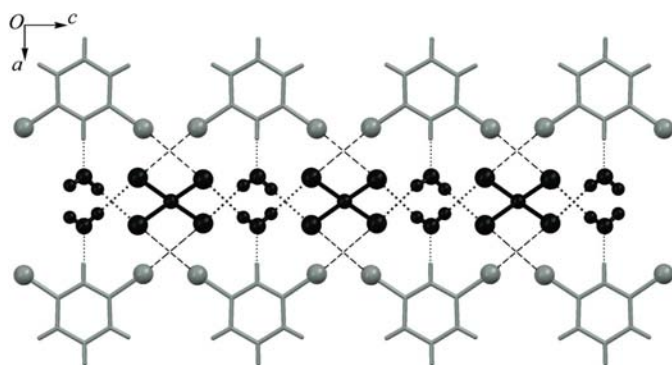
**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The same atom-numbering scheme was applied to compounds (II) and (III). [Symmetry code: (i)  $\frac{3}{2} - x, \frac{1}{2} - y, z$ ]

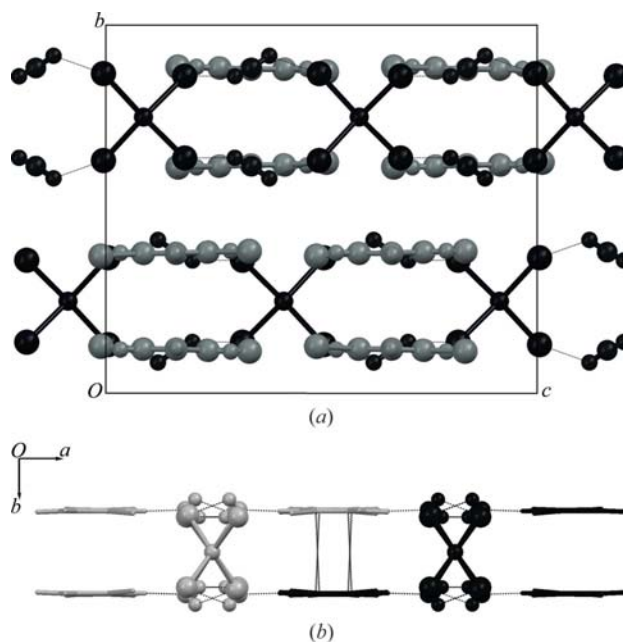
urations, is of interest to us. Attempts to prepare other isomorphous salts of the above failed. The reaction of two equivalents of 2,6-dibromopyridine with one equivalent of the corresponding  $M^{II}$  salt in the presence of excess aqueous HBr gave compounds (I), (II) and (III) in 90, 84 and 82% yield, respectively. The introduction of Br atoms at the 2- and 6-positions increases the basicity at the ring N atom (Al-Far & Ali, 2007a). Therefore, the resulting protonated 2,6-dibromopyridine was expected to create many important centres of interaction with the bromidometal anions, e.g.  $N-H \cdots Br$ ,  $(\pi)C-H \cdots Br$  and possibly aryl-aryl stacking.

The title compounds are isomorphous and crystallize in the orthorhombic space group  $Pccn$ . The asymmetric unit consists of one cation, one half anion, which lies across a crystallographic  $C_2$  axis, and one water molecule (Fig. 1). The anions all have a significantly distorted tetrahedral geometry. The unique  $M-Br$  distances are 2.3770 (8)/2.3797 (8), 2.5803 (5)/2.5947 (5) and 2.5928 (7)/2.6215 (7) Å for (I), (II) and (III), respectively. The  $Br-M-Br$  angles are in the ranges 99.24 (2)–128.09 (2), 102.90 (3)–117.970 (16) and 102.03 (3)–118.19 (2)° for (I), (II) and (III), respectively. These distances and angles are in accordance with previously reported values for corresponding  $[MBr_4]^{2-}$ -containing complexes (Coffey *et al.*, 2000; Al-Far & Ali, 2008; Ali *et al.*, 2006). The bond distances and angles in the planar cations in each structure are in the normal range (Allen *et al.*, 1987).

The  $[MBr_4]^{2-}$  anions and water molecules, which act as bridging units between the anions, form co-operative infinite chains parallel to the crystallographic  $c$  axis through  $M-Br \cdots H-O-H \cdots Br-M$  intermolecular interactions (Fig. 2, and Tables 1, 2 and 3). These chains are further connected to the cations, leading to 'ribbons' (Fig. 2), the connecting unit also being  $H_2O$  molecules *via* short  $(\pi)N-H \cdots OH_2$  intermolecular hydrogen bonds. Within the ribbons,  $Br \cdots Br$  halogen bonding plays a significant and complementary role in bringing all these interacting moieties together (Fig. 2). This type of interaction results from  $C-Br \cdots Br-M$  contacts in which the  $Br \cdots Br$  distances (Table 4) are in the



**Figure 2**  
A packing view of (I), projected down  $b$ , showing the ribbons parallel to  $c$  resulting from the hydrogen-bonding interactions (dotted lines) within the chains of anions and water molecules (in black) and with the cations (in grey). The  $Br \cdots Br$  interactions between anions and cations are also indicated (dashed lines).



**Figure 3**  
(a) The overall packing diagram of (I), showing a layered arrangement of cations and anions (cations in grey). (b) Two layers are shown, where the cations from each are further connected to each other parallel to the  $a$  axis *via* an aryl-aryl face-to-face motif ( $\pi-\pi$  stacking) (viewed down the crystallographic  $c$  axis). One layer is shown in black and the other in grey. Intermolecular interactions are indicated by dotted lines.

range 3.3928 (7)–3.5744 (9) Å, significantly less than the sum of the van der Waals radii (3.7 Å). It is worth mentioning that halide-halide interactions of the type  $M-Br \cdots Br-M$  are absent since the shortest contact in the series [4.3394 (10) Å in (III)] is much larger than the sum of the commonly accepted van der Waals radii.

The discussed ribbons, in turn, interact with neighbouring ones *via* aryl-aryl face-to-face interactions ( $\pi-\pi$  stacking) between almost parallel oppositely oriented pyridinium cations, giving rise to layers parallel to the  $ac$  plane (Fig. 3a). The distances between the centroids ( $C_g$ ) of adjacent rings are 3.533 (3), 3.601 (3) and 3.598 (4) Å for  $C_g(x, y, z) \cdots C_g(\frac{1}{2} - x, \frac{1}{2} - y, z)$  in (I), (II) and (III), respectively. The angles between the centroid-centroid line and the perpendicular distance line between planes are calculated to be 2.3, 7.7 and 7.6° in (I), (II) and (III), respectively.

Intermolecular interactions result in two distinguishable regions in the lattice (Fig. 3b). One is hydrophobic, which represents the cation layers that interact *via* offset face-to-face  $\pi-\pi$  stacking interactions. The other is the hydrophilic region, which represents the zone where  $C-Br \cdots Br-M$ ,  $H-O-H \cdots Br-M$  and  $N-H \cdots OH_2$  interactions are assembled.

## Experimental

All three title compounds were synthesized by dissolving 2,6-dibromopyridine (2 mmol) in 95% EtOH (10 ml, with warming) and an additional 2 ml of HBr (60%). The solution was added slowly with

constant stirring to a warm solution of CuBr<sub>2</sub>, CdBr<sub>2</sub> or HgCl<sub>2</sub> (1 mmol) dissolved in EtOH (10 ml). The resulting mixture was refluxed for 2 h, cooled undisturbed at room temperature and allowed to evaporate slowly until crystals appeared (generally within a few days). The products were as follows: (2,6-dbpH)<sub>2</sub>[CuBr<sub>4</sub>]·2H<sub>2</sub>O, (I), brown crystals, yield 90%; (2,6-dbpH)<sub>2</sub>[CdBr<sub>4</sub>]·2H<sub>2</sub>O, (II), colourless parallelepiped crystals, yield 84%; (2,6-dbpH)<sub>2</sub>[HgBr<sub>4</sub>]·2H<sub>2</sub>O, (III), colourless crystals, yield 82%.

### Compound (I)

#### Crystal data

(C<sub>5</sub>H<sub>4</sub>Br<sub>2</sub>N)<sub>2</sub>[CuBr<sub>4</sub>]·2H<sub>2</sub>O  
*M<sub>r</sub>* = 894.97  
 Orthorhombic, *Pccn*  
*a* = 10.2861 (7) Å  
*b* = 13.4443 (9) Å  
*c* = 15.7523 (11) Å  
*V* = 2178.4 (3) Å<sup>3</sup>  
*Z* = 4  
 Mo *K*α radiation  
 μ = 15.68 mm<sup>-1</sup>  
*T* = 296 K  
 0.22 × 0.16 × 0.12 mm

#### Data collection

Bruker–Siemens SMART APEX diffractometer  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)  
*T<sub>min</sub>* = 0.130, *T<sub>max</sub>* = 0.255  
 19097 measured reflections  
 1921 independent reflections  
 1426 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.067

#### Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.033  
*wR*(*F*<sup>2</sup>) = 0.088  
*S* = 1.03  
 1921 reflections  
 106 parameters  
 H-atom parameters constrained  
 Δρ<sub>max</sub> = 1.32 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.49 e Å<sup>-3</sup>

### Compound (II)

#### Crystal data

(C<sub>5</sub>H<sub>4</sub>Br<sub>2</sub>N)<sub>2</sub>[CdBr<sub>4</sub>]·2H<sub>2</sub>O  
*M<sub>r</sub>* = 943.83  
 Orthorhombic, *Pccn*  
*a* = 10.6168 (7) Å  
*b* = 13.5358 (9) Å  
*c* = 15.6473 (11) Å  
*V* = 2248.6 (3) Å<sup>3</sup>  
*Z* = 4  
 Mo *K*α radiation  
 μ = 15.19 mm<sup>-1</sup>  
*T* = 296 K  
 0.16 × 0.16 × 0.04 mm

#### Data collection

Bruker–Siemens SMART APEX diffractometer  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)  
*T<sub>min</sub>* = 0.111, *T<sub>max</sub>* = 0.551  
 20158 measured reflections  
 2034 independent reflections  
 1607 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.068

#### Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.027  
*wR*(*F*<sup>2</sup>) = 0.064  
*S* = 1.04  
 2034 reflections  
 105 parameters  
 H-atom parameters constrained  
 Δρ<sub>max</sub> = 0.43 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.39 e Å<sup>-3</sup>

### Compound (III)

#### Crystal data

(C<sub>5</sub>H<sub>4</sub>Br<sub>2</sub>N)<sub>2</sub>[HgBr<sub>4</sub>]·2H<sub>2</sub>O  
*M<sub>r</sub>* = 1032.01  
 Orthorhombic, *Pccn*  
*a* = 10.6328 (7) Å  
*b* = 13.5144 (9) Å  
*c* = 15.6141 (11) Å  
*V* = 2243.7 (3) Å<sup>3</sup>  
*Z* = 4  
 Mo *K*α radiation  
 μ = 21.11 mm<sup>-1</sup>  
*T* = 296 K  
 0.22 × 0.20 × 0.14 mm

**Table 1**

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...O1	0.86	1.74	2.602 (6)	177
O1—H1'...Br1 <sup>i</sup>	0.88	2.45	3.298 (4)	160
O1—H2'...Br2 <sup>ii</sup>	0.89	2.59	3.271 (4)	134
C4—H4...Br1 <sup>iii</sup>	0.93	3.02	3.662 (7)	128
C5—H5...Br1 <sup>iii</sup>	0.93	3.08	3.703 (6)	126

Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z$ .

**Table 2**

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...O1	0.86	1.78	2.639 (4)	174
O1—H1'...Br1 <sup>i</sup>	0.91	2.59	3.425 (3)	152
O1—H2'...Br2 <sup>ii</sup>	0.78	2.75	3.363 (3)	137
C4—H4...Br1 <sup>iii</sup>	0.93	3.00	3.658 (5)	129
C5—H5...Br1 <sup>iii</sup>	0.93	3.07	3.685 (4)	125

Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z$ .

**Table 3**

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

<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...O1	0.86	1.78	2.634 (7)	175
O1—H1'...Br1 <sup>i</sup>	0.90	2.58	3.412 (5)	154
O1—H2'...Br2 <sup>ii</sup>	0.81	2.74	3.364 (5)	136
C4—H4...Br1 <sup>iii</sup>	0.93	3.01	3.664 (7)	129
C5—H5...Br1 <sup>iii</sup>	0.93	3.09	3.699 (7)	125

Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z$ .

**Table 4**

Comparative contact distances (Å) and angles (°) for halogen bonding in isomorphous complexes (I), (II) and (III).

	(I)	(II)	(III)
Br2...Br4 <sup>i</sup>	3.5744 (9)	3.4418 (7)	3.4346 (9)
Br1...Br3 <sup>iv</sup>	3.5396 (9)	3.3928 (7)	3.3956 (10)
Br2...Br4 <sup>i</sup> —C	172	173	174
Br1...Br3 <sup>iv</sup> —C	174	176	177

Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z$ ; (iv)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ .

#### Data collection

Bruker–Siemens SMART APEX diffractometer  
 Absorption correction: numerical (*SADABS*; Bruker, 2001)  
*T<sub>min</sub>* = 0.019, *T<sub>max</sub>* = 0.051  
 13744 measured reflections  
 2024 independent reflections  
 1535 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.061

#### Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.031  
*wR*(*F*<sup>2</sup>) = 0.068  
*S* = 1.03  
 2024 reflections  
 105 parameters  
 H-atom parameters constrained  
 Δρ<sub>max</sub> = 0.94 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.68 e Å<sup>-3</sup>

H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93 Å, and constrained to ride on their parent atoms, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N). The H atoms of the water molecules were located in difference Fourier maps and their positions were initially

refined with O—H and H···H distance restraints of 0.90 (2) and 1.45 (2) Å, respectively. In the final refinements, the positions of these H atoms were held fixed, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . There is some disorder in the water molecules in all three structures, reflected in the fact that the displacement ellipsoids for the water O atoms are quite elongated in a direction perpendicular to the molecular plane, particularly in (I). However, refinement of the water O atoms over several locations with partial occupancy did not improve the picture and a single site model with a large displacement parameter was preferred.

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE-Plus* (Bruker, 2001); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *XS* in *SHELXTL* (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 and Al al-Bayt University are thanked for financial support. We also thank Dr Brendan Twamley for his help in collecting data (University of Idaho).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3107). Services for accessing these data are described at the back of the journal.

## References

- Al-Far, R. & Ali, B. F. (2007a). *Acta Cryst.* **C63**, m137–m139.  
Al-Far, R. & Ali, B. F. (2007b). *J. Chem. Crystallogr.* **37**, 333–341.  
Al-Far, R. & Ali, B. F. (2008). *J. Chem. Crystallogr.* **38**, 373–379.  
Ali, B. F. & Al-Far, R. (2007). *Acta Cryst.* **C63**, m451–m453.  
Ali, B. F., Al-Far, R. & Al-Sou'oud, K. (2006). *J. Chem. Crystallogr.* **36**, 523–529.  
Allen, F. H., Hoy, V. J., Howard, J. A. K., Thalladi, V. R., Desiraju, G. R., Wilson, C. C. & McIntyre, G. J. (1997). *J. Am. Chem. Soc.* **119**, 3477–3480.  
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.  
Awwadi, F. F., Willett, R. D., Peterson, K. A. & Twamley, B. (2007). *J. Phys. Chem. A*, **111**, 2319–2328.  
Bruker (2001). *SADABS* (Version 2.03), *SMART* (Version 5.625) and *SAINTE-Plus* (Version 6.22). Bruker AXS Inc., Madison, Wisconsin, USA.  
Chakravarthy, V. & Guloy, A. M. (1997). *Chem. Commun.* pp. 697–698.  
Coffey, T. J., Landee, C. P., Robinson, W. T., Turnbull, M. M., Winn, M. & Woodward, F. M. (2000). *Inorg. Chim. Acta*, **303**, 54–60.  
Cui, Y., Ren, J., Chen, G., Yu, W.-C. & Qian, Y. (2000). *Acta Cryst.* **C56**, e552–e553.  
Desiraju, G. R. (1997). *Chem. Commun.* pp. 1475–1482.  
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*. Oxford University Press.  
Dolling, B., Gillon, A., Orpen, A. G., Starbuck, J. & Wang, X.-M. (2001). *Chem. Commun.* pp. 567–568.  
Haddad, S. F., AlDaamen, M. A. & Willett, R. D. (2006). *Inorg. Chim. Acta*, **359**, 424–432.  
Hunter, C. A. (1994). *Chem. Soc. Rev.* **2**, 101–109.  
Lacroix, P. G., Clement, R., Nakatani, K., Zyss, J. & Ledoux, I. (1994). *Science*, **263**, 658–660.  
Luque, A., Sertucha, J., Castillo, O. & Román, P. (2001). *New J. Chem.* **25**, 1208–1214.  
Panunto, T. W., Urbanczyk-Lipkowska, Z., Johnson, R. & Etter, M. C. (1987). *J. Am. Chem. Soc.* **109**, 7786–7797.  
Robinson, J. M. A., Philp, D., Harris, K. D. M. & Kariuki, B. M. (2000). *New J. Chem.* **24**, 799–806.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.