

A new polymorph of 1,4-bis(imidazol-1-ylmethyl)benzene dihydrate and its hydrogen-bonded fivefold interpenetrated CdSO₄ network

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Received 17 September 2008

Accepted 24 November 2008

Online 27 November 2008

Single crystals of a new polymorph of 1,4-bis(imidazol-1-ylmethyl)benzene dihydrate (bix·2H₂O), C₁₄H₁₄N₄·2H₂O, have been obtained by the hydrothermal method. The asymmetric unit is composed of two independent half-bix molecules, one on an inversion center and one on a twofold axial site, and two water molecules. The disordered water

molecules link into discrete tetrameric water units *via* two O—H···O hydrogen bonds, forming planar R₄⁴(8) rings. These tetrameric water units and bix molecules are further linked by two O—H···N hydrogen bonds into a three-dimensional network in which an R₂₀²⁰(106) hydrogen-bonded ring is observed. These large rings lead to the formation of a fivefold interpenetrated network. If both the tetrameric water units and the bix molecules can be regarded as connected nodes, one single three-dimensional net can then be rationalized as a CdSO₄ network. This study indicates that topological methodology can be applied in some cases in order to understand the inherent characteristics of some hydrogen-bonded supramolecular assemblies.

Comment

The crystal structure of another polymorph of the title compound (bix·2H₂O) has been reported previously [Cambridge Structural Database (Allen, 2002) refcode PUVQIG (Hoskins *et al.*, 1997*b*; Abrahams *et al.*, 1998)]. Interestingly, crystallization of bix *via* the hydrothermal method leads to a structure in the monoclinic space group C2/c with Z = 8 [polymorph (II)], in contrast to the previously reported structure [polymorph (I)] in the space group P2₁/n with Z = 2, which was obtained by recrystallization from water. In this communication, we report the differences between these two polymorphs and give an illustration of their topological classification.

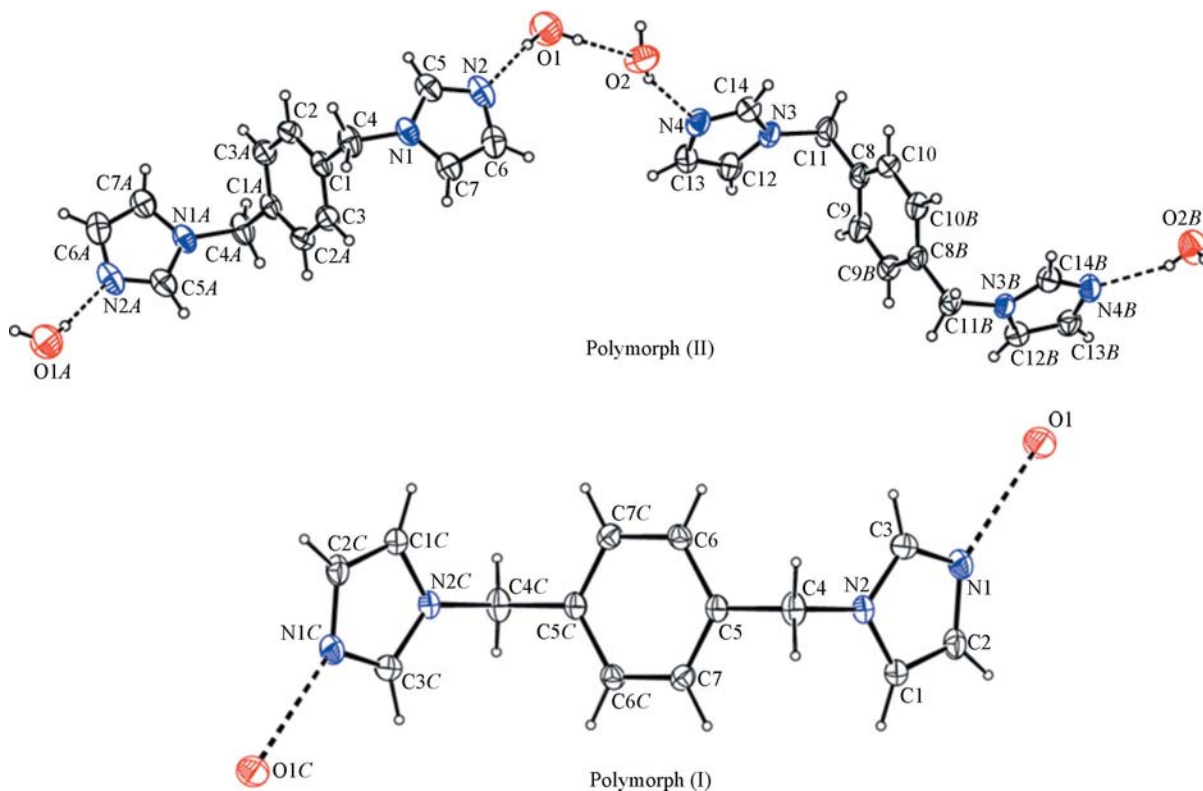
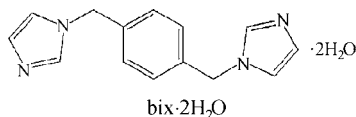


Figure 1

The molecular structures of bix·2H₂O in polymorphs (I) and (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. In polymorph (II), atoms labeled with the suffixes *A* and *B* are at the symmetry positions $(-x + 1, -y + 1, -z)$ and $(-x + 3, y, -z + \frac{3}{2})$, respectively. The minor components of the disordered water molecules have been omitted for clarity. In (I), atoms labeled with the suffix *C* are at the symmetry position $(-x, -y + 2, -z + 1)$.

As a flexible ligand, bix has often been used in the synthesis of metal–organic frameworks as a linker molecule (Hoskins *et al.*, 1997*a*; Abrahams *et al.*, 2002; Carulli *et al.*, 2005; Wen *et al.*, 2005; Zhang *et al.*, 2005) and in the construction of



hydrogen-bonded supramolecular assemblies as hydrogen-bonding acceptors (Ma & Coppens, 2004; Ma *et al.*, 2004; Shen *et al.*, 2004; Aakeröy *et al.*, 2005, 2006; Zhang *et al.*, 2007). Recently, as a result of our interest in exploring the self-assembling nature of carboxylic acids with Lewis bases (Meng *et al.*, 2007; Meng, Lin & Li, 2008; Meng, Xiao, Wang & Liu, 2008; Meng, Xiao, Zhang & Zhou, 2008), we have resynthesized the N-containing Lewis base bix by the standard procedure (Hoskins *et al.*, 1997*b*).

Single-crystal X-ray diffraction reveals that there are two independent half-bix molecules and two water molecules in the selected asymmetric unit of polymorph (II) (Fig. 1). In the N1-containing bix molecule, the two halves are related by an inversion center at $(\frac{1}{2}, \frac{1}{2}, 0)$. However, the two halves in the N2-containing bix molecule are related by a twofold axis. In contrast, the asymmetric unit of polymorph (I) consists of only one water molecule and half a bix molecule whose two halves are related by an inversion center at $(0, 1, \frac{1}{2})$. Besides this, the cell volume (2956.0 \AA^3) in polymorph (II) is *ca* four times that in polymorph (I) (733.4 \AA^3). The water molecules in (II) are linked into a discrete tetrameric $R_4^4(8)$ water ring (Fig. 2) by O–H···O hydrogen bonds. Conversely, water molecules in (I) are linked into one-dimensional water chains $[\text{O} \cdots \text{O} = 2.728(2) \text{ \AA}$ and $2.782(2) \text{ \AA}$; symmetry codes: $-x, -y + 2, -z;$

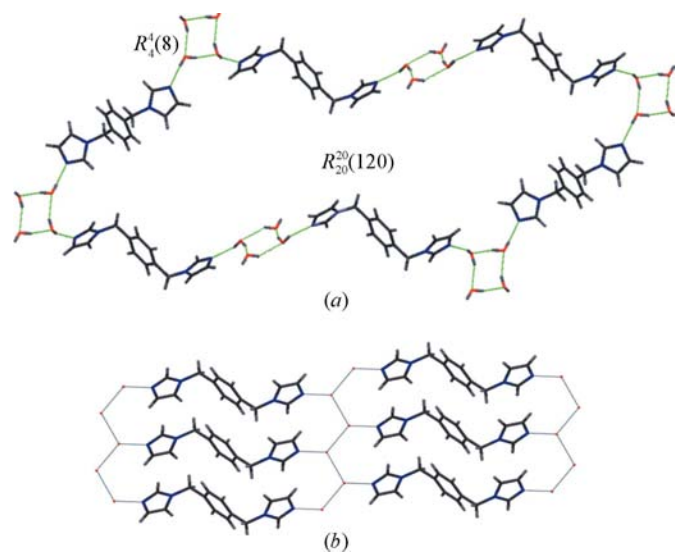


Figure 2

Parts of the crystal structures of bix·2H₂O in (a) polymorph (II) and (b) and polymorph (I), showing the formation of the $R_4^4(8)$ and $R_{20}^{20}(106)$ hydrogen-bond rings in (II) and the one-dimensional water chain running parallel to the [100] direction in (I). Hydrogen bonds are shown as dashed lines. The minor components of the disordered water molecules in (II) have been omitted for clarity.

$-x - 1, -y + 2, -z]$ running parallel to the [100] direction (Fig. 2). These apparent differences may mainly be attributed to: (i) the crystallization conditions, *i.e.* temperature and pressure, and (ii) the flexibility stemming from the $-\text{CH}_2-$ group (Zhang *et al.*, 2007).

The crystal packings of polymorphs (I) and (II) are also very different from each other. In (II), bix and water molecules are linked by O–H···O and O–H···N hydrogen bonds (Table 1) into a continuous three-dimensional network. Two types of hydrogen-bonded rings are formed; one is the $R_4^4(8)$ ring as mentioned above and the other is a very large $R_{20}^{20}(106)$ hydrogen-bond ring (Bernstein *et al.*, 1995), which is constructed *via* O–H···N hydrogen bonds. Topological analysis indicates that if one considers the tetrameric water units to be four-connected nodes and the bix molecules to be bridges (Fig. 3*a*), one single net can then be rationalized as a three-dimensional net with CdSO₄ topology. Fig. 3(*b*) reveals the topology displayed by this structure, with short and long Schläfli symbols $6^5.8$ and $6.6.6.6.6_2^*$, respectively (* means there are no rings for this angle; Batten, 2001; Batten & Robson, 1998). Further analysis indicates that five independent three-dimensional networks of this type related by a translation vector of *ca* 2.1436 \AA along the [100] direction make up the final fivefold interpenetrated network (Fig. 3*b*). These interpenetrated networks are strengthened by π – π and C–H··· π interactions [$\text{Cg}1 \cdots \text{Cg}2^{\text{ii}} = 3.934(2) \text{ \AA}$, $\text{Cg}3 \cdots \text{Cg}3^{\text{iii}} = 3.593(2) \text{ \AA}$, and $\text{H}3 \cdots \text{Cg}3^{\text{iv}} = 2.95 \text{ \AA}$, $\text{C}3 \cdots \text{Cg}3^{\text{iv}} = 3.829(2) \text{ \AA}$ and $\text{C}3-\text{H}3 \cdots \text{Cg}3^{\text{iv}} = 158^\circ$; Cg1, Cg2 and Cg3 are the centroids of the rings involving atoms C1, C8 and N4, respectively; symmetry codes: (ii) $x - 1, y, z - 1$; (iii) $-x + 2, y, -z + \frac{3}{2}$; (iv) $-x + 2, y, -z + \frac{1}{2}$]. In contrast, bix molecules in

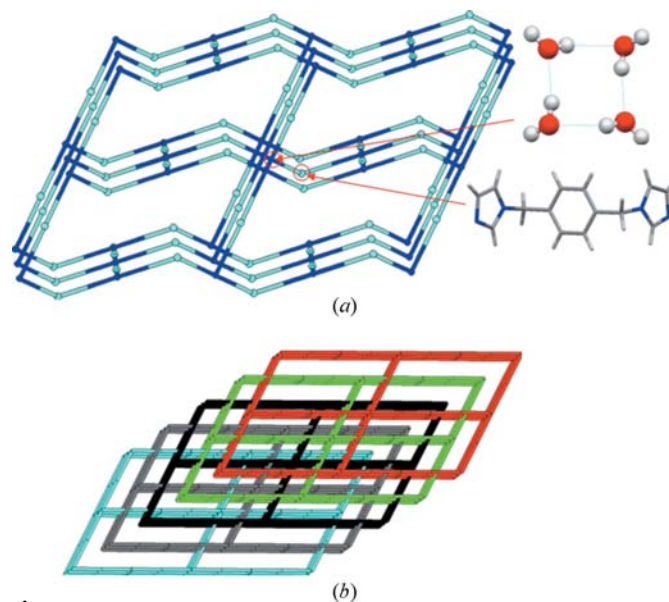
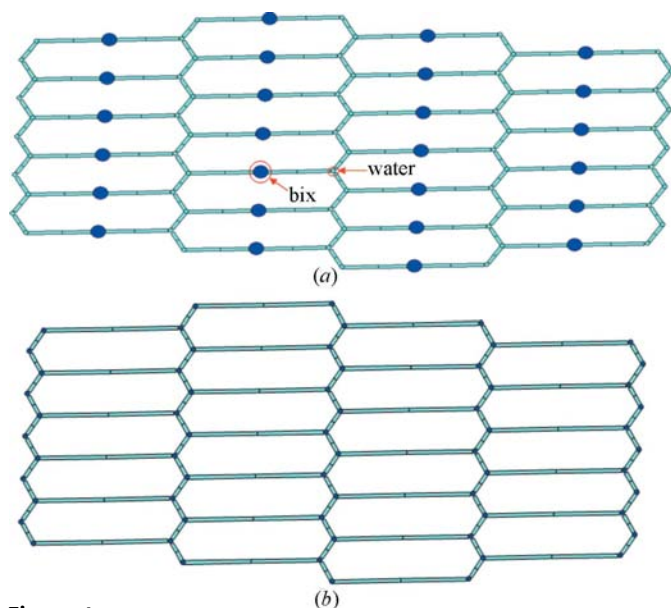


Figure 3

Simplifications of the crystal structure of bix·2H₂O in polymorph (II), showing (a) a schematic view of the formation of a single three-dimensional network and (b) a schematic view of the formation of the fivefold interpenetrated network. [In (a), in the electronic version of the paper, blue and aqua balls represent $R_4^4(8)$ water units and bix molecules, respectively.]

**Figure 4**

Simplifications of the crystal structure of $\text{bix} \cdot 2\text{H}_2\text{O}$ in polymorph (I), showing (a) a schematic view of the formation of the two-dimensional network running parallel to the (010) plane and (b) a schematic view of the Shubnikov hexagonal plane net. [In (a), in the electronic version of the paper, blue and aqua balls represent bix and water molecules, respectively.]

polymorph (I) are joined together by the only water–imidazole $\text{O} \cdots \text{N}$ [2.821 (2) Å] hydrogen bond, which originates from two sides of the one-dimensional water chain, resulting in a simple two-dimensional sheet running parallel to the (010) plane (Fig. 4a). We can regard the two-dimensional sheet as a Shubnikov hexagonal plane net with a total Schläfli symbol of 6^3 (Fig. 4b). The neighbouring sheets are linked by $\text{C1} - \text{H1} \cdots \text{O1}(-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ interactions into a simple three-dimensional network. No other interactions are observed in polymorph (I).

Experimental

The title compound was prepared according to the literature method of Hoskins *et al.* (1997b). A sample (30.0 mg) was sealed in a 23 ml Teflon-lined stainless steel autoclave, heated at 400 K for 2 d under autogenous pressure and cooled slowly to room temperature. Block-shaped single crystals suitable for X-ray diffraction were produced at the bottom of the autoclave.

Crystal data

$\text{C}_{14}\text{H}_{14}\text{N}_4 \cdot 2\text{H}_2\text{O}$	$V = 2956.0$ (4) Å ³
$M_r = 274.32$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 10.7178$ (8) Å	$\mu = 0.09$ mm ⁻¹
$b = 17.9925$ (14) Å	$T = 299$ (2) K
$c = 15.3662$ (12) Å	$0.30 \times 0.20 \times 0.20$ mm
$\beta = 94.006$ (2)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	9245 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	3369 independent reflections
$T_{\min} = 0.965$, $T_{\max} = 0.983$	2237 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.140$
 $S = 1.04$
 3369 reflections
 224 parameters
 12 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.13$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1}-\text{H1A} \cdots \text{N2}$	0.824 (10)	2.030 (18)	2.848 (7)	172 (9)
$\text{O1}-\text{H1B} \cdots \text{O2}$	0.822 (10)	2.10 (5)	2.815 (16)	145 (8)
$\text{O2}-\text{H2A} \cdots \text{N4}$	0.823 (10)	2.10 (4)	2.869 (13)	157 (9)
$\text{O2}-\text{H2B} \cdots \text{O1}^i$	0.822 (10)	2.03 (5)	2.811 (17)	158 (11)
$\text{O1}'-\text{H1C} \cdots \text{N2}$	0.822 (10)	2.06 (3)	2.868 (10)	170 (13)
$\text{O1}'-\text{H1D} \cdots \text{O2}'$	0.820 (10)	2.15 (7)	2.77 (2)	132 (8)
$\text{O2}'-\text{H2C} \cdots \text{N4}$	0.818 (10)	2.09 (2)	2.902 (17)	172 (11)
$\text{O2}'-\text{H2D} \cdots \text{O1}^i$	0.820 (10)	1.82 (3)	2.625 (17)	165 (11)

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

In polymorph (II), the water molecules were both disordered over two positions. Because of the existence of discrete hydrogen-bond networks, the disorder parameters of the molecules containing atoms O1 and O2 were coupled and their final occupancies were refined to be 0.59 (1) and 0.41 (1) for the major and minor components, respectively. All H atoms bonded to C atoms were positioned geometrically, with C–H distances of 0.93 (aromatic) and 0.97 Å (methylene), and treated as riding, with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{C})$. H atoms bonded to water O atoms were found in difference maps and refined with the restraints $\text{O}-\text{H} = 0.82$ (1) Å and $\text{H} \cdots \text{H} = 1.35$ (1) Å, and the constraint $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003), Mercury (Bruno *et al.*, 2002) and DIAMOND (Brandenburg, 2004); software used to prepare material for publication: PLATON.

This work received financial support mainly from the National Key Fundamental Project (grant No. 2002CCA-00500).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3264). Services for accessing these data are described at the back of the journal.

References

- Aakeröy, C. B., Desper, J., Leonard, B. & Urbina, J. F. (2005). *Cryst. Growth Des.* **5**, 865–873.
- Aakeröy, C. B., Salmon, D. J., Smith, M. M. & Desper, J. (2006). *Cryst. Growth Des.* **6**, 1033–1042.
- Abrahams, B. F., Hoskins, B. F., Robson, R. & Slizys, D. A. (1998). *Acta Cryst.* **C54**, 1666–1668.
- Abrahams, B. F., Hoskins, B. F., Robson, R. & Slizys, D. A. (2002). *CrystEngComm*, **4**, 478–482.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Batten, S. R. (2001). *CrystEngComm*, **18**, 1–7.
- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

- Brandenburg, K. (2004). *DIAMOND*. Release 3.0. Crystal Impact GbR, Bonn, Germany.
- Bruker (2001). *SMART* (Version 5.628) and *SAINTE-Plus* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Carculli, L., Ciani, G. & Proserpio, D. M. (2005). *Cryst. Growth Des.* **5**, 37–39.
- Hoskins, B. F., Robson, R. & Slizys, D. A. (1997a). *Angew. Chem. Int. Ed. Engl.* **36**, 2336–2338.
- Hoskins, B. F., Robson, R. & Slizys, D. A. (1997b). *J. Am. Chem. Soc.* **119**, 2952–2953.
- Ma, B. Q. & Coppens, P. (2004). *Cryst. Growth Des.* **4**, 1377–1385.
- Ma, B. Q., Ferreira, L. F. V. & Coppens, P. (2004). *Org. Lett.* **6**, 1087–1090.
- Meng, X.-G., Lin, Z.-D. & Li, A.-M. (2008). *Acta Cryst.* **C64**, o322–o325.
- Meng, X.-G., Xiao, Y.-L., Wang, Z.-L. & Liu, C.-L. (2008). *Acta Cryst.* **C64**, o53–o57.
- Meng, X.-G., Xiao, Y.-L., Zhang, H. & Zhou, C.-S. (2008). *Acta Cryst.* **C64**, o261–o263.
- Meng, X.-G., Zhou, C.-S., Wang, L. & Liu, C.-L. (2007). *Acta Cryst.* **C63**, o667–o670.
- Sheldrick, G. M. (1997). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shen, X. J., Chen, H. L., Yu, F., Zhang, Y. C., Yang, X. H. & Li, Y. Z. (2004). *Tetrahedron Lett.* **45**, 6813–6817.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wen, L. L., Dang, D. B., Duan, C. Y., Li, Y. Z., Tian, Z. F. & Meng, Q. J. (2005). *Inorg. Chem.* **44**, 7161–7170.
- Zhang, J., Gembicky, M., Messerschmidt, M. & Coppens, P. (2007). *Chem. Commun.* pp. 2399–2401.
- Zhang, L., Lü, X. Q., Chen, C. L., Tan, H. Y., Zhang, H. X. & Kang, B. S. (2005). *Cryst. Growth Des.* **5**, 283–287.