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## Key indicators

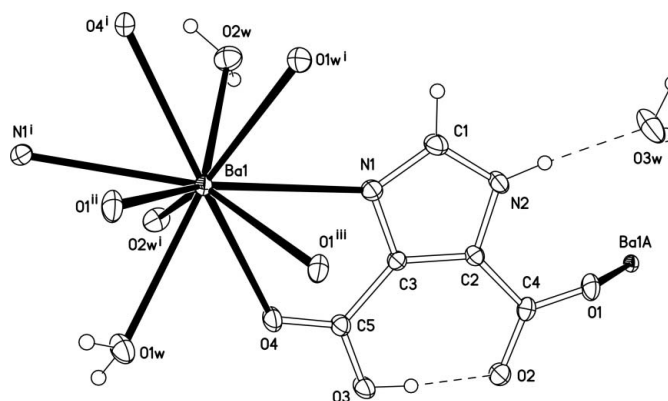
Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å  
 $R$  factor = 0.016  
 $wR$  factor = 0.037  
Data-to-parameter ratio = 13.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A two-dimensional brick-wall layer barium(II)  
coordination polymer: poly[[tetraaquabarium(II)-  
di- $\mu$ -1*H*-imidazole-4,5-dicarboxylato] dihydrate]

In the title two-dimensional coordination polymer,  $\{[\text{Ba}(\text{H}_2\text{IDC})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$  ( $\text{H}_2\text{IDC}^-$  is the 1*H*-imidazole-4,5-dicarboxylate monoanion,  $\text{C}_5\text{H}_3\text{N}_2\text{O}_4^-$ ), each  $\text{Ba}^{\text{II}}$  atom, which lies on a crystallographic twofold rotation axis, is ten-coordinated by four O atoms and two N atoms from different  $\text{H}_2\text{IDC}^-$  ligands, as well as four water molecules, thus defining a hexadecahedron. Four  $\text{Ba}^{\text{II}}$  atoms are linked by four different  $\text{H}_2\text{IDC}^-$  ligands to produce a centrosymmetric macrocyclic structure, leading to an extended two-dimensional brick-wall open framework. Furthermore, there are  $\pi$ - $\pi$  stacking interactions between adjacent parallel imidazole rings in the layer structure, and a three-dimensional supramolecular network is constructed *via* hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions.

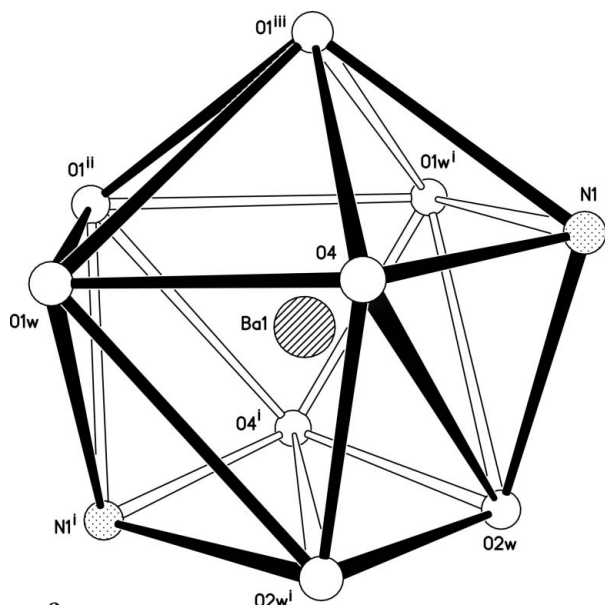
Received 24 October 2005  
Accepted 31 October 2005  
Online 5 November 2005

## Comment

The construction of coordination polymers and networks by the self-assembly of polydentate ligands and metal ions is a rapidly growing area of research (Andrea, 2003). *N*-Heterocyclic carboxylic acids, such as 1*H*-imidazole-4,5-dicarboxylic acid ( $\text{H}_3\text{IDC}$ ), are well known as efficient N/O donors with versatile binding abilities and hydrogen bonding.  $\text{H}_3\text{IDC}$  can be successively deprotonated to generate  $\text{H}_2\text{IDC}^-$ ,  $\text{HIDC}^{2-}$  and  $\text{IDC}^{3-}$  anions, and hence may result in a variety of structural topologies (Liu *et al.*, 2004; Xiao *et al.*, 2004). Some transition metal complexes with one-dimensional chain structures for Mn, Cu and Cd (Zhang *et al.*, 2004; Gao, Gu *et al.*, 2004; Gao, Liu *et al.*, 2004), and two-dimensional layer structures for Mn and Fe (Gao *et al.*, 2005; Xu *et al.*, 2004), have been reported to date. Compared with the extensively investigated transition metal coordination polymers, it is

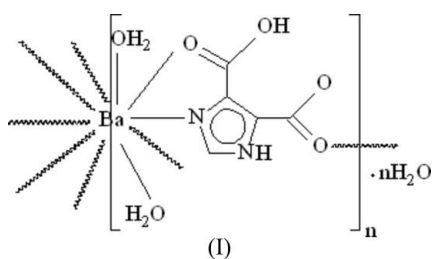


**Figure 1**  
ORTEP plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i)  $-x + 1, y, -z + \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (A)  $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .]

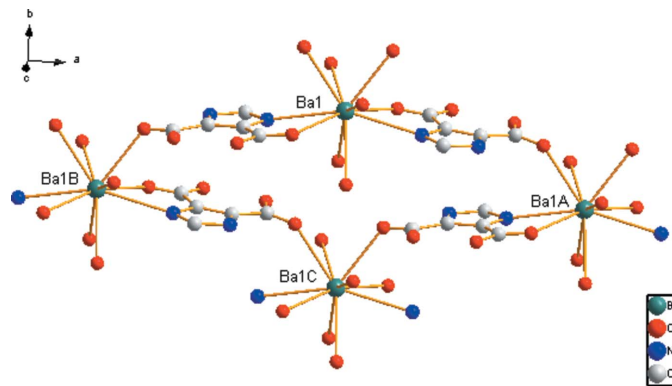


**Figure 2**  
Hexadecahedral coordination of the Ba atom in the title complex. [Symmetry codes: (i)  $-x + 1, y, -z + \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ .]

surprising to see the relatively small number of alkaline earth coordination polymers. Recently, we have reported the structure of a mononuclear calcium complex (Gao, Zhang *et al.*, 2004), in which the  $\text{Ca}^{\text{II}}$  atom shows an eight-coordinated distorted bicapped triangular prismatic configuration and the  $\text{H}_3\text{IDC}$  ligand acts in a bidentate chelating mode. In order to study further the behavior of alkaline earth metals with the  $\text{H}_3\text{IDC}$  ligand, we obtained a two-dimensional brick-wall layer barium coordination polymer,  $[\text{Ba}(\text{H}_2\text{IDC})_2(\text{H}_2\text{O})_4]_n \cdot 2n\text{H}_2\text{O}$ , (I), for which the synthesis and structure are reported here.



As shown in Fig. 1, the crystal structure is composed of a  $[\text{Ba}(\text{H}_2\text{IDC})_2(\text{H}_2\text{O})_4]$  complex and two uncoordinated water molecules; the carboxylate ( $\text{H}_2\text{IDC}^-$ ) ligand bears a formal charge of  $-1$  and binds in a tridentate coordination mode, and the free carboxylate atoms O2 and O3, and atom N2 and water O3w form two of the hydrogen bonds (Table 2). The  $\text{Ba}^{\text{II}}$  atom occupies a special position having crystallographic twofold rotation symmetry. Each  $\text{Ba}^{\text{II}}$  atom is ten-coordinated by four O atoms and two N atoms from different  $\text{H}_2\text{IDC}^-$  ligands, as well as four water molecules, thus defining a hexadecahedron (Fig. 2). The angles around the  $\text{Ba}^{\text{II}}$  atom are distributed over a broad range,  $56.46(4)$ – $163.52(7)^\circ$  (Table 1). The  $\text{Ba}-\text{O}_{\text{carboxylate}}$  distances fall in the range  $2.8629(15)$ –



**Figure 3**  
The macrocyclic structure formed by four  $\text{Ba}^{\text{II}}$  atoms and four different  $\text{H}_2\text{IDC}^-$  anions. H atoms and free water molecules have been omitted. [Symmetry codes: (A)  $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (B)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (C)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ .]

$2.8793(14) \text{ \AA}$ , and are considerably shorter than the maximum  $\text{Ba}-\text{O}$  value [ $3.161(2) \text{ \AA}$ ] in a reported Ba complex (Bouayad *et al.*, 1995). The dihedral angles between the carboxylate groups and the imidazole ring are  $2.3(5)^\circ$  (C4 group) and  $4.5(5)^\circ$  (C5 group).

The  $\text{H}_2\text{IDC}^-$  ligand displays two different kinds of coordination behavior, distinguished by the direction of the  $\text{Ba}-\text{O}$  bonds relative to the carboxylate plane. First, the ligand binds to one  $\text{Ba}^{\text{II}}$  atom in an  $N,O$ -bidentate coordination mode through imidazole atom N1 and carboxylate atom O4, forming a five-membered chelate ring. Secondly, the ligand acts in a monodentate coordination mode through carboxylate atom O1, the  $\text{Ba1} \cdots \text{Ba1A}$  separation being  $9.597(3) \text{ \AA}$  (symmetry codes for  $\text{Ba} \cdots \text{Ba}$  separations are as in Fig. 3). Consequently, as a result of these individual mono- and bidentate modes, a centrosymmetric macrocyclic structure is formed by four  $\text{Ba}^{\text{II}}$  atoms and four different  $\text{H}_2\text{IDC}^-$  anions (Fig. 3), the  $\text{Ba1} \cdots \text{Ba1C}$  and  $\text{Ba1A} \cdots \text{Ba1B}$  separations being  $6.765(3)$  and  $17.962(3) \text{ \AA}$ , respectively. As a consequence of the  $\text{H}_2\text{IDC}^-$  bridges, polymeric (I) has an extended two-dimensional brick-wall layer structure, with alternating organic and inorganic sheets (Fig. 4).

There are  $\pi-\pi$  stacking interactions between adjacent parallel imidazole rings, the centroid-centroid separation being  $3.735(3) \text{ \AA}$ . Furthermore, the water molecules, uncoordinated imidazole N2 atom and carboxyl O atoms form intermolecular hydrogen bonds (Table 2), consolidating the crystal structure and leading to a three-dimensional supra-molecular network.

## Experimental

The title polymeric complex was prepared by the reaction of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (2.40 g, 10 mmol) and  $\text{H}_3\text{IDC}$  (1.54 g, 10 mmol) in aqueous solution. The mixture was sealed in a 50 ml Teflon-lined stainless steel bomb and held at 423 K for five days. The bomb was then allowed to cool naturally to room temperature, and colorless prismatic crystals of (I) were obtained. Analysis calculated for  $\text{C}_{10}\text{H}_{18}\text{BaN}_4\text{O}_{14}$ : C 21.62, H 3.27, N 10.08%; found: C 21.65, H 3.25, N 10.11%.

Crystal data

[Ba(C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O  
*M<sub>r</sub>* = 555.61  
 Monoclinic, *C2/c*  
*a* = 17.962 (4) Å  
*b* = 6.7649 (14) Å  
*c* = 14.892 (3) Å  
 $\beta$  = 95.22 (3)°  
*V* = 1802.0 (7) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 2.048 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 7944 reflections  
 $\theta$  = 3.2–27.5°  
 $\mu$  = 2.29 mm<sup>-1</sup>  
*T* = 295 (2) K  
 Prism, colorless  
 0.35 × 0.24 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)  
*T<sub>min</sub>* = 0.521, *T<sub>max</sub>* = 0.665  
 8564 measured reflections

2069 independent reflections  
 1947 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.018  
 $\theta_{max}$  = 27.5°  
*h* = -23 → 23  
*k* = -8 → 8  
*l* = -18 → 19

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.016  
*wR* (*F*<sup>2</sup>) = 0.037  
*S* = 1.10  
 2069 reflections  
 153 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 2.0363P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.33 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.46 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ba1–N1	2.9662 (16)	Ba1–O2w <sup>i</sup>	2.8501 (15)
Ba1–N1 <sup>ii</sup>	2.9662 (16)	Ba1–O4	2.8629 (15)
Ba1–O1 <sup>ii</sup>	2.8793 (14)	Ba1–O4 <sup>i</sup>	2.8629 (15)
Ba1–O1 <sup>iii</sup>	2.8793 (14)	O1–C4	1.241 (2)
Ba1–O1w	2.9104 (15)	O2–C4	1.273 (2)
Ba1–O1w <sup>i</sup>	2.9104 (15)	O3–C5	1.298 (2)
Ba1–O2w	2.8501 (15)	O4–C5	1.224 (2)
O1 <sup>ii</sup> –Ba1–N1	135.72 (4)	O2w–Ba1–O1w	143.96 (4)
O1 <sup>ii</sup> –Ba1–N1 <sup>i</sup>	68.47 (4)	O2w–Ba1–O1w <sup>i</sup>	77.45 (4)
O1 <sup>ii</sup> –Ba1–O1 <sup>iii</sup>	68.98 (5)	O2w <sup>i</sup> –Ba1–O2w	67.13 (6)
O1 <sup>ii</sup> –Ba1–O1w	66.93 (4)	O2w–Ba1–O4	104.15 (4)
O1 <sup>ii</sup> –Ba1–O1w <sup>i</sup>	78.87 (4)	O4–Ba1–N1 <sup>i</sup>	119.46 (4)
O1w–Ba1–N1	115.40 (5)	O4–Ba1–N1	56.46 (4)
O1w–Ba1–N1 <sup>i</sup>	73.82 (5)	O4–Ba1–O1 <sup>ii</sup>	120.79 (4)
O1w <sup>i</sup> –Ba1–O1w	138.44 (6)	O4–Ba1–O1 <sup>iii</sup>	74.00 (4)
O2w–Ba1–N1	71.21 (5)	O4–Ba1–O1w <sup>i</sup>	125.14 (4)
O2w–Ba1–N1 <sup>i</sup>	88.24 (5)	O4–Ba1–O1w	61.72 (4)
O2w–Ba1–O1 <sup>iii</sup>	131.81 (4)	O4 <sup>i</sup> –Ba1–O4	163.52 (7)
O2w–Ba1–O1 <sup>ii</sup>	134.99 (4)	N1 <sup>i</sup> –Ba1–N1	155.55 (6)

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

Table 2

Hydrogen-bond geometry (Å, °).

<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>
O3–H3...O2	0.85 (2)	1.62 (2)	2.4635 (19)	173 (3)
N2–H2...O3w	0.86	1.92	2.775 (2)	175
O1w–H1w1...O2 <sup>ii</sup>	0.85 (2)	1.93 (2)	2.7752 (19)	174 (2)
O1w–H1w2...O4 <sup>iv</sup>	0.85 (3)	2.09 (3)	2.880 (2)	156 (2)
O2w–H2w1...O3w <sup>v</sup>	0.84 (3)	2.36 (3)	3.102 (3)	148 (2)
O2w–H2w2...O1 <sup>vi</sup>	0.84 (2)	2.15 (2)	2.980 (2)	170 (2)
O3w–H3w2...O1w <sup>vi</sup>	0.85 (3)	2.14 (2)	2.965 (2)	163 (3)
O3w–H3w1...O2w <sup>vii</sup>	0.85 (2)	2.24 (2)	2.951 (2)	142 (2)
O3w–H3w1...O2 <sup>viii</sup>	0.84 (2)	2.52 (2)	3.173 (2)	135 (2)

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

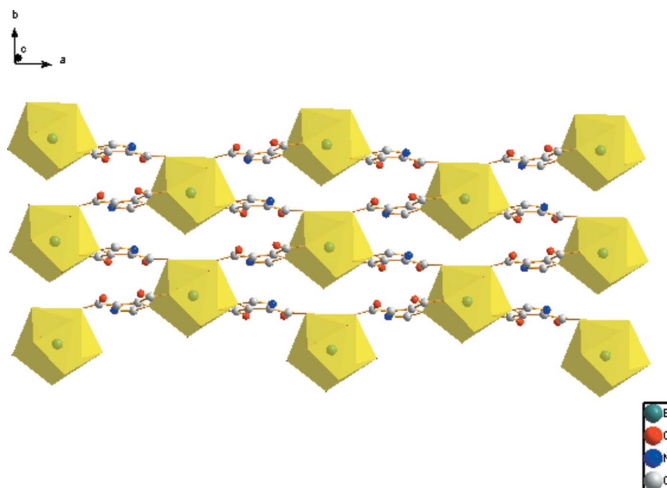


Figure 4

A two-dimensional layer of the title complex. Hydrogen bonds, H atoms and uncoordinated water molecules have been omitted.

H atoms on C and N atoms were placed in calculated positions, with C–H = 0.93 Å, N–H = 0.86 Å and *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(C,N), and were refined in the riding-model approximation. Oxygen-bound H atoms were located in a difference Fourier map and refined with O–H and H...H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and *U<sub>iso</sub>*(H) = 1.5*U<sub>eq</sub>*(O).

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (1054 G036) and Heilongjiang University for supporting this study.

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