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Poly[[sesqui[μ_2-1,4-bis(imidazol-1-ylmethyl)benzene-κ^2N:N'](carbonato-κ^2O,O')copper(**II**)] 1,4-bis(imidazol-1-ylmethyl)benzene hemisolvate pentahydrate]

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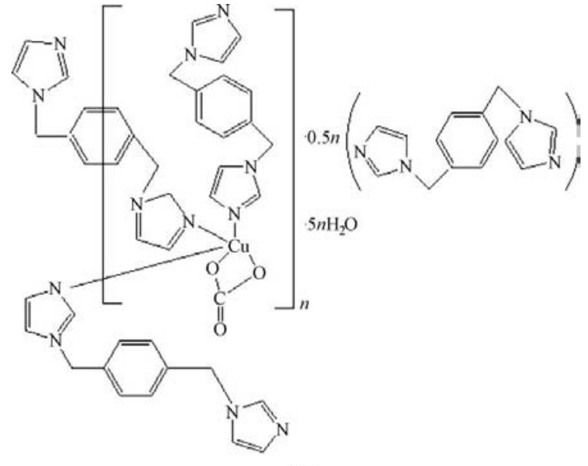
The asymmetric unit of the title compound, $\{[Cu(CO_3)(C_{14}H_{14}N_4)_{1.5}]\cdot 0.5C_{14}H_{14}N_4\cdot 5H_2O\}_n$, contains one Cu^{II} cation in a slightly distorted square-pyramidal coordination environment, one CO_3^{2-} anion, one full and two half 1,4-bis(imidazol-1-ylmethyl)benzene (bix) ligands, one half-molecule of which is uncoordinated, and five uncoordinated water molecules. One of the coordinated bix ligands and the uncoordinated bix molecule are situated about centers of symmetry, located at the centers of the benzene rings. The coordinated bix ligands link the copper(II) ions into a $[Cu(bix)_{1.5}]_n$ molecular ladder. These molecular ladders do not form interpenetrated ladders but are arranged in an *ABAB* parallel terrace, *i.e.* with the ladders arranged one above another, with sequence *A* translated with respect to *B* by 8 Å. To best of our knowledge, this arrangement has not been observed in any of the molecular ladder frameworks synthesized to date. The coordination environment of the Cu^{II} atom is completed by two O atoms of the CO_3^{2-} anion. The framework is further strengthened by extensive O—H···O and O—H···N hydrogen bonds involving the water molecules, the O atoms of the CO_3^{2-} anion and the N atoms of the bix ligands. This study describes the first example of a molecular ladder coordination polymer based on bix and therefore demonstrates further the usefulness of bix as a versatile multidentate ligand for constructing coordination polymers with interesting architectures.

Comment

Owing to their fascinating properties and potential applications to gas storage, molecular sieves, size- or shape-selective catalysis, and ion exchange (Noro *et al.*, 2000; Eddaoudi *et al.*, 2002) in functional materials, the construction of organic–inorganic open framework complexes with variable cavities or channels has attracted considerable interest in the past decade (Tong *et al.*, 1999; Wu *et al.*, 2006; Zhang *et al.*, 2006). These studies have shown that the careful selection of appropriate multidentate bridging ligands is helpful not only for tailoring polymer architectures effectively but also for realizing various applications. The use of long bidentate nitrogen ligands has afforded very interesting structural motifs, such as double helices (Carlucci *et al.*, 1997), multiple sheets (Hennigar *et al.*, 1997), interpenetrated ladders (Fujita *et al.*, 1998) and other noteworthy species. Many of the architectures reported to date, however, are based on rigid linear linker bidentate nitrogen ligands, with efforts only recently being focused on the use of ligands showing conformational flexibility (Carlucci *et al.*, 2000). In addition, the design of coordination polymers from flexible ligands is highly influenced by factors such as the nature of coordination of the metal ion, the length and flexibility of the organic ligand, the metal–ligand ratio, and the possible influences of the counter-anion and solvent. Recently, we have begun to work on the architectures of polymeric structures containing flexible ligands. We describe here the synthesis and structure of a new metal–organic molecular ladder, (I), formed from 1,4-bis(imidazol-1-ylmethyl)benzene (bix) ligands and copper sulfate.



(I)

X-ray diffraction analysis reveals that the title complex is a unique 'parallel terrace' molecular ladder structure. Each Cu center is five-coordinated, with one N atom from a bix ligand located in the apical position, and two bix N atoms and two O atoms from the CO_3^{2-} anion located in the basal plane, as shown in Fig. 1. The τ value for the coordination environment of the Cu atom is 0.36, showing that the Cu atom is in a slightly distorted square-pyramidal arrangement [τ ranges between 0 and 1 for square-pyramidal and trigonal bipyramidal structures, respectively (Addision & Rao, 1984)]. The Cu—N distances range from 1.963 (5) to 2.123 (5) Å, and the Cu—O distances are 1.966 (3) and 1.993 (3) Å (Table 1). The bix ligands link the copper(II) ions into a $[Cu(bix)_{1.5}]_n$ ladder. The bix ligands adopt two different conformations (*A* and *B*) in the

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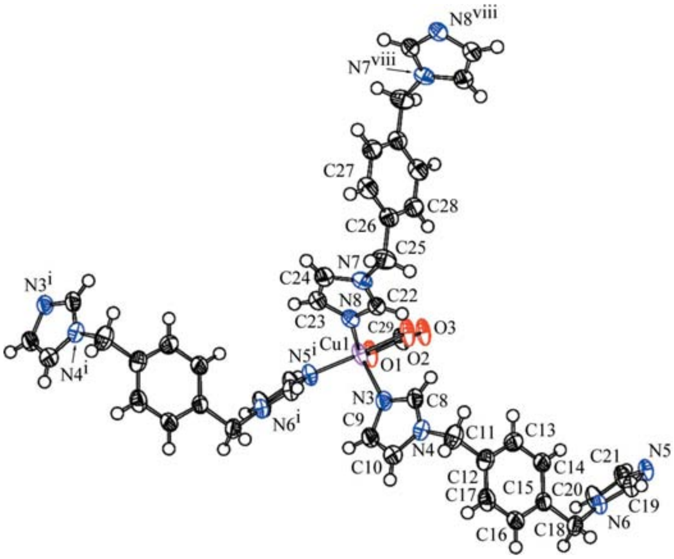

Figure 1
The local coordination around the Cu^{II} ion in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - 1, y - 1, z$; (viii) $-x - 1, -y, -z + 1$.]

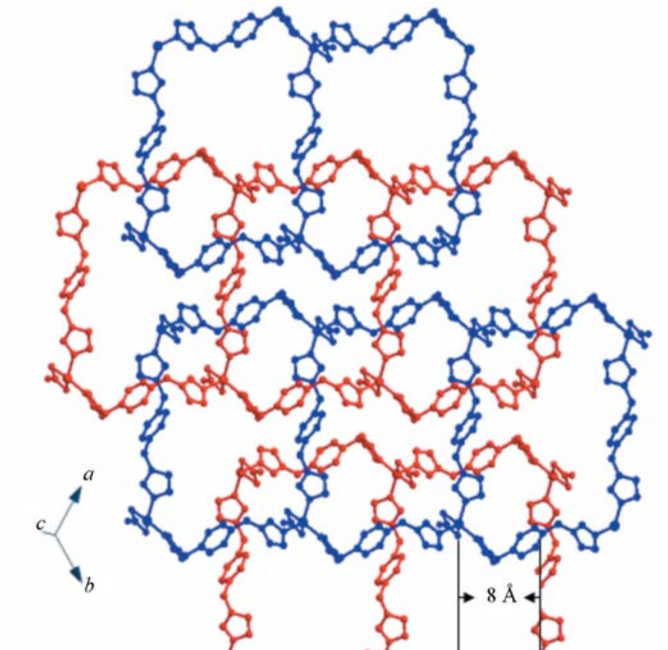

Figure 2
The parallel terrace arrangement of the molecular ladder in (I). H atoms, uncoordinated bix ligands and water molecules have been omitted for clarity.

ladder; the sides of the ladder adopt conformation *A*, with a dihedral angle between the two imidazole rings of 46.1 (3)°, and the rungs of the ladder adopt conformation *B*, where the dihedral angle between the two imidazole rings is 0°, as the two imidazole rings are related by a centre of inversion. The CO_3^{2-} ligands not only complete the coordination geometry of Cu^{II} but also act to balance the charge in the structure.

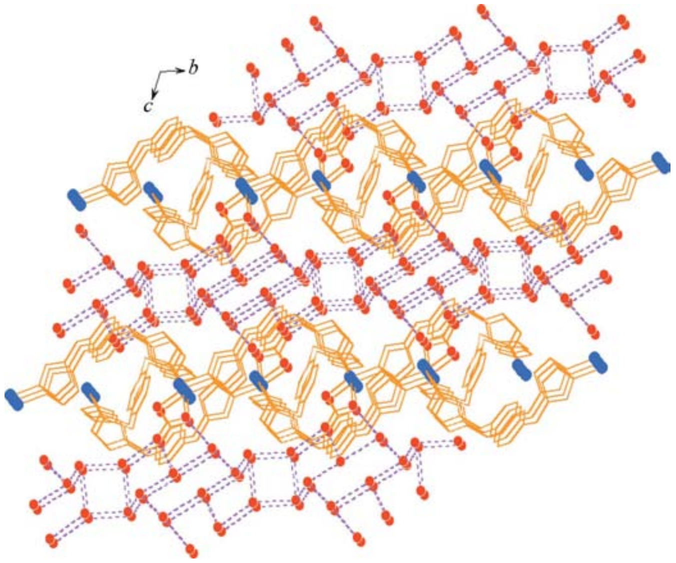

Figure 3
The crystal packing of (I). Hydrogen bonds are shown as dashed lines and uncoordinated bix ligands and H atoms have been omitted for clarity.

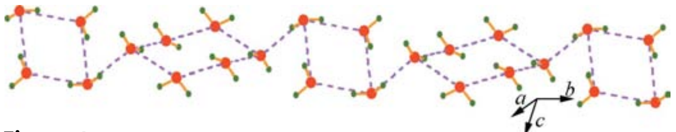

Figure 4
The one-dimensional water chains in (I). Dashed lines represent hydrogen bonds.

Generally, molecular ladders occur in a T-shaped unit and exhibit the phenomenon of interpenetration (Fujita *et al.*, 1995; Blake *et al.*, 1997). Large cavities between the rungs of the ladders encourage the inclusion of discrete symmetry-related ladders. Interpenetration was found to be perpendicular to the orientation of the original ladder to generate a three-dimensional polycatenated structure (Hennigar *et al.*, 1997). Another interpenetrating example of a molecular ladder was described by Blake *et al.* (1997). The packing of polymer (I) is very interesting. As shown in Fig. 2, the molecular ladders do not form an interpenetrated structure. Each ladder has two ladders above it, so as to fill the spaces between the rungs of the ladder, and the ladders are arranged in an *ABAB* parallel terrace sequence as *A* is translated with respect to *B* by *ca* 8 Å. To the best of our knowledge, this fascinating (one-dimensional-to-one-dimensional) parallel terrace array shows a type of arrangement of molecular ladder that has not been observed in any of the molecular ladder frameworks synthesized to date. The structure is further stabilized by extensive O—H···N hydrogen bonds (Table 2) involving the water molecules, the carbonate O atoms and the N atoms of the bix ligands, as shown in Fig. 3. When O—H···O hydrogen bonds between the uncoordinated water molecules and the CO_3^{2-} ligands, and O—H···N hydrogen bonds between the uncoordinated water molecules and the bix ligands are omitted, one-dimensional water chains emerge. As shown in Fig. 4, the one-dimensional water chain is built up from four- and six-membered rings arranged alternately. The one-dimensional water chain structure constitutes a potential form of water that is poorly understood (Liu & Xu, 2005). Many fundamental biological processes appear to depend on the unique properties of water chains. However, the role of the structural constraints in stabilizing one-dimensional chains is not fully established (Cheruzel *et al.*, 2003). The one-dimensional water chains reported here represent a rare example.

Finally, it is worth mentioning that the CO_3^{2-} anion may either be formed by an *in situ* oxidation reaction from the bix ligand or originate from atmospheric carbon dioxide, as there were no carbon complexes except the bix ligands and carbon dioxide in the starting reaction mixture. The C29—O1 [1.289 (5) Å], C29—O2 [1.276 (5) Å] and C29—O3 [1.241 (5) Å] bond lengths and the O1—C29—O2 [113.3 (4)°], O2—C29—O3 [122.3 (4)°] and O1—C29—O3 [124.4 (4)°] angles for the CO_3^{2-} anion are comparable with those reported in the complex (carbonato-$\kappa^2 O,O'$)bis(propane-1,3-diyldiamine-$\kappa^2 N,N'$)cobalt(III) chloride monohydrate (Zhu & Chen, 1999). When using $CuCO_3$ instead of $CuSO_4$, the title compound could not be obtained, indicating that SO_4^{2-} may play an important role in the formation of the title compound, although it does not appear in the molecular formula of the final compound.

Experimental

A mixture of $CuSO_4 \cdot 5H_2O$ (0.50 mmol, 0.14 g), bix (1.00 mmol, 0.24 g) and water (15 ml) was stirred vigorously while the pH value was adjusted to 6 by the addition of 10% NaOH. The mixture was then heated at 433 K for 3 d in a sealed 25 ml Teflon-lined stainless steel vessel under autogenous pressure. After cooling to room temperature at a rate of 50 K h^{-1}, blue prismatic crystals were isolated, which were washed with ethanol and dried in air (yield 42%, based on Cu). Elemental analyses found: C 50.45, H 5.72, N 16.21%; calculated: C 50.47, H 5.55, N 16.23%. IR (KBr, cm^{-1}): 3415 (*m*), 3102 (*m*), 1645 (*m*), 1566 (*s*), 1521 (*w*), 1442 (*m*), 1386 (*m*), 1300 (*m*), 1245 (*m*), 1090 (*m*), 1024 (*m*), 952 (*w*), 878 (*w*), 848 (*w*), 742 (*w*), 718 (*w*), 659 (*m*), 622 (*w*), 517 (*w*), 466 (*w*).

Crystal data

$[Cu(CO_3)(C_{14}H_{14}N_4)_{1.5}] \cdot 0.5C_{14}H_{14}N_4 \cdot 5H_2O$
$M_r = 690.22$
Triclinic, $P\overline{1}$
$a = 12.2286$ (2) Å
$b = 12.4976$ (7) Å
$c = 12.951$ Å
$\alpha = 103.759$ (15)°
$\beta = 98.726$ (12)°
$\gamma = 118.767$ (9)°
$V = 1600.8$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.74$ mm^{-1}
$T = 293$ (2) K
0.20 × 0.15 × 0.05 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.875$, $T_{max} = 0.963$
12466 measured reflections
7352 independent reflections
5723 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.120$
$S = 1.02$
7352 reflections
49 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N5^{i}	1.963 (3)	Cu1—N8	2.041 (3)
Cu1—O2	1.966 (3)	Cu1—N3	2.123 (5)
Cu1—O1	1.993 (3)		
N5^{i}—Cu1—O2	163.80 (13)	O1—Cu1—N8	141.92 (15)
N5^{i}—Cu1—O1	98.53 (13)	N5^{i}—Cu1—N3	94.9 (2)
O2—Cu1—O1	65.57 (13)	O2—Cu1—N3	94.3 (2)
N5^{i}—Cu1—N8	96.19 (13)	O1—Cu1—N3	112.5 (2)
O2—Cu1—N8	95.13 (14)	N8—Cu1—N3	100.90 (19)

Symmetry code: (i) $x-1, y-1, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O5*W*	0.83 (16)	2.40 (11)	2.780 (10)	108 (10)
O1*W*—H1*WB*···O1^{ii}	0.86 (5)	1.87 (5)	2.722 (8)	170 (13)
O2*W*—H2*WA*···O3^{iii}	0.83 (10)	1.88 (6)	2.687 (9)	163 (10)
O2*W*—H2*WB*···O1*W*^{iv}	0.82 (5)	2.29 (9)	2.964 (14)	140 (10)
O3*W*—H3*WA*···O5*W*^{v}	0.84 (10)	2.02 (5)	2.834 (9)	163 (10)
O3*W*—H3*WB*···O4*W*^{vi}	0.85 (9)	2.00 (5)	2.803 (9)	160 (10)
O4*W*—H4*WA*···O3	0.84 (10)	2.00 (6)	2.779 (8)	156 (10)
O4*W*—H4*WB*···O3*W*^{vii}	0.83 (4)	2.21 (5)	3.012 (10)	162 (9)
O5*W*—H5*WA*···O2*W*	0.84 (5)	1.99 (5)	2.808 (10)	166 (10)
O5*W*—H5*WB*···N1^{i}	0.86 (5)	2.09 (6)	2.868 (10)	151 (9)

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

C-bound H atoms were positioned geometrically and treated using a riding model, fixing the C—H bond lengths at 0.97 and 0.93 Å for CH_2 and aromatic CH groups, respectively [$U_{iso}(H) = 1.2U_{eq}(C)$]. Water H atoms were located from difference maps and refined with O—H distance restraints of 0.86 (5) Å [$U_{iso}(H) = 1.2U_{eq}(O)$].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3087). Services for accessing these data are described at the back of the journal.

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