

catena-Poly[[[μ -1,4-bis(imidazol-1-ylmethyl)benzene- $\kappa^2N^3:N^{3'}$]]bis[di-chlorocopper(II)]-bis[μ -1,4-bis(imidazol-1-ylmethyl)benzene]-1:1' $\kappa^2N^3:N^3$;2:2' $\kappa^2N^3:N^3$]

Tao Li,^{a,b} Sheng-Min Hu^a and Shao-Wu Du^{a*}

^aState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and ^bGraduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China
Correspondence e-mail: swdu@fjirsm.ac.cn

Received 9 May 2005

Accepted 22 June 2005

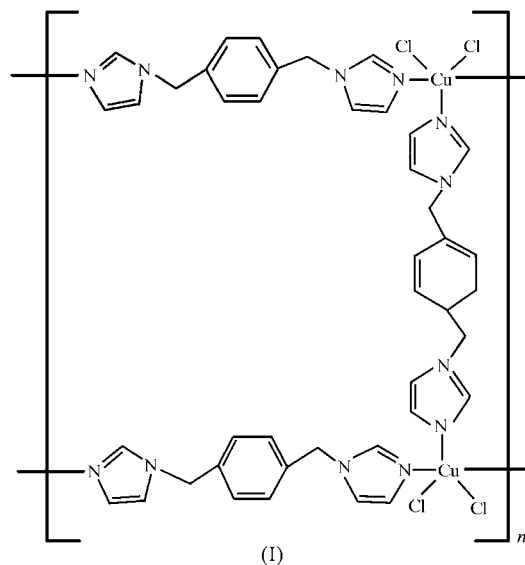
Online 10 August 2005

The title compound, $[\text{Cu}_2\text{Cl}_4(\text{bix})_3]_n$ [bix is 1,4-bis(imidazol-1-ylmethyl)benzene, $\text{C}_{14}\text{H}_{14}\text{N}_4$], has been synthesized by the hydrothermal method. The copper(II) center has a five-coordinate trigonal-bipyramidal geometry. Each bix ligand binds with two Cu^{II} ions, forming ladder-like structures which are connected by π - π stacking interactions to form a two-dimensional network.

Comment

In recent years, many strategies have been employed in the synthesis of polymeric architectures with nitrogen-containing heterocyclic ligands, which may play a determining role in the control of the structures (Fujita *et al.*, 1994; Lu *et al.*, 1999; Ho *et al.*, 1999; Meng *et al.*, 2004). One of the most fruitful choices consists in making good use of imidazole and its derivatives (Carlucci, Ciani & Proserpio, 2004; Liu & Li, 2003; Su *et al.*, 2002, 2003). For example, by reactions with silver nitrate and zinc nitrate hexahydrate, the highly flexible ligand 1,4-bis(imidazole-1-ylmethyl)benzene provided low-dimensional complexes with remarkable polyrotaxane-like polymers $[\text{Ag}_2(\text{bix})_3(\text{NO}_3)_2]$ and $[\text{Zn}(\text{bix})_2(\text{NO}_3)_2] \cdot 4.5\text{H}_2\text{O}$ (Hoskins *et al.*, 1997*a,b*). Recently, there has been growing interest in bix complexes as a result of their intriguing frameworks (Abrahams *et al.*, 1998, 2002; Carlucci, Ciani, Proserpio & Spadacini, 2004; Shen *et al.*, 1999; Zhao *et al.*, 2002). In previous research, the syntheses of the bix compounds were all performed in solution at room temperature because the bix ligand is readily soluble in CH_3OH , CHCl_3 or acetone. In order to investigate further the influence of bix ligands on the final frameworks, we synthesized a one-dimensional ladder-like copper(II) polymer, *viz.* $[\text{Cu}_2(\text{bix})_3\text{Cl}_4]_n$ (I), by hydrothermal reaction of

copper(II) chloride dihydrate with the bix ligand. Unlike other bix complexes, the bix ligands in compound (I) not only act as long linkers that interconnect the parallel chains but also construct the supramolecular architecture by π - π stacking interactions between the aromatic imidazole rings. As a result, this one-dimensional compound forms a two-dimensional network.



Compound (I) contains ladder-like chains, as shown in Fig. 1, in which the chloride ligands are coordinated to the copper(II) center, preventing the formation of an extended framework. The copper(II) center has a five-coordinate trigonal-bipy-

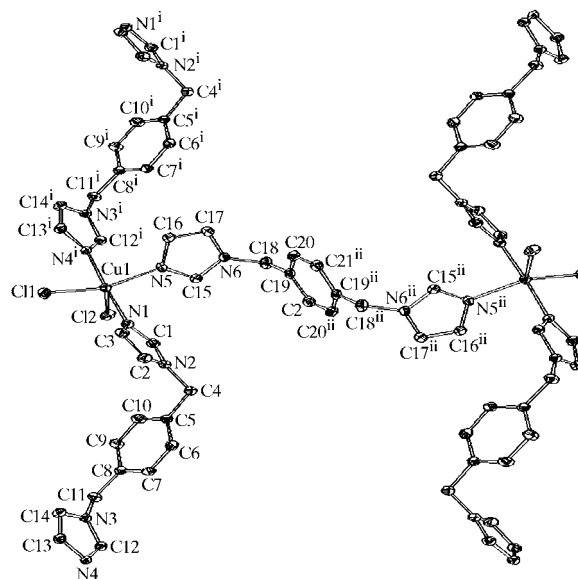


Figure 1

A section of the crystal structure of the title compound. Displacement ellipsoids are plotted at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x, 1 - y, 1 - z$.]

ramidal geometry, with one N atom of a bix ligand and two chloride anions in the basal plane, and with the other two N atoms in *trans* axial positions completing the coordination environment (Table 1). Atoms N5, Cl1 and Cl2 are coplanar, but the angles around the Cu atom are rather different, the largest being 144.34 (8)° (Table 1), far from the expected value of 120° of a regular trigonal bipyramid. In the axial direction, the N1–Cu1–N4ⁱ angle is close to linearity [176.17 (10)°; symmetry code: (i) $x - 1, y, z - 1$]. There are two different types of μ_2 -bridging bix ligands in the compound. The first type uses the N atoms of the apical positions to build up a linear subunit, *viz.* bix–Cu–bix. Two of these subunits are then connected by the N atoms located in the equatorial plane, giving a ladder-like coordination polymer with a large grid of 13.893 × 14.170 Å (metal-to-metal distance; Fig. 2). The grid-like Cu₄(bix)₄ units can be viewed as the basic building block of the structure, in which the apices are occupied by the Cu^{II} ions and the sides by the bix ligands.

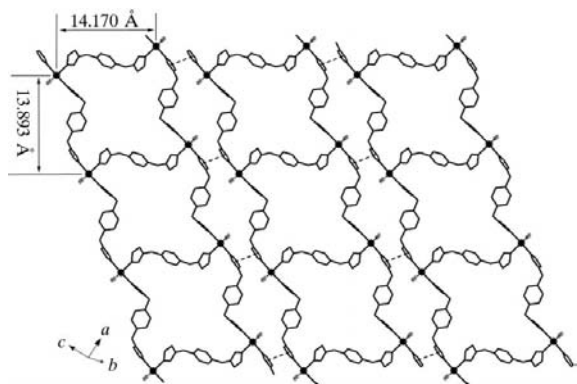


Figure 2
The ladder-like square grid and two-dimensional molecular networks formed by π – π stacking interactions (dashed lines).

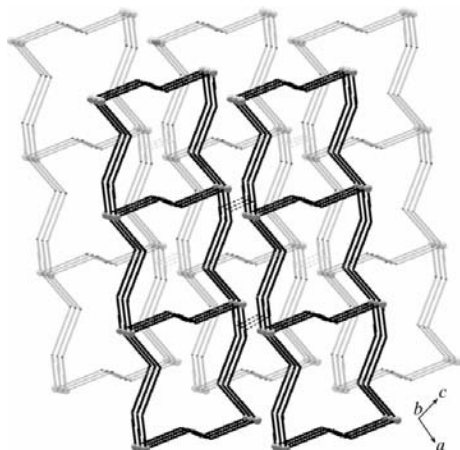


Figure 3
The packing of the grid layers of the title compound.

The basic grid is puckered and can be described as chair-like in shape, although all the Cu atoms in the ladder are strictly planar. This shape is understandable because the sp^3 configuration of the –CH₂– spacer forces the bix ligand to be non-linear, generating the non-linear grid sides and thereby the reclining chair-shaped grids. The N–C–C angles of the bix ligands in (I) are 112.2 (2), 112.3 (2) and 113.8 (2)°, while the bridging ligands in this ladder-like structure all adopt the *trans* conformation, and the dihedral angles between planes N1/C1/N2/C3/C2 and C5–C10, N3/C12/N4/C13/C14 and C5–C10, and N5/C15/N6/C17/C16 and C19/C20/C21ⁱⁱ/C19ⁱⁱ/C20ⁱⁱ/C21 are 99.3, 94.4, and 104.7°, respectively [symmetry code: (ii) $-x, 1 - y, 1 - z$]. These structure data clearly depict the non-linear configuration of the bix ligand in (I). The striking feature of the structure of (I) is that the aromatic imidazole ring of one chain parallel to a symmetry-related (symmetry code: $1 - x, 2 - y, -z$) adjacent chain interacts with an offset face-to-face separation of *ca* 3.4 Å and a centroid–centroid distance of 3.659 (1) Å, indicating significant π – π interactions (Dance & Scudder, 1995). The double chains are thus organized into two-dimensional molecular networks by π – π stacking interactions (Fig. 2). The grid layers are closely stacked in an offset fashion along the *b* direction, the cavity of each layer being blocked by the neighboring layers (Fig. 3).

Experimental

Bix dihydrate was prepared as described by Hoskins *et al.* (1997b). Compound (I) was synthesized hydrothermally under autogenous pressure. A mixture of CuCl₂·2H₂O (0.085 g, 0.5 mmol), bix dihydrate (0.14 g, 0.5 mmol) and water (8 ml) was sealed in a stainless steel reactor with a Teflon liner, and was heated to 393 K for two days. After slow cooling to room temperature, light-blue block-shaped crystals of (I) were obtained as a major phase by filtration; these were washed with distilled water and finally dried in air (70% yield). Analysis calculated for (I): C 38.41, H 3.15, N 12.50%; found: C 38.13, H 3.15, N 12.65%. IR (KBr pellet): 3446 (s), 3105 (w), 1631 (m), 1520 (s), 1425 (w), 1384 (m), 1286 (w), 1243 (m), 1111 (s), 1092 (s), 1029 (w), 950 (w), 859 (w), 827 (w), 773 (w), 749 (m), 716 (w), 660 (m), 622 (w).

Crystal data

[Cu ₂ Cl ₄ (C ₁₄ H ₁₄ N ₄) ₃]	Z = 2
<i>M_r</i> = 491.89	<i>D_x</i> = 1.560 Mg m ^{−3}
Triclinic, <i>P</i> $\bar{1}$	Mo K α radiation
<i>a</i> = 9.752 (5) Å	Cell parameters from 2262 reflections
<i>b</i> = 9.894 (6) Å	θ = 3.1–27.5°
<i>c</i> = 11.685 (6) Å	μ = 1.32 mm ^{−1}
α = 105.963 (5)°	<i>T</i> = 293 (2) K
β = 99.760 (7)°	Block, blue
γ = 98.062 (3)°	0.25 × 0.10 × 0.10 mm
<i>V</i> = 1047.3 (10) Å ³	

Data collection

Rigaku Mercury 70 diffractometer	3590 reflections with <i>I</i> > 2σ(<i>I</i>)
ω scans	<i>R</i> _{int} = 0.027
Absorption correction: multi-scan	θ _{max} = 27.5°
(<i>CrystalClear</i> ; Rigaku, 2000)	<i>h</i> = −12 → 12
<i>T</i> _{min} = 0.766, <i>T</i> _{max} = 0.876	<i>k</i> = −12 → 11
8202 measured reflections	<i>l</i> = −10 → 15
4736 independent reflections	

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.093$
 $S = 1.06$
 4736 reflections
 271 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 0.7403P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	1.982 (3)	Cu1—Cl1	2.332 (1)
Cu1—N4 ⁱ	2.009 (3)	Cu1—Cl2	2.565 (2)
Cu1—N5	2.086 (3)		
N1—Cu1—N4 ⁱ	176.17 (10)	Cl1—Cu1—Cl2	113.93 (4)
N1—Cu1—N5	90.24 (10)	N2—C4—C5	112.2 (2)
N4 ⁱ —Cu1—N5	86.39 (10)	N3—C11—C8	113.9 (3)
N5—Cu1—Cl1	144.36 (8)	N6—C18—C19	112.3 (2)
N5—Cu1—Cl2	101.68 (8)		

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

All H atoms were placed at calculated positions and treated as riding on their parent atoms [$C-H = 0.93$ and 0.97 \AA , and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

This work was supported by grants from the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences (CAS), The Ministry of Science and Technology of

China (grant No. 001CB108906), and the National Science Foundation of China (grant No. 20333070).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1091). Services for accessing these data are described at the back of the journal.

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