

## Poly[di- $\mu_3$ -chloro- $\mu_2$ -*trans*-1,2-di-4-pyridylethylene-dicopper(I)]: a two-dimensional organic–inorganic hybrid constructed from linear CuCl clusters and bridging ligands

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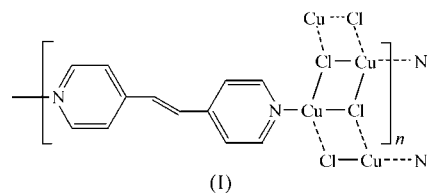
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The structure of the title compound,  $[\text{Cu}_2\text{Cl}_2(\text{C}_{12}\text{H}_{10}\text{N}_2)]_n$ , contains infinite CuCl staircase-like chains, which lie about inversion centres. The *trans*-1,2-di-4-pyridylethylene molecules also lie about inversion centres and connect the CuCl chains through Cu–N coordination bonds into a two-dimensional organic–inorganic hybrid network. The planar sheets are stacked along the *c* axis and associated through weak C–H $\cdots$ Cl interactions. The results show a reliable structural motif with controllable separation of the CuCl chains by variation of the length of the ligand.

### Comment

Designed synthesis of metal-organic coordination polymers by employing various metal centres and polyfunctional ligands has attracted increasing interest in recent years because of the novel electronic, optical, magnetic and catalytic properties of these polymers (Janiak, 2003; Kitagawa *et al.*, 2004). In the case of reaction systems containing inorganic species, the coordination polymers may form in an organic–inorganic hybrid fashion. Coordinate covalent bonds or non-covalent interactions, such as hydrogen bonds and  $\pi$ – $\pi$  interactions, are useful tools to connect inorganic and organic components (Graham & Pike, 2000; Mitzi *et al.*, 1995). The choice of metal coordination units used as building blocks is crucial to the assembly of the supramolecular networks, since the geometric and topological characteristics of these units determine the structures of the products. The Cu<sup>I</sup>–halide/organoamine system is of interest because of the preference for the formation of predictable copper(I)–halide motifs, including zigzag chains (Wang *et al.*, 2005), rack chains (Begley *et al.*, 1994) and staircases (Blake, Brooks, Champness, Cooke, Crew *et al.*, 1999; Aakeröy *et al.*, 2000), which can be propagated through the coordination of organic N-donor ligands to form

network structures. It has been demonstrated that the ligand geometry can affect the type of Cu<sup>I</sup>–halide framework. For example, Cu<sup>I</sup>–halide polymers in a staircase form have been observed for linear bidentate ligands such as pyrazine (pyz) and 4,4'-bipyridine (bpy) (Kawata *et al.*, 1998; Lu *et al.*, 1999), while a tridentate triazine ligand results in the formation of a columnar polymer (Blake, Brooks, Champness, Cooke, Deveson *et al.*, 1999). These results led us to examine the effects of 1,2-di-4-pyridylethylene (bpe), a longer analogue of 4,4'-bipyridine, on the structure of a Cu<sup>I</sup>–halide hybrid polymer. We report here the structure of  $[(\text{CuCl})_2(\text{bpe})]_n$  (I), which exhibits an organic–inorganic layered structure formed by the assembly of a one-dimensional CuCl staircase and the bridging ligand.



Compound (I) was prepared as described in the *Experimental*, and the resulting dark-yellow crystals suggested that (I) is a cuprous product; this was established by crystal structure analysis. The formation of the coordination polymer  $[\text{Cu}_4\{1,4\text{-C}_6\text{H}_4(\text{COO})_2\}_3(\text{bpy})_2]_n$ , with mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup> subunits from the Cu<sup>II</sup> salt under a similar solvothermal condition (Lo *et al.*, 2000), and of the polymer  $[(\text{CuCl})_2(\text{bpy})]_n$ , from hydrothermal reaction of Cu<sup>II</sup> chloride (Lu *et al.*, 1999), have shown that both ethanol and aromatic amine may act as reducing agents for Cu<sup>II</sup> reduction at high temperature.

In the structure of (I), as shown in Fig. 1, atom Cu1 is coordinated to three Cl1 atoms and atom N1 from the bpe ligand in a distorted tetrahedral environment (Table 1), showing the typical character of the monovalent copper ion. Each Cl1 atom binds three Cu1 atoms in a  $\mu_3$ -fashion, thus generating a polymeric CuCl staircase-like chain. The bpe ligand is planar, with an inversion centre lying at the mid-point of the ethylene bond. The polymeric CuCl chains arranged parallel to each other are interconnected through the bridging bpe molecules into a two-dimensional layered network (Fig. 2). The bridging ligands are stacked in such a way that  $\pi$ – $\pi$  interactions between the pyridine rings may be maximized, with a centroid-to-plane separation of 3.46 Å, which further stabilizes the network structure.

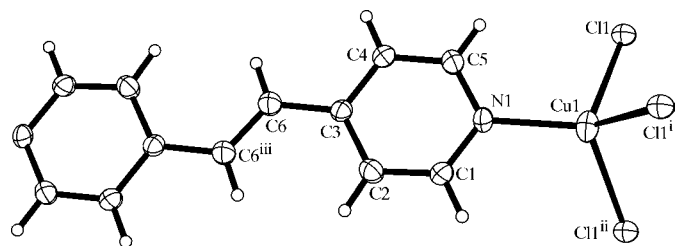


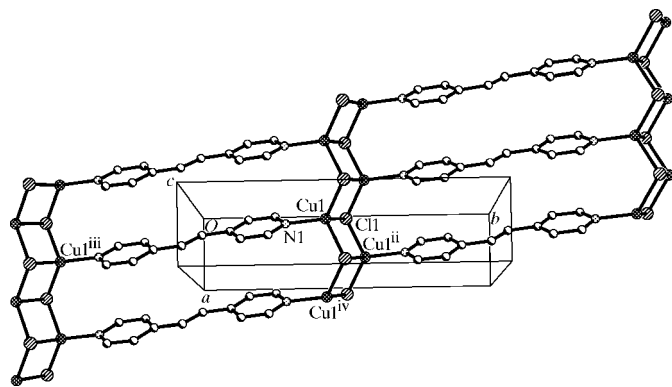
Figure 1

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + 1, -y, -z + 1$ .]

There are three types of Cu···Cu separations that are structurally significant. One is the shortest contact of 2.975 (2) Å between atoms Cu1 and Cu1<sup>ii</sup> (see Fig. 2 for symmetry codes) within the CuCl staircase, which implies a weak Cu···Cu interaction. This interaction seems to be enhanced as the size of the bridging ligand decreases, as indicated by the corresponding values of 2.936 (1) Å in [(CuCl)<sub>2</sub>(bpy)]<sub>n</sub> (Lu *et al.*, 1999) and 2.889 (2) Å in [(CuCl)<sub>2</sub>(pyz)]<sub>n</sub> (Kawata *et al.*, 1998). The second is the separation of Cu1 and Cu1<sup>iv</sup> of 3.796 (1) Å along the staircase, which corresponds to the short axis of the unit cell. This distance is a good match with π–π interaction between the bridging ligands. In the case of [(CuI)<sub>2</sub>(bpe)]<sub>n</sub> (Blake, Brooks, Champness, Cooke, Crew *et al.*, 1999), the corresponding distance is a little longer [4.1000 (8) Å], leading to a relatively weak π–π interaction between the pyridine rings, with a centroid-to-plane distance of 3.59 Å. The third is the separation of atoms Cu1 and Cu1<sup>iii</sup> between adjacent CuCl staircases [13.377 (5) Å]. A comparison with the corresponding values of 11.099 and 6.781 Å in [(CuCl)<sub>2</sub>(bpy)]<sub>n</sub> and [(CuCl)(pyz)]<sub>n</sub>, respectively, shows that the separation of the CuCl staircases can be effectively governed by the length of the bridging ligands. This distance can also be extended by the use of hydrogen-bonded dimeric ligands (Aakerøy *et al.*, 2000). Thus, it is a predictable and adjustable aspect of this family of structures.

The two-dimensional networks are stacked along the *c* axis at *c* = 0 and  $\frac{1}{2}$ . Adjacent sheets are staggered with respect to one another by half a translation along the *b* axis, so that ethylene atom C6 is located near atom Cl1 from a neighbouring sheet to form a weak C–H···Cl contact. The H···Cl(–*x*, *y* –  $\frac{1}{2}$ , –*z* +  $\frac{1}{2}$ ) distance of 2.95 Å is at the limit of van der Waals radii (Bondi, 1964), but the C–H···Cl angle of 157° is within the range of acceptable values for hydrogen bonds (Taylor & Kennard, 1982). This C–H···Cl interaction may benefit the stacking of the planar sheets in an *ABAB* fashion.

In summary, the two-dimensional hybrid network with the CuCl staircase as building block and the bpe ligand as spacer can be readily constructed from the reduction reaction of Cu<sup>II</sup> under solvothermal conditions. The results indicate that the



**Figure 2**  
A view of the two-dimensional network, showing the one-dimensional CuCl staircases linked by bpe ligands. [Symmetry codes: (ii) –*x* + 1, –*y* + 1, –*z* + 1; (iii) –*x* + 1, –*y*, –*z* + 1; (iv) *x* + 1, *y*, *z*.]

structural motif is stable and repeatable, and that it is possible to control the separations of Cu atoms by changing the sizes of the ligands, thus leading to changes in the properties of the compounds.

### Experimental

A mixture of Cu(BF<sub>4</sub>)<sub>2</sub> (0.2 mmol), bpe (0.2 mmol), HCl (0.2 mmol) in water (9 ml), and ethanol (3 ml) was stirred, adjusted to a pH of 9.6 with triethylamine, and then transferred to and sealed in a 25 ml Teflon-lined reaction vessel, which was heated at 433 K for 3 d. The vessel was cooled to room temperature at a rate of 10 K h<sup>–1</sup>. The resulting dark-yellow plate-shaped crystals were filtered off, washed and dried in air (yield 34%).

#### Crystal data

[Cu <sub>2</sub> Cl <sub>2</sub> (C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> )]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 380.20	<i>D<sub>x</sub></i> = 2.026 Mg m <sup>–3</sup>
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 3.7965 (11) Å	<i>μ</i> = 3.82 mm <sup>–1</sup>
<i>b</i> = 15.078 (5) Å	<i>T</i> = 293 (2) K
<i>c</i> = 10.972 (4) Å	Plate, dark yellow
<i>β</i> = 97.082 (6)°	0.36 × 0.26 × 0.15 mm
<i>V</i> = 623.3 (4) Å <sup>3</sup>	

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer	3304 measured reflections
<i>φ</i> and <i>ω</i> scans	1238 independent reflections
Absorption correction: multi-scan (SAINT; Bruker, 2003)	840 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>T<sub>min</sub></i> = 0.332, <i>T<sub>max</sub></i> = 0.604 (expected range = 0.310–0.564)	<i>R<sub>int</sub></i> = 0.053
	<i>θ<sub>max</sub></i> = 26.1°

#### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.055	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0513 <i>P</i> ) <sup>2</sup> ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.120	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>S</i> = 1.05	(Δ/σ) <sub>max</sub> < 0.001
1238 reflections	Δρ <sub>max</sub> = 0.49 e Å <sup>–3</sup>
82 parameters	Δρ <sub>min</sub> = –0.42 e Å <sup>–3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1–N1	1.999 (4)	Cu1–Cl1	2.5420 (17)
Cu1–Cl1 <sup>i</sup>	2.3235 (16)	Cu1–Cu1 <sup>ii</sup>	2.9752 (17)
Cu1–Cl1 <sup>iii</sup>	2.4003 (17)	Cu1–Cu1 <sup>i</sup>	2.9848 (17)
N1–Cu1–Cl1 <sup>i</sup>	122.94 (13)	N1–Cu1–Cl1	103.53 (13)
N1–Cu1–Cl1 <sup>iii</sup>	111.45 (13)	Cl1 <sup>i</sup> –Cu1–Cl1	104.47 (5)
Cl1 <sup>i</sup> –Cu1–Cl1 <sup>iii</sup>	106.96 (6)	Cl1 <sup>iii</sup> –Cu1–Cl1	106.04 (5)

Symmetry codes: (i) –*x*, –*y* + 1, –*z* + 1; (ii) –*x* + 1, –*y* + 1, –*z* + 1.

All H atoms were located from difference maps and treated as riding atoms, with C–H distances of 0.93 Å and *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(parent).

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); 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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3011). Services for accessing these data are described at the back of the journal.

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## References

- Aakeröy, C. B., Beatty, A. M. & Lorimer, K. R. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3869–3872.
- Begley, M. J., Eisenstein, O., Hubberstey, P., Jackson, S., Russell, C. E. & Walton, P. H. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1935–1942.
- Blake, A. J., Brooks, N. R., Champness, N. R., Cooke, P. A., Crew, M., Deveson, A. M., Hanton, L. R., Hubberstey, P., Fenske, D. & Schröder, M. (1999). *Cryst. Eng.* **2**, 181–195.
- Blake, A. J., Brooks, N. R., Champness, N. R., Cooke, P. A., Deveson, A. M., Fenske, D., Hubberstey, P., Li, W.-S. & Schröder, M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2103–2110.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1998). *SMART*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2003). *SAINTE*. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.
- Graham, P. M. & Pike, R. D. (2000). *Inorg. Chem.* **39**, 5121–5132.
- Janiak, C. (2003). *Dalton Trans.* pp. 2781–2804.
- Kawata, S., Kitagawa, S., Kumagai, H., Iwabuchi, S. & Katad, M. (1998). *Inorg. Chim. Acta*, **267**, 143–145.
- Kitagawa, S., Kitaura, R. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
- Lo, S. M.-F., Chui, S. S.-Y., Shek, L.-Y., Lin, Z., Zhang, X. X., Wen, G.-H. & Williams, I. D. (2000). *J. Am. Chem. Soc.* **122**, 6293–6294.
- Lu, J. Y., Cabrera, B. R., Wang, R.-J. & Li, J. (1999). *Inorg. Chem.* **38**, 4608–4611.
- Mitzi, D. B., Wang, S., Feild, C. A., Chess, C. A. & Guloy, A. M. (1995). *Science*, **267**, 1473–1476.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Taylor, R. & Kennard, O. J. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Wang, X.-Q., Cheng, J.-K., Wen, Y.-H., Zhang, J., Li, Z.-J. & Yao, Y.-G. (2005). *Inorg. Chem. Commun.* **8**, 897–899.