

## A novel three-dimensional copper(I) coordination polymer constructed from a copper–bromide net and nicotinic acid ligands

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Received 8 December 2008

Accepted 19 December 2008

Online 10 January 2009

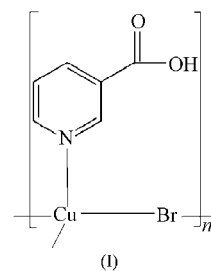
The title compound, poly[ $\mu_3$ -bromido-(pyridine-3-carboxylato- $\kappa N$ )copper(I)], [CuBr(C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>)]<sub>n</sub>, is a novel coordination polymer based on a copper–bromide net and nicotinic acid ligands. The asymmetric unit contains one copper(I) ion, one bromide ligand and one nicotinic acid ligand, all on general positions. The Cu<sup>I</sup> atom is tetrahedral and coordinated by three bridging Br atoms and the N atom from the nicotinic acid ligand. The Cu–Br units form alternating six-membered chair-patterned rings in net-like layers. The attached nicotinic acid units point alternately up and down. The layers are assembled into a three-dimensional network *via* intermolecular O–H...O and C–H...Br hydrogen-bonding interactions.

### Comment

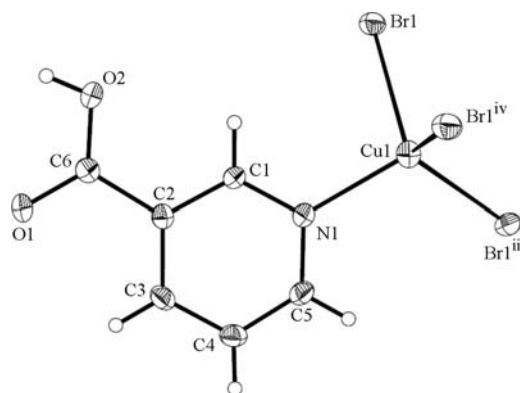
Metal halides have been of increasing interest for their rich photoluminescent properties and intriguing topologies (Subramanian & Hoffmann, 1992; Ye *et al.*, 2005; Lu, 2003; Cheng *et al.*, 2005). In the past decade, experiments have proved that an effective approach for increasing the dimensionality is to use aromatic multidentate bridging N-donor molecules to link the oligomers into one-, two- or three-dimensional coordination polymers (Zhong *et al.*, 2000; Larionova *et al.*, 2000). In the structural investigations of compounds of nicotinic acid, it has been found that nicotinic acid can act as such a multidentate ligand (Luo *et al.*, 2004; Evans & Lin, 2001; Li *et al.*, 2007) with versatile binding and coordination modes. A novel net-like two-dimensional copper(I) coordination polymer, (I), resulted from the hydrothermal treatment of CuBr with nicotinic acid in alkaline aqueous solution.

As depicted in Fig. 1, the asymmetric unit consists of one copper(I) ion, one bromide ligand and one nicotinic acid ligand per asymmetric unit. The Cu<sup>I</sup> center has a tetrahedral coordination geometry defined by three Br atoms and one N

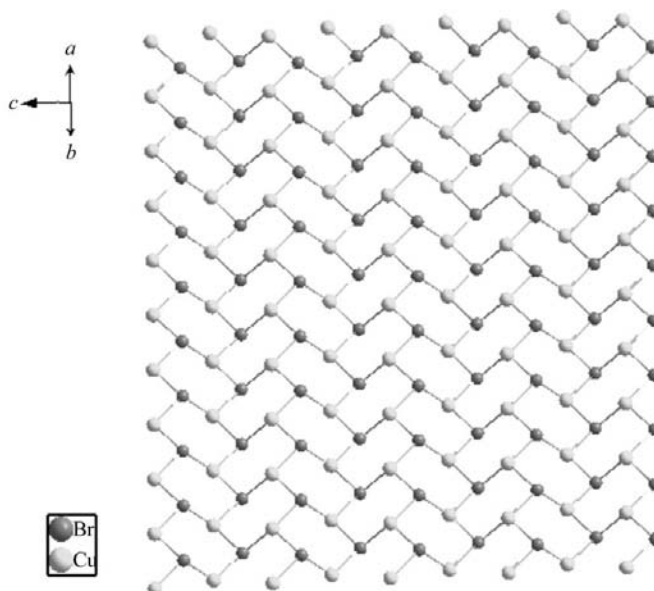
atom from the nicotinic acid ligand. The Cu–Br unit forms an alternating six-membered chair-patterned ring. The ring is



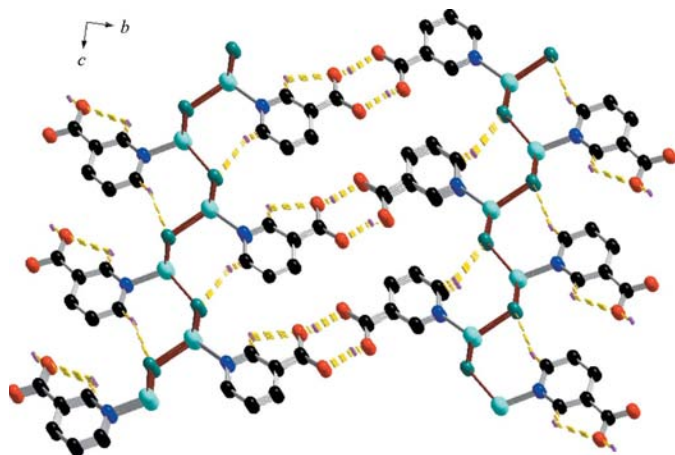
further extended into a net-like layer (Fig. 2) through edge-sharing. Each Cu atom is bonded to nicotinic acid ligands arranged alternately pointing up and down around the ring. Finally, these layers are further assembled into a three-dimensional supramolecular network *via* intermolecular O–H...O and C–H...Br hydrogen-bonding stacking inter-



**Figure 1**  
A perspective view of the asymmetric unit of (I). [Symmetry codes: (iii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $x - 1, y, z$ .]



**Figure 2**  
A view of a net-like layer of Cu–Br units in (I).



**Figure 3**  
A three-dimensional view of (I) in the *bc* plane. Hydrogen bonds are shown as dashed lines.

actions (Fig. 3). The overall structural motif in (I) is unprecedented.

Copper(I) halide complexes with nitrogen bases have long been of interest because of the diversity of structure types formed (Gill *et al.*, 1976; Camus *et al.*, 1975; Healy *et al.*, 1983, 1989). Typically, either discrete tetranuclear clusters (Dyason *et al.*, 1985) or polymers are produced (Healy *et al.*, 1989; Graham *et al.*, 1989). The two common polymer frameworks are often termed the ‘chain’ and the ‘stair’. The ‘chain’ polymer has linear chains consisting of  $-(\text{Cu}X)-$  repeat units. These chains can form two-dimensional sheets when the pendant ligands are bidentate, by bridging of Cu atoms in adjacent chains (as seen in the polymer  $[\text{CuClPz}]$ ; Pz is pyrazine; Moreno *et al.*, 1995). Alternatively, the ‘stair’ polymer has square  $-(\text{Cu}_2X_2)-$  units that form the step of a stair (Healy *et al.*, 1989; Massaux *et al.*, 1971; Jasinski *et al.*, 1985; Wilsson & Oskarsson, 1985). However, the title compound differs from these ‘chain’ and ‘stair’ frameworks, forming a net-like layer constructed by edge-sharing of  $-(\text{CuBr})-$  alternating six-membered chair-patterned rings.

## Experimental

A mixture of cuprous bromide (0.14 g, 1 mmol), nicotinic acid (0.134 g, 1 mmol), NaOH (0.06 g, 1.5 mmol) and water (12 ml) was placed in a 23 ml Teflon reactor, which was heated to 433 K for 3 d and then cooled to room temperature at a rate of  $10 \text{ K h}^{-1}$ . The crystals obtained were washed with water and dried in air (yield 0.33 g, 90.2%).

### Crystal data

$[\text{CuBr}(\text{C}_6\text{H}_5\text{NO}_2)]$	$V = 741.03 (2) \text{ \AA}^3$
$M_r = 266.56$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 3.8738 (5) \text{ \AA}$	$\mu = 8.28 \text{ mm}^{-1}$
$b = 30.379 (4) \text{ \AA}$	$T = 273 (2) \text{ K}$
$c = 6.3055 (1) \text{ \AA}$	$0.24 \times 0.19 \times 0.15 \text{ mm}$
$\beta = 93.001 (1)^\circ$	

### Data collection

Bruker APEXII area-detector diffractometer	9966 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1604 independent reflections
$T_{\min} = 0.169$ , $T_{\max} = 0.295$	1314 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	2 restraints
$wR(F^2) = 0.092$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 1.05 \text{ e \AA}^{-3}$
1604 reflections	$\Delta\rho_{\text{min}} = -0.73 \text{ e \AA}^{-3}$
101 parameters	

**Table 1**

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

Br1—Cu1 <sup>i</sup>	2.4242 (8)	Br1—Cu1	2.4806 (8)
Br1—Cu1 <sup>ii</sup>	2.4757 (9)		
Cu1 <sup>i</sup> —Br1—Cu1 <sup>ii</sup>	110.02 (3)	Br1 <sup>iii</sup> —Cu1—Br1 <sup>iv</sup>	112.26 (3)
Cu1 <sup>i</sup> —Br1—Cu1	116.48 (3)	N1—Cu1—Br1	102.93 (10)
Cu1 <sup>ii</sup> —Br1—Cu1	102.81 (3)	Br1 <sup>iii</sup> —Cu1—Br1	118.84 (3)
N1—Cu1—Br1 <sup>iii</sup>	110.51 (10)	Br1 <sup>iv</sup> —Cu1—Br1	102.81 (3)
N1—Cu1—Br1 <sup>iv</sup>	108.64 (11)		

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

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 $\cdots$ Br1 <sup>v</sup>	0.93	2.87	3.716 (4)	152
O2—H2 $\cdots$ O1 <sup>vi</sup>	0.82	1.82	2.620 (5)	166

Symmetry codes: (v)  $x - 1, y, z + 1$ ; (vi)  $-x + 2, -y, -z$ .

H atoms were placed at calculated positions and were treated as riding on their parent atoms, with  $C-H = 0.93 \text{ \AA}$  and  $O-H = 0.82 \text{ \AA}$ , and with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$  and  $1.5U_{\text{eq}}(\text{O})$ .

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The authors are grateful to the Natural Science Foundation of Zhejiang Province (grant No. Y407081) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3010). Services for accessing these data are described at the back of the journal.

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