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A polymeric ladder complex: *catena*-poly[[[μ-4,4′-bipyridyl-bis[aqua-(*p*-aminobenzoato)copper(II)]]-di-μ-4,4′-bipyridyl] dinitrate tetrahydrate]

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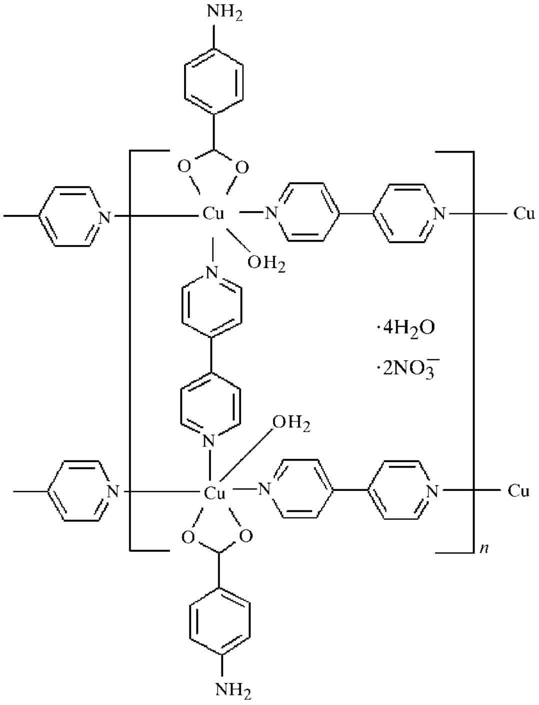
The title polymeric ladder complex, $\{[Cu_2(C_7H_6NO_2)_2(C_{10}H_8N_2)_3(H_2O)_2](NO_3)_2\cdot 4H_2O\}_n$, has been synthesized and spectroscopically characterized. The polymeric nature of the compound involves two non-equivalent 4,4′-bipyridyl ligands acting as almost orthogonal bridges joining the metal coordination Jahn–Teller-distorted octahedra, and forming ladders packed under the influence of hydrogen bonds involving the uncoordinated amino group of the *p*-aminobenzoate ligand, the NO_3^- anion and the water molecules.

Comment

The application of metal atoms as key elements in the self-assembly of arrays has emerged as an area of great interest over the past a few years (Fujita, 1998; Leininger *et al.*, 2000). A series of one-, two- and three-dimensional frameworks with novel topologies and potential properties has been obtained by binding metal ions of specific coordination geometry with rigid or flexible bridging ligands, such as 4,4′-bipyridine (Tong *et al.*, 2000; Lu *et al.*, 1998; Yaghi *et al.*, 1997), 1,3,5-benzenetricarboxylic acid (Plater *et al.*, 1999), pyrazine (Carlucci *et al.*, 1995), carboxyl-4-pyridine (MacGillivray *et al.*, 1998), terephthalate (Lo *et al.*, 2000), 1,2-bis(4-pyridyl)ethylene (Carlucci *et al.*, 1999*a*; Jung *et al.*, 1998), 1,4-bis(4-pyridyl)-butadiyne (Blake *et al.*, 1997), 1,2-bis(4-pyridyl)ethane (Carlucci *et al.*, 2000), 1,2-bis(4-pyridyl)ethyne (Carlucci *et al.*, 1999*b*), 3,6-bis(pyridin-3-yl)-1,2,4,5-tetrazine (Withersby *et al.*, 1999), *N*,*N*′-*p*-phenylenedimethylenebis(pyridin-4-one) (Goodgame *et al.*, 1995) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (Fujita *et al.*, 1998). Although many of these complex structures were obtained by chance to a certain extent, many polymers with specifically designed topologies have also been documented (Lehn & Rigault, 1998; Fujita *et al.*, 1995; Noro *et al.*, 2000). Recently, a systematic attempt has been made to determine the relationship between the molar ratio and the type of metal ions and ligands. The main focus of interest is on their remarkable structures and the self-assembly processes which brought them about (Beissel *et al.*, 1996).

Recently, we have undertaken a series of investigations into metal-directed self-assembly, with the principal aim of obtaining supramolecular compounds or ordered coordination polymers. From this, a rigid organic ligand, *p*-aminobenzoate, has been chosen as a building block to react with transition metal ions, and a series of coordination polymers with different topological structures have been generated. We report here the title polymeric ladder complex, (I), where the amino group of the *p*-aminobenzoate is uncoordinated.



(I)

The present X-ray crystal structure analysis indicates that complex (I) is made up of a molecular ladder formed by the metal complex, nitrate anions and lattice water molecules. As illustrated in Fig. 1, the coordination geometry around each Cu^{II} atom is Jahn–Teller-distorted octahedral, where atoms O1*W* and O1, from an aqua ligand and the carboxyl group of the *p*-aminobenzoate, respectively, occupy the axial positions, and atom O2 from the carboxyl group of the *p*-aminobenzoate, atom N1 from one 4,4′-bipyridyl (4,4′-bipy) moiety, and atoms N2 and N3*A* from two different 4,4′-bipy ligands comprise the equatorial plane. Selected bond distances and angles are given in Table 1.

It is noted that *p*-aminobenzoate acts as a bidentate chelating ligand in (I) (coordinated *via* the anionic carboxylate group), forming the lateral arm of the molecular ladders, with the amino group uncoordinated. Two 4,4′-bipy ligands and one *p*-aminobenzoate group form a T-shaped unit, producing a molecular ladder which extends along the whole crystal

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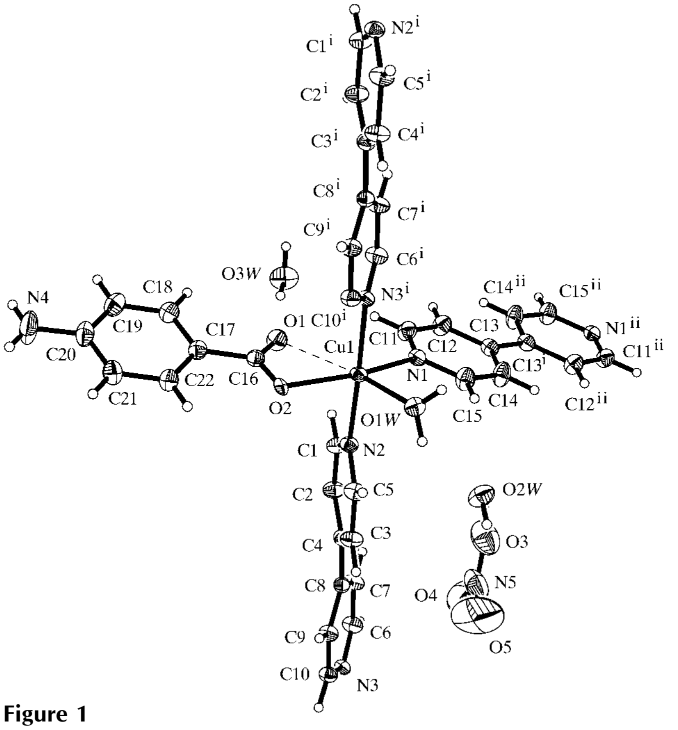

Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 2 - y, 1 - z$.]

through the μ_2-4,4′-bipy bridge (Fig. 2). The dihedral angle between the two pyridyl rings of the 4,4′-bipy ligand along the rail of the ladder is 27.5 (1)°, and that between the pyridyl ring of the 4,4′-bipy on the rung and the phenyl ring of the *p*-aminobenzoate is 16.9 (1)°. It is notable that the lateral arms of each molecular ladder are threaded into the $[Cu_4(4,4'\text{-bipy})_4]$ squares of adjacent molecular ladders, and each $[Cu_4(4,4'\text{-bipy})_4]$ square includes two aromatic rings belonging to two *p*-aminobenzoate groups of adjacent molecular ladders, which propagate in opposite directions and are parallel to each other. In addition, there are hydrogen-bonding interactions between the amino H atom of the *p*-aminobenzoate and an O atom of one nitrate anion (Table 2).

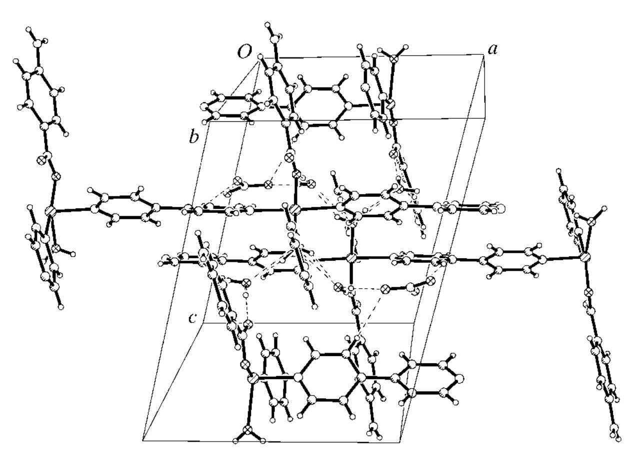

Figure 2
A perspective view of the crystal packing of (I). The hydrogen-bond contacts are shown as dashed lines.

This structural pattern is similar to that recently reported by Chen and co-workers (Tong *et al.*, 2000), who used *p*-hydroxybenzoate anions as building blocks that acted as the corresponding arms. In that case, the coordination geometry of the Cu^{II} atoms is also described as distorted octahedral, where two O atoms from an asymmetrically chelating carboxyl group of a *p*-hydroxybenzoate anion have analogous M—O lengths [Cu—O = 1.992 (2) and 2.466 (3) Å] to those in (I). Moreover, the hydroxyl group of the *p*-hydroxybenzoate anion is also uncoordinated, but is involved in different hydrogen-bonding interactions, namely with one O atom of a nitrate anion, compared with the amino group in (I).

Experimental

To a stirred solution of $Cu(NO_3)_2\cdot 4H_2O$ (0.260 g, 1.0 mmol) in methanol (10 ml), 4,4′-bipy (0.156 g, 1.0 mmol) and sodium *p*-aminobenzoate (0.157 g, 1.0 mmol) in methanol (15 ml) were added. The mixture was refluxed for 2 h and the precipitate was filtered off and dried *in vacuo* (yield: 81%). Analysis calculated for $C_{22}H_{24}CuN_5O_8$: C 47.57, H 4.32, N 12.61; found: C 47.52, H 4.22, N 12.69%. Spectroscopic analysis, IR (KBr, diffuse reflectance, ν, cm^{-1}): 3386, 1686, 1610, 1540, 1018.

Crystal data

$[Cu_2(C_7H_6NO_2)_2(C_{10}H_8N_2)_3(H_2O)_2](NO_3)_2\cdot 4H_2O$
$M_r = 1100.00$
Monoclinic, $P2_1/c$
$a = 11.102$ (2) Å
$b = 15.478$ (3) Å
$c = 14.493$ (3) Å
$\beta = 104.75$ (1)°
$V = 2408.4$ (8) Å^3
$Z = 2$
$D_x = 1.517$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6531 reflections
$\theta = 2.5$–27.1°
$\mu = 0.96$ mm^{-1}
$T = 293$ (2) K
Prism, dark blue
0.40 × 0.25 × 0.25 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.749$, $T_{max} = 0.786$
12 286 measured reflections
4245 independent reflections
3623 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$
$h = -13 \rightarrow 12$
$k = -11 \rightarrow 18$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.112$
$S = 1.08$
4245 reflections
344 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2 + 0.2627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

The H-atom coordinates of three water molecules were located using the *HYDROGEN* program (Nardelli, 1999). The positions of all other H atoms were fixed geometrically, with distances as follows:

Table 1
Selected geometric parameters (Å, °).

Cu1—O2′	1.98 (2)	Cu1—N3$^{\rm i}$	2.07 (4)
Cu1—N3′$^{\rm i}$	2.00 (3)	Cu1—O1*W*	2.2776 (18)
Cu1—N2	2.016 (2)	N3—Cu1$^{\rm ii}$	2.07 (3)
Cu1—N1	2.047 (2)	N3′—Cu1$^{\rm ii}$	2.00 (3)
Cu1—O2	2.05 (3)		
O2′—Cu1—N3′$^{\rm i}$	84.0 (15)	N2—Cu1—N3$^{\rm i}$	177.6 (14)
O2′—Cu1—N2	90.9 (8)	N1—Cu1—N3$^{\rm i}$	92.4 (9)
N3′$^{\rm i}$—Cu1—N2	174.9 (9)	O2—Cu1—N3$^{\rm i}$	93.5 (10)
O2′—Cu1—N1	165.9 (7)	O2′—Cu1—O1*W*	97.6 (7)
N3′$^{\rm i}$—Cu1—N1	97.0 (8)	N3′$^{\rm i}$—Cu1—O1*W*	84.6 (9)
N2—Cu1—N1	88.00 (8)	N2—Cu1—O1*W*	95.87 (8)
N3′$^{\rm i}$—Cu1—O2	89.7 (13)	N1—Cu1—O1*W*	96.51 (8)
N2—Cu1—O2	85.3 (7)	O2—Cu1—O1*W*	104.6 (10)
N1—Cu1—O2	158.4 (10)	N3$^{\rm i}$—Cu1—O1*W*	86.4 (14)
O2′—Cu1—N3$^{\rm i}$	88.1 (13)		

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*B*···O3$^{\rm i}$	0.86	2.41	3.255 (5)	166
N4—H4*B*···O4$^{\rm i}$	0.86	2.53	3.240 (7)	141
O1*W*—H1*WB*···O2*W*	0.85	1.97	2.702 (3)	143
O1*W*—H1*WA*···O3*W*$^{\rm ii}$	0.85	1.95	2.755 (3)	158
O2*W*—H2*WA*···O3	0.85	1.97	2.817 (4)	173
O2*W*—H2*WB*···O2$^{\rm iii}$	0.85	2.09	2.89 (4)	155
O3*W*—H3*WB*···O4$^{\rm iv}$	0.85	2.16	2.881 (5)	143

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$.

C—H = 0.96 Å, N—H = 0.86 Å and O—H = 0.85 Å. One O atom of the *p*-aminobenzoate (O2 and O2′) and one N atom of the 4,4′-bipy (N3 and N3′) were found to be disordered over two sites, with occupancies of 0.60 (9) and 0.40 (9).

Data collection: *SMART* (Bruker, 2000; cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); 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: NA1636). Services for accessing these data are described at the back of the journal.

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