Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

An alternating copolymer containing trigonal planar homocoordinated copper(I) ions: *catena*-poly[[[bis[μ-(*E*)-1,2-bis(1-ethyl-1*H*-benzimidazol-2-yl)ethene-$\kappa^2N^3:N^{3'}$]dicopper(I)]-μ-(*E*)-1,2-bis(1-ethyl-1*H*-benzimidazol-2-yl)ethene-$\kappa^2N^3:N^{3'}$] bis(perchlorate) acetonitrile disolvate]

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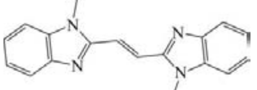
Received 4 October 2007
Accepted 23 January 2008
Online 19 April 2008

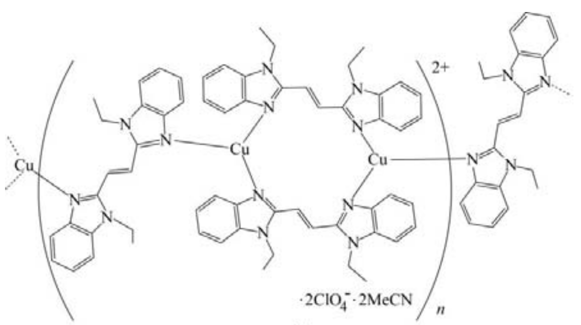
The structure of the title salt, $\{[Cu_2(C_{20}H_{20}N_4)_3](ClO_4)_2\cdot 2CH_3CN\}_n$, consists of linear $[Cu^I_2L_3]$ polymer chains [L is (*E*)-1,2-bis(1-ethyl-1*H*-benzimidazol-2-yl)ethene], which extend along the c cell direction, interspersed with disordered perchlorate ions and acetonitrile solvent molecules. In a given chain, each Cu^I ion exhibits distorted trigonal planar coordination to three L ligands; two of these are linked to adjacent Cu^I ions to form dimeric units containing 14-membered rings that adopt a twisted-loop configuration, stabilized by π–π interactions between the ethene fragments of the two ligands. The dimeric units exhibit diad symmetry (twofold axis sites in $I2/a$) and are linked by a third, centrosymmetric, S-shaped L ligand (inversion centers in $I2/a$) to form the copolymer chain. When viewed along the b cell direction, the 14-membered rings appear as vacant ellipses that form channels parallel to the b axis. The walls of the channels are formed by the benzimidazole fragments of the dimeric units. This study of a novel alternating copolymer containing homocoordinated Cu^I ions demonstrates further the usefulness of bis(benzimidazoles) as versatile bidentate ligands.

Comment

Our long-standing interest in the chemistry of bis(imidazoles), bis(benzimidazoles) and their complexes with metal ions has demonstrated the usefulness of these species as geometrically constraining ligands (Stibrany *et al.*, 2004), proton sponges (Stibrany *et al.*, 2002), polymerization catalysts (Stibrany *et al.*, 2003; Stibrany & Kacker, 2002) and agents to study electron transfer (Knapp *et al.*, 1990; Xie *et al.*, 1999). An effort to prepare a coordination complex of Cu^{II} and L, where L is (*E*)-1,2-bis(1-ethyl-1*H*-benzimidazol-2-yl)ethene, yielded instead, *via* a redox reaction, an amorphous mass and a few low-quality crystals of the title salt, $[Cu^I_2L_3](ClO_4)_2\cdot 2CH_3CN$, (I). High-quality crystals, one of which was used for the structure determination reported here, were obtained in good yield by the direct reaction of $Cu^I(ClO_4)$ and L in acetonitrile.



L



(I)

The structure of (I) consists of $Cu^I{}_2L_2$ dimeric units bridged by ligands L to form linear polymeric chains interspersed with disordered perchlorate counter-ions and acetonitrile solvent molecules. In addition to a perchlorate ion and an acetonitrile solvent molecule, the asymmetric unit (Fig. 1) contains a Cu^I ion bonded to the imine N atoms (N13 and N33) of two L ligands. Only half of the ligand containing N33 is unique, and the cation portion of the asymmetric unit can be viewed as

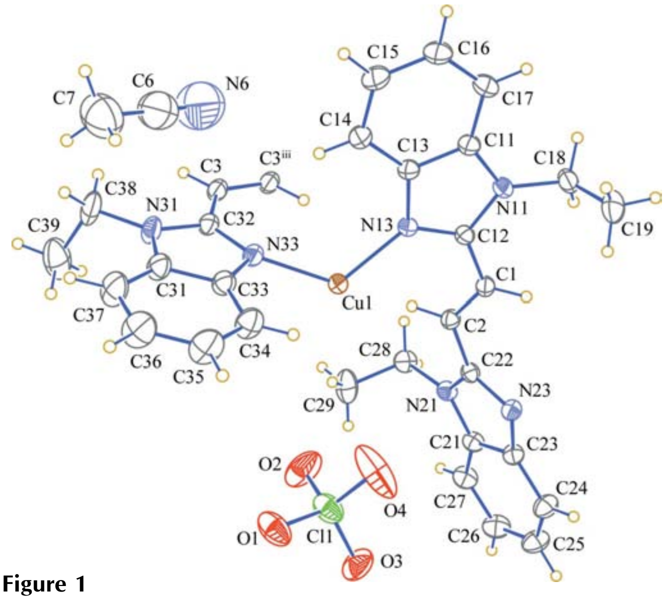


Figure 1
A view of the asymmetric unit, showing 30% probability displacement ellipsoids and the atom-numbering scheme. Only the major component of the disordered perchlorate ion is shown. [Symmetry code: (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$.]

containing a Cu$^{\rm I}$ ion and three half-ligands (ethylbenzimidazole fragments containing one ethene atom), which we designate as etbzim1, etbzim2 and etbzim3 for the fragments containing atoms N13, N23 and N33, respectively.

In forming the polymer chain, both ligands utilize crystallographic symmetry. Ligands *L* derived from etbzim3 are centrosymmetrically related (4*d* sites in *I*2/*a*), with the inversion centers located at the mid-points of the ethene fragments (atom C3 and its symmetry-related partner in Fig. 1), while ligands generated from etbzim1 and etbzim2 exhibit twofold symmetry (4*e* sites in space group *I*2/*a*). The result is the alternating copolymer chain sketched in the scheme and shown in Fig. 2. Partial removal of the benzimidazole fragments, as in Fig. 3, helps to clarify the connectivity and the linkage along a given chain. Thus, etbzim1 and etbzim2 are linked to adjacent Cu atoms by two S-shaped *L* ligands in a twisted-loop arrangement to yield dimeric units. The two symmetry-related Cu ions in the dimeric units are part of 14-membered rings, which are stabilized by π–π interactions (Janiak, 2000) between the ethene groups, as indicated by the C1$\cdots$C1$'$ and C2$\cdots$C2$'$ distances of 3.399 (3) and 3.351 (3) Å, respectively. A third S-shaped bidentate ligand links the dimers and completes the alternating copolymer cation chain.

At the unique Cu$^{\rm I}$ ion (Fig. 2), a distorted trigonal planar coordination geometry is formed (Table 1), in which the Cu—N33 bond length to etbzim3 is substantially longer than the corresponding Cu—N(imine) bonds to etbzim1 and etbzim2, while the N13—Cu—N23 angle, involving etbzim1 and etbzim2, is substantially larger than those involving etbzim3. Excluding the methyl group atoms and the methylene H atoms, the atoms of a given benzimidazole fragment are essentially coplanar, as expected. As indicated by the metric data in Table 2, the geometric parameters of the three ligands compare well with one another and with those of the unique centrosymmetric benzimidazole fragments in two structures that contain the free *L* ligand (*La*: Stibrany *et al.*, 2005; *Lb*: Stibrany & Potenza, 2006).

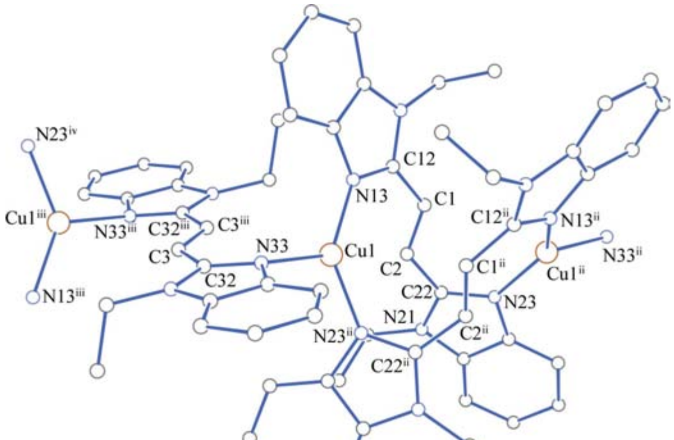


Figure 2
The repeat unit of the cationic alternating copolymer chain in (I). H atoms have been omitted for clarity. [Symmetry codes: (ii) $-x+\frac{1}{2}, y, -z+1$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.]

In the crystal structure (Fig. 4), the polymer strands extend along the *c* cell direction and form layers centered about the planes $x = \frac{1}{4}$ and $\frac{3}{4}$. With crystallographic symmetry taken into account, the repeat unit in the solid state is seen to consist of two dimers and two single-ligand linkers. In Fig. 4, the S-shaped centrosymmetric ligands are clearly seen, while the 14-membered rings, viewed along their diad axes, appear as jagged ellipses. The ellipses outline vacant channels along the *b* cell direction, each with a cross-sectional area of approximately 14 Å^2, with the major and minor axes of the ellipses taken as the Cu$\cdots$Cu$'$ and ethene–ethene π overlap distances, respectively. The perchlorate counter-ions are centered about the planes $x = 0$ and $\frac{1}{2}$, midway between the polymer strands. Along these planes, the perchlorate anions alternate with benzimidazole fragments from bzim3, which extend from the polymer chains along the *a* cell direction. In contrast, the

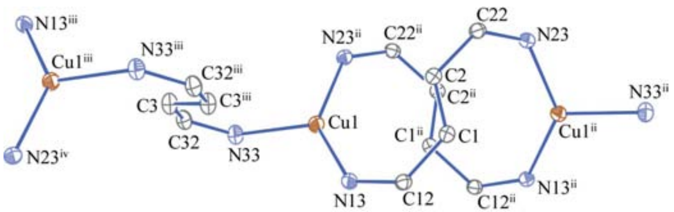


Figure 3
The repeat unit showing only the connectivity of the Cu$^{\rm I}$ ions. The view is approximately normal to the twofold axis of the 14-membered ring. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (ii) $-x+\frac{1}{2}, y, -z+1$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.]

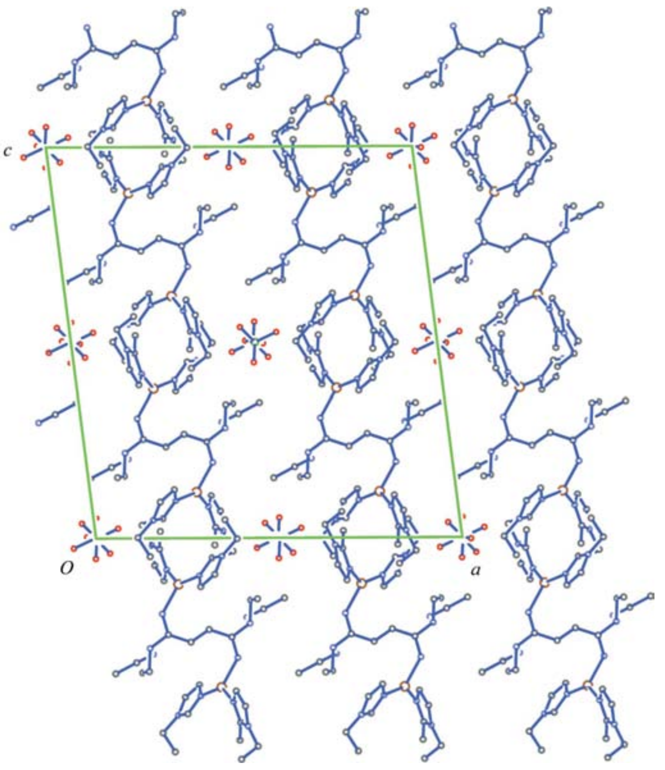


Figure 4
A projection of the structure along the *b* axis constructed using the repeat unit in Fig. 3, augmented by the ethyl groups of the ligand.

benzimidazole fragments bzim1 and bzim2 extend along the *b* cell direction and form the walls of the channels noted above. The perchlorate ions are stabilized somewhat in the crystal structure by several weak C—H···O hydrogen bonds with the benzimidazole fragments. The acetonitrile solvent molecules are associated closely with a given chain (Fig. 4), with the cyano group located near atoms N31, C31, and C32 of etbzim3.

Knowledge of the structure is helpful in suggesting a possible path for the formation and termination of the copolymer chains. In acetonitrile, $CuClO_4$ forms $Cu(NCCH_3)_4^+$ ions. Stepwise replacement of acetonitrile by the stronger imine bases of the bulky *L* ligand could produce the copolymer chains, which may be terminated at Cu by having one or two acetonitrile ligands complete the coordination of a terminal dimer. In support of this possibility, we note that a structure containing trigonal $Cu^I(bbil)(NCCH_3)$ and tetrahedral $Cu^I(bbil)(NCCH_3)_2$ cations in the same crystal, where bbil is a bis(benzimidazole) ligand similar to *L*, has recently been reported (Stibrany & Potenza, 2006).

Structurally characterized polymeric complexes containing trigonally coordinated copper(I) ions are rare. We are aware of four such systems, one with alternating trigonal $CuCl_3$ and tetrahedral $CuCl_4$ units (Andersson & Jagner, 1988), one with N, S and Cl coordination to Cu^I (Devillanova *et al.*, 1998), and two organometallic complexes with trigonal coordination of Cu^I by an olefin and two chloride ions (Baenziger *et al.*, 1964; Goreshnik *et al.*, 2005). In the four complexes noted above, the Cu^I—Cl and Cu^I—S linkages formed with the relatively soft Cl and S ligands range from 2.215 (2) to 2.288 (2) Å, all substantially larger than the Cu^I—N distances in the title complex, which are derived from the hard (stronger) imine bases in the benzimidazole fragments. The lone Cu—N(imine) distance of 1.929 Å in one of the complexes above (Devillanova *et al.*, 1998) compares favorably with those in the title complex.

Lastly, we note that, owing to the steric bulk and limited flexibility of ligands such as *L*, it would seem possible to prepare a variety of polymers similar to that of the title complex with Cu^I and with other metals, such as Ag^I, known to accommodate trigonal coordination easily.

Table 1
Selected geometric parameters (Å, °).

Cu1—N13	1.9473 (14)	Cu1—N33	2.0206 (16)
Cu1—N23^i	1.9642 (14)		
N13—Cu1—N23^i	135.49 (6)	N23—Cu1—N33^i	104.87 (6)
N13—Cu1—N33	119.57 (6)		

Symmetry code: (i) $-x+\frac{1}{2}, y, -z+1$.

Table 2
Comparison of selected bond lengths (Å) in five centrosymmetric ligands with structure *L*: etbzim1, etbzim2, etbzim3, and *La* and *Lb* (see *Comment* for references to *La* and *Lb*).

Bond	etbzim1	etbzim2	etbzim3	*La*	*Lb*
C1—C2	1.327 (2)	1.327 (2)	1.324 (4)	1.332 (4)	1.323 (5)
C1—C12	1.445 (2)	1.448 (2)	1.445 (3)	1.440 (3)	1.449 (3)
N11—C12	1.358 (2)	1.355 (2)	1.366 (2)	1.376 (3)	1.371 (3)
N13—C12	1.333 (2)	1.336 (2)	1.330 (2)	1.321 (3)	1.325 (3)
N11—C11	1.373 (2)	1.376 (2)	1.366 (2)	1.381 (3)	1.389 (3)
N13—C13	1.393 (2)	1.389 (2)	1.383 (2)	1.377 (3)	1.384 (3)
C11—C13	1.393 (2)	1.393 (3)	1.393 (3)	1.404 (3)	1.387 (3)
C11—C17	1.396 (3)	1.392 (2)	1.393 (3)	1.395 (3)	1.395 (3)
C13—C14	1.391 (3)	1.393 (3)	1.390 (3)	1.391 (3)	1.396 (3)
C14—C15	1.382 (3)	1.373 (3)	1.370 (3)	1.372 (4)	1.374 (3)
C16—C17	1.370 (3)	1.375 (3)	1.379 (4)	1.368 (4)	1.373 (4)
C15—C16	1.394 (3)	1.390 (3)	1.388 (4)	1.391 (4)	1.392 (4)

Experimental

A colorless solution of $[Cu(CH_3CN)_4](ClO_4)$ (50 mg, 0.15 mmol) was prepared in acetonitrile (10 ml) and methanol (1 ml). Addition of (*E*)-1,2-bis(1-ethylbenzimidazol-2-yl)ethene (73 mg, 0.22 mmol) yielded a green solution, which was sealed in a jar containing diethyl ether to allow slow vapor diffusion. Orange crystalline prisms formed over a period of several days. The crystals exhibited yellow–green dichroism (yield 62 mg, 59.9%).

Crystal data

$[Cu_2(C_{20}H_{20}N_4)_3](ClO_4)_2\cdot 2C_2H_3N$
$M_r = 678.64$
Monoclinic, *I*2/*a*
$a = 21.834$ (6) Å
$b = 12.948$ (4) Å
$c = 23.502$ (10) Å
$\beta = 97.039$ (4)°
$V = 6594$ (4) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.79$ mm^{-1}
$T = 297$ (1) K
0.47 × 0.25 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.757$, $T_{max} = 1.00$ (expected range = 0.672–0.888)
30631 measured reflections
6478 independent reflections
5414 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.096$
$S = 1.00$
6478 reflections
469 parameters
26 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

H atoms were positioned geometrically and were refined using a riding model, with C—H distances of 0.93–0.97 Å and U_{iso}(H) values of $1.5U_{eq}$(C) for the methyl H atoms and $1.2U_{eq}$(C) for all other H atoms. The perchlorate group exhibited large displacement parameters and was modeled assuming a three-site disorder about a threefold axis; the occupancy factors for the three components were allowed to vary and their summation was set to 1. A total of 26 restraints were employed to ensure convergence of this model.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Version 6.10; Sheldrick, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3116). Services for accessing these data are described at the back of the journal.

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