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## Key indicators

Single-crystal X-ray study  
 $T = 238$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.012$  Å  
Disorder in solvent or counterion  
 $R$  factor = 0.051  
 $wR$  factor = 0.149  
Data-to-parameter ratio = 9.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A chiral facially coordinated  $\text{Cu}^{\text{II}}$  complex derived from a tridentate bis(benzimidazole) ligand: bis[(*S,S*)-1,2-dimethoxy-1,2-bis(1-methylbenzimidazol-2-yl)ethane]copper(II) bis(tetrafluoroborate) acetonitrile disolvate

Crystals of the chiral title salt,  $[\text{Cu}(\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_2)_2](\text{BF}_4)_2 \cdot 2\text{C}_2\text{H}_3\text{N}$ , contain  $\text{Cu}(\text{L}2)_2^{2+}$  cations separated by disordered tetrafluoroborate anions and by acetonitrile solvent molecules. The ligands *L2*, (*S,S*)-1,2-dimethoxy-1,2-bis(1-methylbenzimidazol-2-yl)ethane, coordinate Cu ions facially to yield a distorted and tetragonally elongated octahedral coordination geometry. Coordination affords V- or butterfly-shaped ligands, cations with the overall shape of the letter X, and seven-membered chelate rings which adopt distorted boat conformations. In the crystal structure, the cations form layers parallel to (001), interspersed with layers containing both tetrafluoroborate anions and acetonitrile molecules. Ligands within a given cation, anions and solvate molecules, and cations and anions, are linked by an extensive  $\text{C}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \text{F}$  hydrogen-bonding network. Additionally, cations within a given layer are linked by interionic head-to-tail  $\pi-\pi$  interactions between two benzimidazole fragments along the *a* cell direction and by edge-over-edge  $\text{C}-\text{H} \cdots \pi$  overlap between the remaining two benzimidazole fragments along the *b* cell direction.

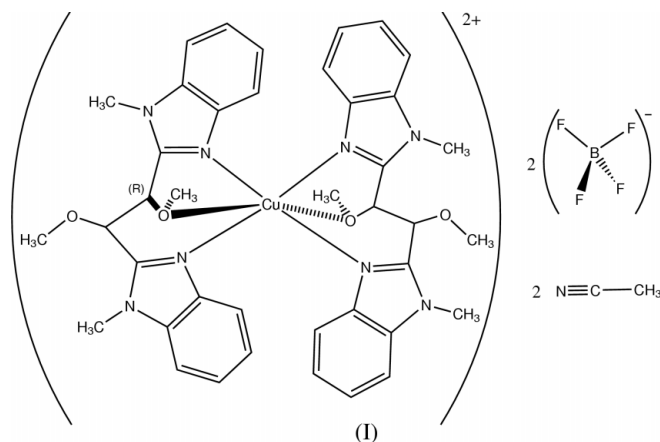
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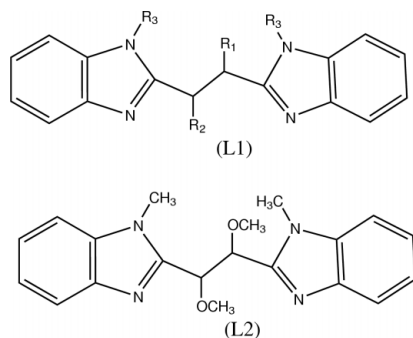
## Comment

For some time, we have been interested in utilizing compounds containing bis(imidazole) or bis(benzimidazole) species bridged by alkyl or aryl groups as geometrically constraining ligands (Stibrany *et al.*, 2004), as agents to study electron self-exchange (Knapp *et al.*, 1990) or as polymerization catalysts (Patil *et al.*, 2003; Stibrany, Schulz *et al.*, 2003).

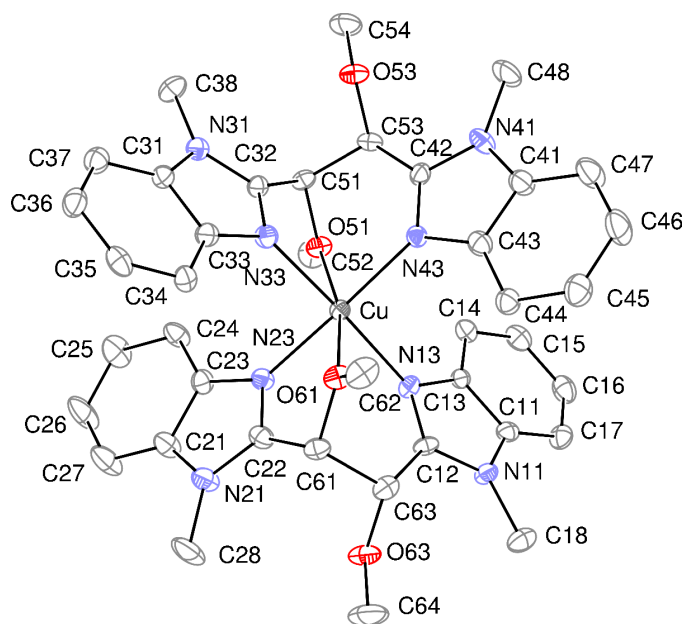


Ethane-bridged bis(benzimidazole) compounds, such as *L1*, can behave as bidentate or tridentate ligands depending on whether  $R_1$  or  $R_2$  can coordinate metal ions. Furthermore, single substituents at  $R_1$  and  $R_2$  create stereogenic centers,

which suggests the possibility of using these species in applications for which chirality is important. This class of ligands is particularly versatile in terms of the coordination geometries they afford when complexed to metal ions. With divalent copper, for example, coordination geometries including square-planar  $[\text{Cu}(\text{L}1)_2]^{2+}$ , with  $R_1 = R_2 = R_3 = \text{H}$ ; van Albada *et al.*, 1999], tetrahedral  $[\text{Cu}(\text{L}1)\text{Cl}_2]$  and  $[\text{Cu}(\text{L}1)\text{Br}_2]$ , with  $R_1 = R_2 = \text{H}$ ,  $R_3 = 3,5\text{-dimethoxybenzyl}$  (Broughton *et al.*, 1998);  $[\text{Cu}(\text{L}1)\text{Br}_2]$ , with  $R_1 = R_2 = R_3 = \text{H}$  (van Albada *et al.*, 2000)] and tetragonal  $4 + 2$   $[\text{Cu}(\text{L}1)_2]^{2+}$ , with  $R_1 = \text{OH}$ ,  $R_2 = R_3 = \text{H}$ , and two related structures in which  $R_2$  and  $R_3$  are varied (Isele *et al.*, 2002)] have been reported.

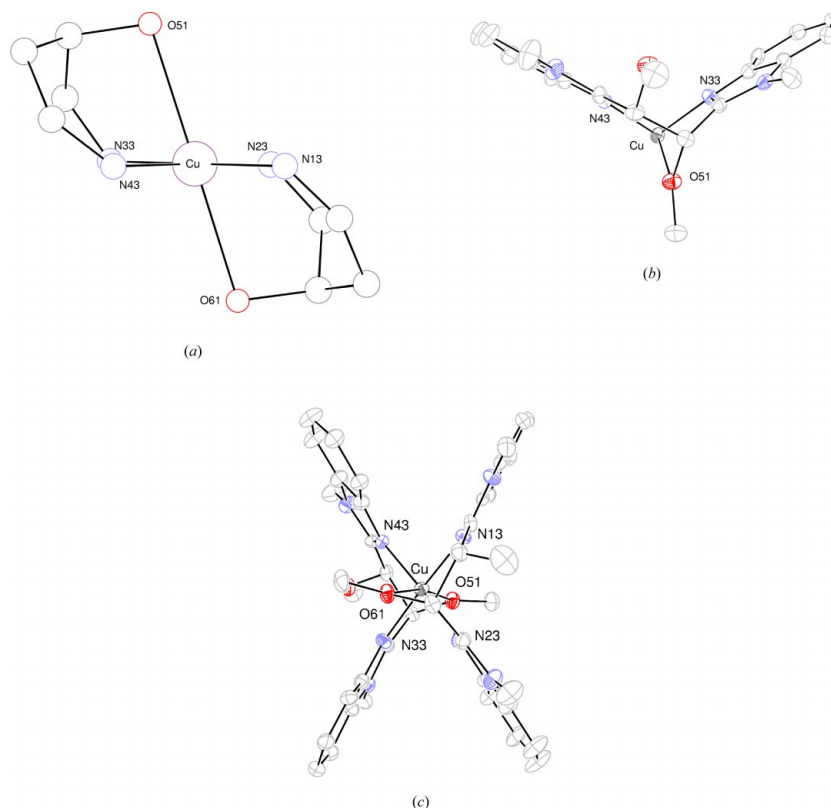


Crystals of the title salt, (I), contain  $\text{Cu}(\text{L}2)_2^{2+}$  cations (Fig. 1) separated by disordered tetrafluoroborate anions and by acetonitrile solvent molecules. Each cation is coordinated

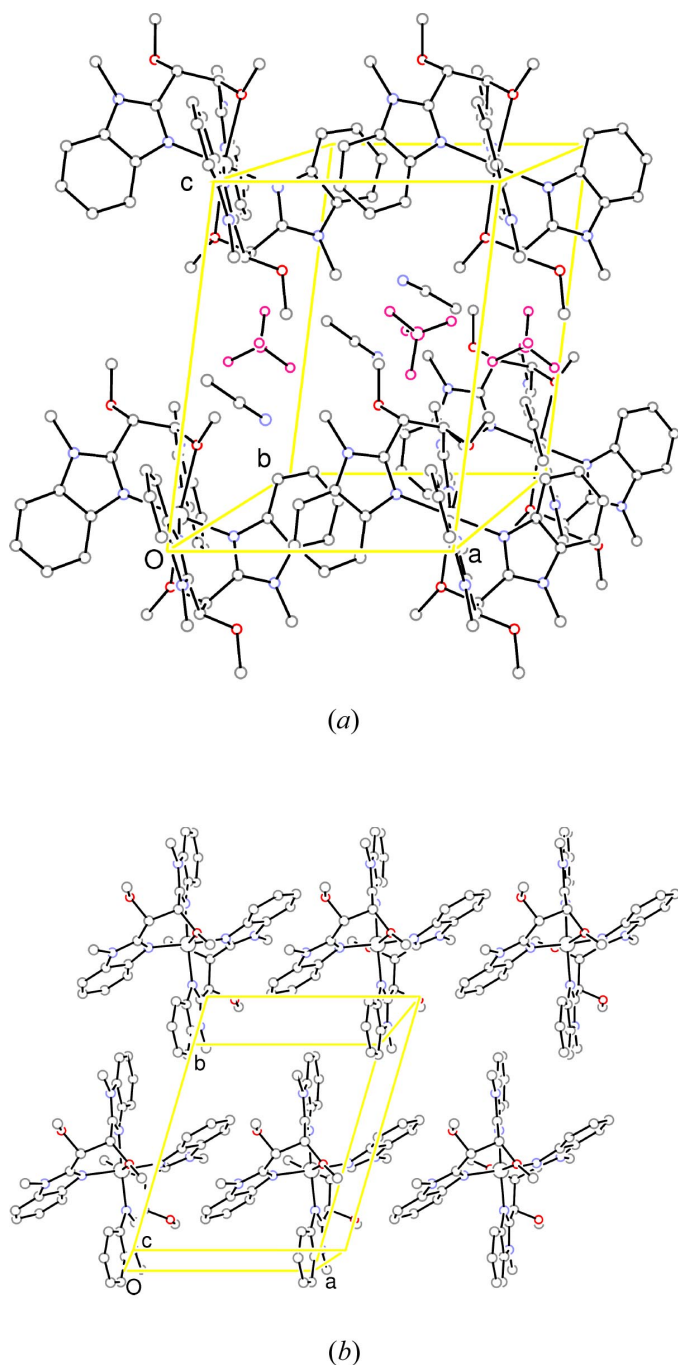


**Figure 1**  
The structure of the cation of (I), showing 25% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

facially by the two imine N atoms and by an ether O atom from each of two ligands of formula *L2* to yield a distorted tetragonal  $4 + 2$  complex in which the N atoms form a nearly square-planar base (Table 1). The axially coordinated O



**Figure 2**  
(a) View of a portion of a cation showing the seven-membered chelate rings and the orientation of the axially coordinated O atoms. (b) View of one of the ligands *L2* chelated to a copper ion. (c) View of a cation in profile. H atoms have been omitted for clarity.



**Figure 3**  
(a) View, approximately along the [010] direction, of the structure. Half of the disordered F atoms have been omitted for clarity. (b) View, along the [001] direction, of a cation layer.

atoms, O51 and O61, are skewed towards the ligand to which they are attached, resulting in an O51–Cu–O61 angle, 169.55 (15)°, which deviates substantially from the ideal value of 180°. Furthermore, the O51–Cu–O61 plane is displaced significantly from the normal to the CuN<sub>4</sub> plane (Fig. 2a). Facial ligation results in three chelate rings per ligand, one five-, one six-, and one seven-membered. The seven-membered rings exhibit distorted boat conformations (Fig. 2a), closely related to one of the four symmetric archetypal forms of seven-membered rings (Allen *et al.*, 1994). Complexation

causes ligands in the present structure to adopt a V- or butterfly-shaped conformation (Fig. 2b), in contrast to the free ligand, which exhibits a stepped conformation in the solid state (Stibrany, Schugar *et al.*, 2003). The ligands are further disposed to give the cations an X-shape when the planar benzimidazole fragments are viewed approximately in profile (Fig. 2c). Similar geometric features have been observed in related bis(benzimidazole)copper(II) complexes (Isele *et al.*, 2002; Broughton *et al.*, 1998). Lastly, we note that ligands in the cations are linked by three weak C–H...O hydrogen bonds between the ether O atoms and the H atoms of the benzene rings from three of the four benzimidazole groups (Table 2).

In the crystal structure, the cations form layers parallel to (001), interspersed with layers containing both tetrafluoroborate anions and acetonitrile molecules (Fig. 3a). Within a given layer (Fig. 3b), the cations exhibit substantial head-to-tail  $\pi$ - $\pi$  overlap between two benzimidazole fragments along the *a* cell direction, as suggested by 14 inter-ring C...C and C...N distances which range from 3.436 (9) to 3.696 (9) Å, all smaller than the value of 3.8 Å, the generally accepted upper limit for face-to-face  $\pi$ -stacking (Janiak, 2000). In the *b* cell direction, the cations exhibit edge-over-edge  $\pi$  overlap, with seven inter-ring C(benzene)...C(benzene) distances ranging from 3.457 (12) to 3.775 (13) Å. The anions and solvent molecules are linked by three weak hydrogen bonds between the F atoms of the tetrafluoroborate groups and the methyl group H atoms of the acetonitrile solvent molecules. Cation and anion layers are linked by an extensive network of C–H...F hydrogen bonds involving the F atoms and the relatively acidic H atoms attached to the C atoms bonded to the ether O atoms, as well as the C atoms attached to the amine N atoms N21 and N31 (Table 2). These interionic hydrogen bonds augment the Coulombic interaction and serve to stabilize the structure further.

## Experimental

A pale-blue solution of 41.6 mg of Cu(BF<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.14 mmol) was prepared in 10 ml of acetonitrile and 2 ml of triethyl orthoformate. Addition of 100 mg of (*S,S*)-1,2-dimethoxy-1,2-bis(1-methylbenzimidazol-2-yl)ethane (0.28 mmol) yielded a green solution, from which purple crystalline prisms formed upon slow evaporation of the solvent. Because the crystals readily lost solvent, a crystal was removed from the mother liquor, glued to a glass fiber, and placed immediately in a stream of cold nitrogen. The crystalline product was collected by filtration and vacuum-dried to give a pale-purple powder (yield: 112 mg, 85.3%). IR (KBr pellet, cm<sup>-1</sup>): 3430 (*br*), 2954 (*w*), 1616 (*w*), 1501 (*m*), 1460 (*m*), 1337 (*m*), 1084 (*s*), 813 (*w*), 754 (*m*).

### Crystal data

[Cu(C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ·2C <sub>2</sub> H <sub>3</sub> N	Z = 1
<i>M<sub>r</sub></i> = 1020.10	<i>D<sub>x</sub></i> = 1.408 Mg m <sup>-3</sup>
Triclinic, <i>P</i> 1	Mo K $\alpha$ radiation
<i>a</i> = 9.2286 (5) Å	Cell parameters from 1009 reflections
<i>b</i> = 11.4896 (6) Å	$\theta$ = 2.8–19.9°
<i>c</i> = 12.0277 (7) Å	$\mu$ = 0.54 mm <sup>-1</sup>
$\alpha$ = 80.517 (4)°	<i>T</i> = 238 (1) K
$\beta$ = 82.803 (4)°	Prism, purple
$\gamma$ = 73.690 (4)°	0.29 × 0.22 × 0.04 mm
<i>V</i> = 1203.07 (11) Å <sup>3</sup>	

Data collection

Bruker SMART CCD area-detector diffractometer	6750 independent reflections
$\varphi$ and $\omega$ scans	5698 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.681$ , $T_{\text{max}} = 1.00$	$\theta_{\text{max}} = 25.1^\circ$
13054 measured reflections	$h = -11 \rightarrow 10$
	$k = -13 \rightarrow 13$
	$l = -11 \rightarrow 14$

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.093P)^2 + 0.5665P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{\AA}^{-3}$
6750 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$
697 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2484 Friedel pairs
	Flack parameter = 0.019 (17)

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu—N23	1.973 (6)	Cu—N13	2.032 (5)
Cu—N33	2.006 (6)	Cu—O51	2.520 (5)
Cu—N43	2.028 (6)	Cu—O61	2.483 (4)
N23—Cu—N33	87.8 (2)	N43—Cu—O61	106.24 (19)
N23—Cu—N43	177.4 (3)	N13—Cu—O61	81.39 (19)
N33—Cu—N43	90.3 (2)	N23—Cu—O51	99.9 (2)
N23—Cu—N13	89.7 (2)	N33—Cu—O51	73.9 (2)
N33—Cu—N13	177.4 (3)	N43—Cu—O51	81.15 (19)
N43—Cu—N13	92.2 (2)	N13—Cu—O51	106.05 (19)
N23—Cu—O61	72.4 (2)	O61—Cu—O51	169.55 (15)
N33—Cu—O61	98.4 (2)		

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C14—H14 $\cdots$ O51	0.93	2.56	3.392 (9)	149
C24—H24 $\cdots$ O51	0.93	2.55	3.311 (9)	140
C34—H34 $\cdots$ O61	0.93	2.51	3.291 (8)	142
C2—H2C $\cdots$ F13A <sup>i</sup>	0.96	2.25	3.189 (18)	166
C4—H4C $\cdots$ F24 <sup>ii</sup>	0.96	2.53	3.45 (3)	162
C4—H4C $\cdots$ F21A <sup>iii</sup>	0.96	2.52	3.16 (3)	124
C28—H28A $\cdots$ F23 <sup>iii</sup>	0.96	2.32	3.050 (15)	132
C38—H38C $\cdots$ F22A	0.96	2.37	3.303 (17)	163
C46—H46 $\cdots$ F24A <sup>iv</sup>	0.93	2.20	3.098 (15)	161
C51—H51 $\cdots$ F22	0.98	2.35	3.323 (13)	171
C51—H51 $\cdots$ F22A	0.98	2.54	3.516 (19)	174
C52—H52A $\cdots$ F14B	0.96	2.39	3.33 (2)	166
C53—H53 $\cdots$ F14A	0.98	2.34	3.31 (2)	171
C53—H53 $\cdots$ F14B	0.98	2.47	3.415 (19)	162
C54—H54C $\cdots$ F12B <sup>v</sup>	0.96	2.46	3.37 (2)	159
C61—H61 $\cdots$ F23 <sup>iii</sup>	0.98	2.26	3.197 (15)	159
C61—H61 $\cdots$ F23A <sup>iii</sup>	0.98	2.38	3.359 (15)	175
C62—H62A $\cdots$ F14B <sup>iii</sup>	0.96	2.49	3.252 (16)	137
C62—H62B $\cdots$ F22 <sup>iii</sup>	0.96	2.36	3.297 (16)	166
C62—H62B $\cdots$ F22A <sup>iii</sup>	0.96	2.50	3.453 (17)	172
C63—H63 $\cdots$ F12A <sup>iii</sup>	0.98	2.55	3.47 (2)	157
C64—H64B $\cdots$ F12A <sup>iii</sup>	0.96	2.42	3.12 (2)	130

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

Crystals of the title complex were prepared using enantiomerically pure *L2* and are, therefore, of necessity chiral, excluding the possibility that the space group is  $P\bar{1}$ . H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.98  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $1.2U_{\text{eq}}(\text{C})$  for all other H atoms. In contrast to the acetonitrile solvent molecules, both tetrafluoroborate groups were found to exhibit disorder and to have rather large displacement parameters for the F atoms [ $U_{\text{eq}} = 0.093(2)\text{--}0.32(3) \text{\AA}^2$ ], suggesting that they are held somewhat loosely in the crystal structure. One tetrafluoroborate group was modeled assuming a two-site disorder about a threefold axis and the other as two restrained  $\text{BF}_4$  units sharing a common B atom. Site-occupancy factors for all F atoms were set equal to 0.5.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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