

A structure with trigonally and tetrahedrally coordinated Cu^I cations: *rac*-(acetonitrile)-[2,2'-bis(1-propyl-1*H*-benzimidazol-2-yl)-biphenyl]copper(I) bis(acetonitrile)-[2,2'-bis(1-propyl-1*H*-benzimidazol-2-yl)-biphenyl]copper(I) bis(perchlorate)

Robert T. Stibrany and Joseph A. Potenza*

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, USA

Correspondence e-mail: potenza@rutchem.rutgers.edu

Key indicators

Single-crystal X-ray study
 $T = 100$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.051
 wR factor = 0.145
 Data-to-parameter ratio = 14.3

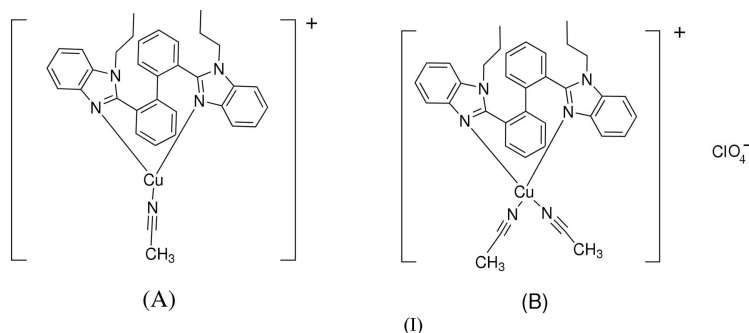
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

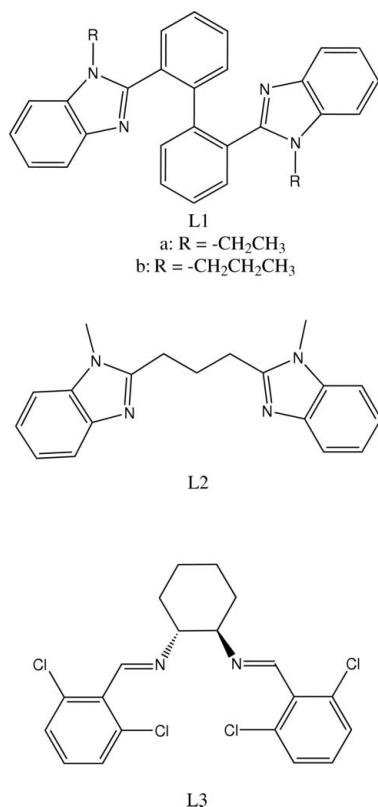
The asymmetric unit of the title salt, $[\text{Cu}(\text{C}_{32}\text{H}_{30}\text{N}_4)(\text{C}_2\text{H}_3\text{N})][\text{Cu}(\text{C}_{32}\text{H}_{30}\text{N}_4)(\text{C}_2\text{H}_3\text{N})_2](\text{ClO}_4)_2$, contains two perchlorate anions and two crystallographically distinct Cu^I complexes, *viz.* $[\text{Cu}(\text{L1b})(\text{acetonitrile})]^+$ (*A*) and $[\text{Cu}(\text{L1b})(\text{acetonitrile})_2]^+$ (*B*), where *L1b* is 2,2'-bis(1-propyl-1*H*-benzimidazol-2-yl)biphenyl. The *A* and *B* cations exhibit approximate trigonal-planar and tetrahedral coordination geometries, respectively. In the solid state, the ligand *L1b* is chiral but the crystal structure is a racemate. The cations form separate, enantiomerically pure columns along the *a*-axis direction. Centrosymmetrically related alternating *R* and *S* columns of *A* and of *B* cations, centered about the planes $y = 0$ and $y = \frac{1}{2}$, respectively, progress along the *c*-axis direction. The perchlorate ions, which form columns along the *a*-axis direction, are linked to the cations by C—H...O hydrogen bonds.

Received 8 November 2006
 Accepted 8 November 2006

Comment

Species such as *L1* (see scheme) behave as proton sponges (Stibrany *et al.*, 2002; Stibrany & Potenza, 2006) and as bidentate ligands that distort coordination geometries from trigonal or square-planar towards tetrahedral (Stibrany *et al.*, 2004). The free ligand *L1a* (see scheme) adopts an unusual twisted clamshell configuration (Stibrany *et al.*, 2003), while $[\text{CuL1a}(\text{CH}_3\text{CN})][\text{BF}_4]$ has found use as a polymerization catalyst (Stibrany & Kacker, 2002). We report here the structure of the title salt, (I), which contains independent three-coordinate $[\text{Cu}(\text{L1b})(\text{CH}_3\text{CN})]^+$ (*A*) (Fig. 1) and four-coordinate $[\text{Cu}(\text{L1b})(\text{CH}_3\text{CN})_2]^+$ (*B*) (Fig. 2) cations, where *L1b* is 2,2'-bis(1-propylbenzimidazol-2-yl)biphenyl, separated by perchlorate anions.





In the *A* and *B* cations of (I), the largest angular deviations from ideal values (Table 1) are associated with the bite angles of ligands *L1b* and with one of the N(imine)–Cu–N(nitrile) angles; these are approximately 10° larger and smaller, respectively, than the ideal values. The nine-membered chelate rings are chiral and, because the crystal structure is centrosymmetric, it is racemic.

The geometrically constraining effect of the ligand *L1b* may be seen by comparing the coordination geometry of cation *A* with that of [Cu(*L2*)(CH₃CN)]⁺ (where *L2* is as shown in the scheme), in which the three N–Cu–N angles (118.0, 120.0 and 121.6°) differ only slightly from the ideal value of 120° [Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) refcode PATVEL (Bernardinelli *et al.*, 1993)].

Co-crystallization of a metal with two or more different coordination geometries is rare, though not unprecedented. For example, a crystal structure has been reported (Dakin *et al.*, 2000) which contains three distinct Cu^I species, namely [Cu(*L3*)(CH₃CN)]⁺, [Cu(*L3*)(CH₃CN)₂]⁺ and a dinuclear cation consisting of two Cu(*L3*) fragments bridged by an *L3* ligand (*L3* is shown in the scheme). Solution studies suggested that the three species isolated are present in solution in only trace amounts, and that their presence in the solid state is favored by equilibria influenced by the crystallization procedure. A similar situation could obtain with (I). Interestingly, [Cu(*L1a*)(CH₃CN)](BF₄) crystallizes as a single three-coordinate complex (Stibrany & Kacker, 2002) under crystallization conditions similar to those for (I).

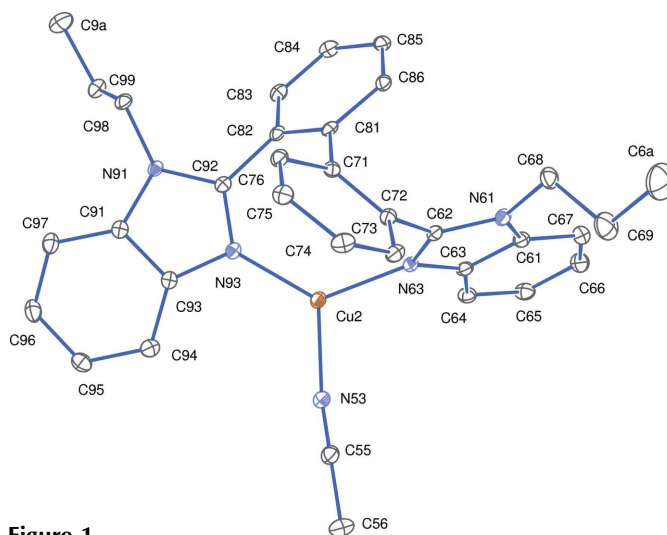


Figure 1
The structure of cation *A* of compound (I), showing 25% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted.

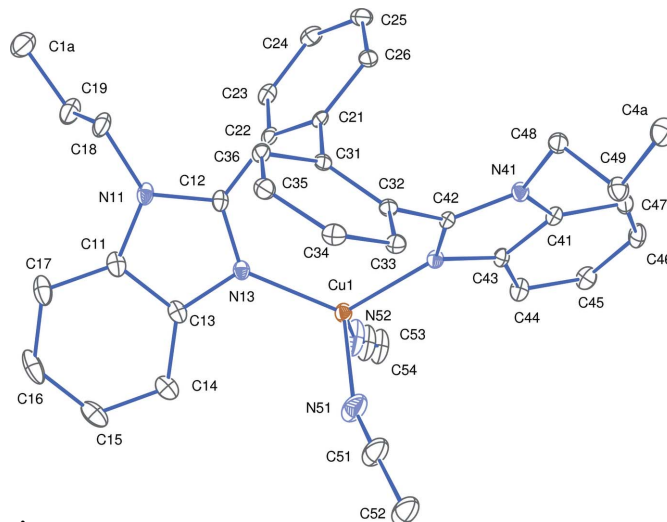


Figure 2
The structure of cation *B* of compound (I), showing 25% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted.

In the crystal structure of (I), cations *A* and *B* stack individually to form enantiomerically pure *R* and *S* columns parallel to the *a*-axis direction (Fig. 3). The cations of a given type are related centrosymmetrically, with alternating *R* and *S* columns of the *A* and *B* cations centered, respectively, about the $y = 0$ and the $y = \frac{1}{2}$ planes. The perchlorate anions also form columns, parallel to the *a* axis. The anions are linked to the cations by a substantial number of C–H...O hydrogen bonds (Table 2).

Experimental

To a flask containing acetonitrile (10 ml), 2,2'-bis(1-propylbenzimidazol-2-yl)biphenyl (111 mg, 0.24 mmol) (Stibrany *et al.*, 2004) was added, followed by the addition of [Cu(CH₃CN)₄](ClO₄) (77 mg, 0.24 mmol). The flask containing the resulting colorless

solution was sealed in a jar which had been partially filled with diethyl ether to allow vapor diffusion. Over a period of several days, colorless plates of the title salt precipitated from solution.

Crystal data

[Cu(C ₃₂ H ₃₀ N ₄)(C ₂ H ₃ N)]-	$\gamma = 88.588 (3)^\circ$
[Cu(C ₃₂ H ₃₀ N ₄)(C ₂ H ₃ N) ₂](ClO ₄) ₂	$V = 3324.5 (10) \text{ \AA}^3$
$M_r = 1390.34$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.389 \text{ Mg m}^{-3}$
$a = 8.8593 (15) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 17.407 (3) \text{ \AA}$	$\mu = 0.78 \text{ mm}^{-1}$
$c = 22.760 (4) \text{ \AA}$	$T = 100 (2) \text{ K}$
$\alpha = 71.424 (3)^\circ$	Plate, colorless
$\beta = 87.901 (3)^\circ$	$0.43 \times 0.38 \times 0.07 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	26871 measured reflections
φ and ω scans	11757 independent reflections
Absorption correction: multi-scan (SADABS; Blessing, 1995)	9415 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.867$, $T_{\max} = 1.00$ (expected range = 0.821–0.947)	$R_{\text{int}} = 0.024$
	$\theta_{\text{max}} = 25.1^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 6.3573P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 1.14 \text{ e \AA}^{-3}$
11757 reflections	$\Delta\rho_{\text{min}} = -1.20 \text{ e \AA}^{-3}$
823 parameters	
H-atom parameters constrained	

Table 1

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

Cu1—N43	2.026 (3)	Cu2—N93	1.944 (3)
Cu1—N13	2.031 (3)	Cu2—N63	1.965 (3)
Cu1—N52	2.033 (4)	Cu2—N53	1.969 (3)
Cu1—N51	2.061 (4)		
N43—Cu1—N13	121.78 (11)	N52—Cu1—N51	110.1 (2)
N43—Cu1—N52	109.74 (14)	N93—Cu2—N63	128.26 (11)
N13—Cu1—N52	108.01 (13)	N93—Cu2—N53	121.74 (12)
N43—Cu1—N51	97.69 (16)	N63—Cu2—N53	108.74 (12)
N13—Cu1—N51	108.88 (13)		

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C18—H18B \cdots O14 ⁱ	0.97	2.54	3.461 (7)	158
C26—H26 \cdots O14 ⁱⁱ	0.93	2.53	3.308 (7)	142
C34—H34 \cdots O14 ⁱⁱⁱ	0.93	2.55	3.337 (6)	143
C54—H54A \cdots O23 ^{iv}	0.96	2.58	3.272 (6)	129
C54—H54B \cdots O22	0.96	2.51	3.039 (7)	115
C56—H56B \cdots O11 ^v	0.96	2.35	3.283 (5)	165
C68—H68B \cdots O22	0.97	2.44	3.320 (6)	151
C86—H86 \cdots O21	0.93	2.58	3.279 (5)	132
C97—H97 \cdots O24 ^{vi}	0.93	2.50	3.425 (5)	174
C98—H98B \cdots O21 ^{vi}	0.97	2.54	3.503 (5)	174

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

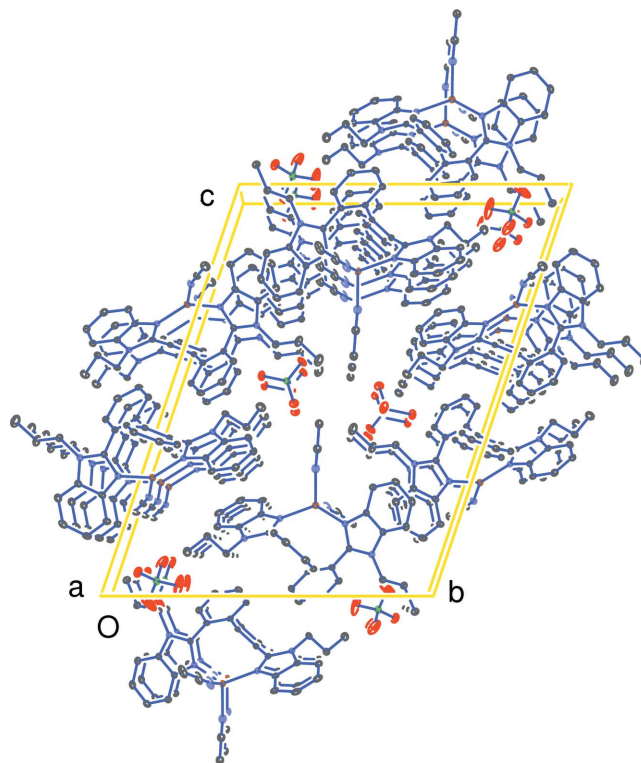


Figure 3

A view of the structure of (I), along the a axis. H atoms have been omitted.

Each asymmetric unit contains a void of 46.1 \AA^3 , the investigation of which in the refined structure using the SQUEEZE algorithm (van der Sluis & Spek, 1990) in *PLATON* (Spek, 2003) yielded a total of 2.3 electrons per void. Voids of the size observed are large enough, in principle, to accommodate water molecules. Adventitious water of solvation has been observed in crystals obtained from acetonitrile in which no special precautions were taken to exclude water, as in the present instance. However, based on the integrated electron density in the voids, we conclude that, if water molecules occupy these spaces, the occupancy factor is likely to be less than 20%. The relatively large value of $wR(F^2)$ may be attributed in part to the voids noted above, in part to an unresolved disorder of one of the perchlorate anions about one of its triad axes, and in part to the fact that the crystals formed as relatively small thin plates. In support of this view, we note that refinement of the structure with a 2θ cutoff of 45° reduced $wR(F^2)$ modestly to 0.131.

H atoms were positioned geometrically and treated as riding, with C—H distances in the range 0.93–0.97 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for methyl groups. In the final difference electron-density map, the highest residual was located 1.14 \AA from perchlorate oxygen atom O14, whilst the deepest hole was located 0.11 \AA from acetonitrile atom C54.

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-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernardinelli, G., Kubel-Pollak, A., Ruttimann, S. & Williams, A. F. (1993). *Z. Kristallogr.* **203**, 135–137.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker (2000). *SHELXTL* (Version 6.10), *SAINT-Plus* (Version 6.02) and *SMART* for Windows NT/2000 (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Dakin, L. A., Ong, P. C., Panek, J. S., Staples, R. J. & Stavropoulos, P. (2000). *Organometallics*, **19**, 2896–2908.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* **A46**, 194–201.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Stibrany, R. T. & Kacker, S. (2002). US Patent 6479425.
- Stibrany, R. T., Lobanov, M. V., Schugar, H. J. & Potenza, J. A. (2004). *Inorg. Chem.* **43**, 1472–1480.
- Stibrany, R. T. & Potenza, J. A. (2006). Private communication (deposition numbers CCDC 604501 and 612691) to the Cambridge Structural Database, 12 Union Road, Cambridge, England.
- Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2002). *Acta Cryst.* **E58**, o1142–o1144.
- Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2003). *Acta Cryst.* **E59**, o693–o695.