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Bis[*N*,*N*′-bis(2,4,6-trimethylphenyl)-1,2-ethanediylidenediamine]copper(I) tetrafluoroborate

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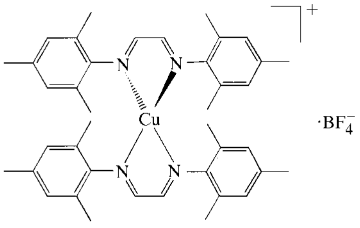
In the title compound, $[Cu(C_{20}H_{24}N_2)_2]BF_4$, the complex cation adopts a distorted tetrahedral structure, the dihedral angle between the least-squares planes of the chelating ligand backbones being 51.1 (2)°. This flattening of the tetrahedral coordination sphere may be driven by the presence of intramolecular π–π stacking interactions between mesityl groups on adjacent ligands.

Comment

The title complex, (I) (Fig. 1), was prepared during our studies of the copper chemistry of bis- and meridional tris-imine ligands (Halcrow *et al.*, 1997; Li *et al.*, 1998; Solanki *et al.*, 1998, 1999). The Cu^{I} ion is four-coordinate, with the four Cu—N bond lengths being crystallographically indistinguishable. While a tetrahedral geometry might be expected for a four-coordinate Cu^{I} centre, the geometry about Cu1 is distorted by the restricted bite of the chelating ligands [the average intra-ligand N—Cu—N angle is 82.43 (8)°]. In addition, the coordination sphere is severely twisted towards planarity, the dihedral angle (θ) between the least-squares planes formed by the atoms Cu1/N2/C3/C4/N5 and Cu1/N24/C25/C26/N27 being 51.1 (2)°; $\theta = 90°$ for an ideal tetrahedron and 0° for a square-planar structure. For comparison, previously reported crystal structures of Cu^{I}–bis-diimine complexes have shown θ values in the range 49–90° (Halcrow *et al.*, 1997, and references therein). The average N—Cu—N angle about Cu1 is 111.94 (15)°, however, which is close to the tetrahedral angle of 109.5°. This suggests that the coordination geometry in this complex is still best thought of as being derived from a tetrahedral arrangement of N-donors.



(I)

There are two intramolecular π–π stacking interactions within the cation, between mesityl rings on adjacent ligands. For the phenyl rings C6–C11 and C28–C33, the dihedral angle between the least-squares mean planes of the two arenes is 4.8 (2)°, the inter-ring spacing is 3.5 Å and the offset between the centroids of the two rings is 0.9 Å. Between C15–C20 and C37–C42, the dihedral angle is 1.3 (2)°, the inter-ring spacing is 3.4 Å and the centroid offset is 0.7 Å. In both cases, the inter-centroid offset distance is smaller than the ideal value of 3 Å for an attractive π–π interaction (Hunter & Sanders, 1990). This probably results from the geometric constraints of the copper ion coordination sphere and suggests that the stacking interactions here should be relatively weak. There are no unusually close intermolecular contacts within the crystal lattice.

It is interesting to compare this structure with that of $[Cu(L)_2][Cu(O_2C_6Cl\text{-}4\text{-}{}^tBu_2\text{-}3,6)_2(thf)]$ [L is *N*,*N*′-bis(*tert*-butyl)-1,2-ethanediylidenediamine and thf is tetrahydrofuran], whose cation adopts a more regular tetrahedral geometry with $\theta = 89°$ (Zakharov *et al.*, 1990). The difference between these two structures may reflect the increased steric bulk of the *tert*-butyl compared with the mesityl ligand substituents, which might prevent a planar twist in the latter complex. Alternatively, the planar distortion in the present structure may be driven by the formation of intramolecular π–π interactions.

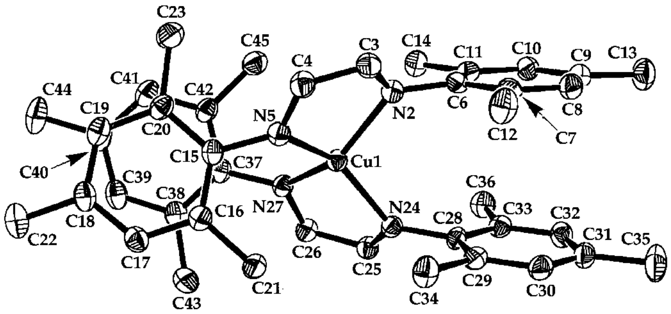


Figure 1
The molecular structure of the complex cation with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed. H atoms have been omitted for clarity.

Experimental

The diimine ligand was prepared by refluxing glyoxal with two molar equivalents of 2,4,6-trimethylaniline in aqueous methanol. The resultant pale-yellow precipitate was used without further purification. The title complex was obtained by the treatment of $[Cu(NCMe)_4]BF_4$ with two molar equivalents of the above yellow solid in MeCN. After filtration and concentration of this solution, dark-green crystals were obtained by vapour diffusion of Et_2O. Found: C 65.1, H 6.6, N 7.5%; calculated for $C_{40}H_{48}BCuF_4N_4$: C 65.3, H 6.6, N 7.6%.

Crystal data

$[Cu(C_{20}H_{24}N_2)_2]BF_4$
$M_r = 735.17$
Orthorhombic, $P2_12_12_1$
$a = 14.1107$ (2) Å
$b = 15.5953$ (2) Å
$c = 16.6469$ (2) Å
$V = 3663.33$ (8) Å^3
$Z = 4$
$D_x = 1.333$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 50 861 reflections
$\theta = 1.0$–$26.4°$
$\mu = 0.651$ mm^{-1}
$T = 150$ (2) K
Square prism, dark green
0.40 × 0.33 × 0.27 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Area-detector scans (see text)
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.781$, $T_{\max} = 0.844$
50 861 measured reflections

4180 independent reflections (plus 3320 Friedel-related reflections)
7151 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 26.38°$
$h = -17 \rightarrow 17$
$k = -19 \rightarrow 19$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.073$
$S = 1.013$
7500 reflections
497 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 1.2582P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.013 (7)

The BF_4^- anion is disordered over two orientations: B46—F50, with an occupancy of 0.6, and B51—F55, with an occupancy of 0.4. All B—F distances were restrained to 1.38 (2) Å and F···F distances were restrained to 2.25 (2) Å. All non-H atoms, including both orientations of the disordered anion, were refined anisotropically, while H atoms were placed in calculated positions and refined using a riding model.

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	2.0202 (15)	Cu1—N5	2.0219 (16)
Cu1—N24	2.0232 (15)	Cu1—N27	2.0253 (15)
N2—Cu1—N24	108.29 (6)	N2—Cu1—N27	145.34 (6)
N2—Cu1—N5	82.30 (6)	N24—Cu1—N27	82.56 (6)
N24—Cu1—N5	145.46 (6)	N5—Cu1—N27	107.66 (6)

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1996); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1389). Services for accessing these data are described at the back of the journal.

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