

Tetrakis[1-(3-chloropropyl)-1,2,4-triazole- κ N⁴]bis(tetrafluoroborato- κ F)-copper(II)Allison M. Mills,^{a*} Kristel Flinzner,^b Arno F. Stassen,^b
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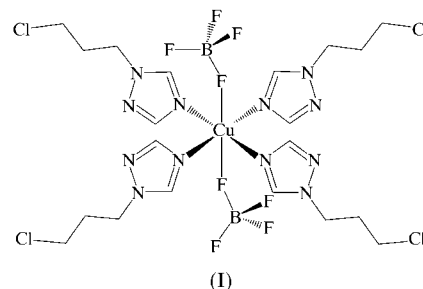
In the title complex, [Cu(BF₄)₂(1tpc)₄] [1tpc is 1-(3-chloropropyl)-1,2,4-triazole, C₅H₈ClN₃], the copper(II) centres reside in a tetragonally distorted octahedral coordination environment. Four 1tpc ligands are coordinated to the metal atom *via* the N4 atom of the triazole rings in a square-planar arrangement, with Cu–N bond lengths in the range 2.002 (2)–2.019 (2) Å. Two tetrafluoroborate anions, in the axial positions above and below the square plane, are weakly coordinated to the copper(II) centre, with Cu–F distances of 2.4009 (18) and 2.5096 (18) Å.

Comment

Coordination complexes of triazole and tetrazole derivatives have recently generated considerable interest as spin-cross-over compounds with potential applications in information storage or molecular switching (Dova *et al.*, 2001; Haasnoot, 2000; Stassen *et al.*, 2000). The donor strengths of triazole and tetrazole ligands are in the proper range to allow thermally induced transitions between the paramagnetic high-spin and diamagnetic low-spin states of octahedrally coordinated iron(II) (Haasnoot, 2000; Stassen, undated). For example, [Fe(teec)₆](BF₄)₂ [teec is 1-(2-chloroethyl)tetrazole] undergoes a two-step spin transition upon cooling (Dova *et al.*, 2001). In the present study, a new 1-(haloalkyl)triazole ligand, *viz.* 1-(3-chloropropyl)-1,2,4-triazole (1tpc), was synthesized. Since complexation of iron(II) with 1tpc did not produce single crystals, a copper(II) complex was prepared instead as a viable structural model.

The molecular structure of the title complex, [Cu(BF₄)₂(1tpc)₄] (I), is presented in Fig. 1, and selected geometric parameters are listed in Table 1. In the monomeric complex, copper(II) is at the centre of a distorted octahedral coordination sphere composed of four equatorial 1tpc ligands and

two axial tetrafluoroborate anions. The 1tpc ligands are coordinated to the metal *via* the less sterically hindered N4 atom of the triazole rings at normal Cu–N distances of 2.002 (2)–2.019 (2) Å. The *trans*-tetrafluoroborate ligands are weakly, and asymmetrically, coordinated at long Cu–F distances of 2.4009 (18) and 2.5096 (18) Å. The geometry of this tetragonally elongated coordination polyhedron is similar to that observed in other *d*⁹ CuN₄F₂ complexes, for example, [Cu(Him)₄(BF₄)₂]·2hmpa [Him is imidazole and hmpa is hexamethylphosphoramide; Su *et al.*, 1992; Cu–N 2.004 (3)–2.005 (4) Å and Cu–F 2.506 (4) Å].



The *cis*-N–Cu–F [85.11 (8)–98.28 (9)°] and *trans*-F–Cu–F [172.68 (7)°] angles involving the loosely coordinated tetrafluoroborate ligands deviate significantly from ideal octahedral values. The arrangement of the 1tpc *N*-donor atoms about the metal, on the other hand, is nearly ideally square planar; the *cis*-N–Cu–N angles range from 88.80 (10) to 90.83 (9)° and sum to 360.0 (2)°. However, since the copper(II) centre occupies a general position, each of the coordinated 1tpc ligands is crystallographically unique. The planes of the triazole rings are tilted at dihedral angles ranging

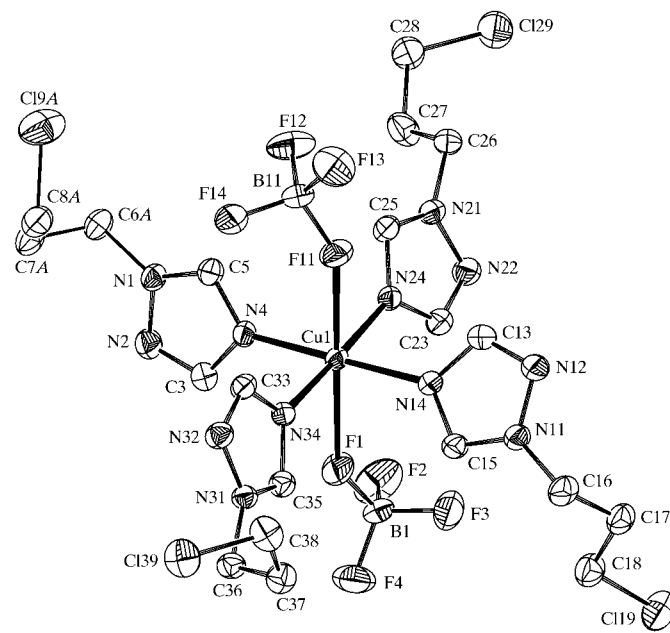


Figure 1
PLATON/ORTEP representation (Spek, 2002) of (I) with displacement ellipsoids at the 50% probability level. Only the major component of the disordered 3-chloropropyl chain is shown. H atoms have been omitted for clarity.

from 50.05 (14) to 73.64 (14)° with respect to the CuN₄ coordination plane, and the flexible 3-chloropropyl substituents adopt different conformations. The side chain of one ligand is disordered between two possible conformations, with *gauche* and *anti* orientations of the terminal Cl atom, respectively, in a 0.857 (3):0.143 (3) ratio.

In the crystal structure of (I), the copper(II) centres of the mononuclear complexes are well separated, with a closest distance of 8.8079 (5) Å. Accordingly, (I) exhibits paramagnetic behaviour from 2 to 300 K; magnetic susceptibility data measured as a function of temperature fit the Curie law, with a Curie constant of $C = 0.412 \text{ cm}^3 \text{ K mol}^{-1}$. The effective magnetic moment is 1.82 μ_B , comparable to the spin-only moment of 1.73 μ_B predicted for a single unpaired electron per d^9 ion. The anisotropic g factors ($g_{\text{perp}} = 2.06$ and $g_{\text{par}} = 2.25$) and hyperfine splitting constant ($A_{\text{par}} = 16.7 \text{ mT}$), determined from the electron paramagnetic resonance (EPR) spectrum of (I), are consistent with a tetragonally elongated octahedral geometry at the copper(II) centre (van Albada *et al.*, 1999; Hathaway, 1987). In the ligand field spectrum of (I), the metal $d-d$ transitions occur at $17.8 \times 10^3 \text{ cm}^{-1}$, in the usual range for CuN₄X₂ chromophores (van Albada *et al.*, 1999; Hathaway, 1987; Su *et al.*, 1992).

Experimental

The 1-(3-chloropropyl)-1,2,4-triazole (1tpc) ligand was synthesized by the following procedure. An excess of sodium methoxide (0.1 mol, 5.4 g) was added to a solution of 1,2,4-triazole (0.035 mol, 2.42 g) in ethanol (80 ml). The triazolite solution was then added slowly to a solution of 1,3-dichloropropane (0.14 mol, 15.8 g) in ethanol (80 ml). After refluxing for 5 d, the reaction mixture was filtered to remove the precipitated sodium chloride, then evaporated under reduced pressure to remove the ethanol. The residue was extracted into 2-propanol, and after evaporating the solvent, 1tpc was isolated as a yellow oil. ¹H NMR (300 MHz, DMSO): δ 8.52 (s), 7.96 (s), 4.31 (t), 2.23 (q), 3.60 (t) p.p.m. The title complex was prepared by adding a solution of Cu(BF₄)₂·4H₂O (0.33 mmol, 0.10 g) in water (2 ml) to a solution of 1tpc (1.0 mmol, 0.15 g) in ethanol (2 ml). Light-blue crystals suitable for X-ray analysis grew within a few days upon partial evaporation of the solvent. Elemental analysis found (calculated) for C₂₀H₃₂B₂Cl₄CuF₈N₁₂: C 29.5 (29.3), N 20.8 (20.5), H 3.9% (3.9%).

Crystal data

[Cu(BF ₄) ₂ (C ₅ H ₈ ClN ₃) ₄]	$Z = 2$
$M_r = 819.54$	$D_x = 1.632 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.8647$ (2) Å	Cell parameters from 60 147 reflections
$b = 13.3168$ (3) Å	$\theta = 1.0\text{--}27.5^\circ$
$c = 15.1469$ (4) Å	$\mu = 1.06 \text{ mm}^{-1}$
$\alpha = 72.1540$ (8)°	$T = 150$ (2) K
$\beta = 78.6200$ (9)°	Plate, light blue
$\gamma = 88.3480$ (15)°	$0.27 \times 0.18 \times 0.06 \text{ mm}$
$V = 1667.63$ (7) Å ³	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.049$
φ and ω scans	$\theta_{\text{max}} = 27.5^\circ$
26 534 measured reflections	$h = -11 \rightarrow 11$
7607 independent reflections	$k = -17 \rightarrow 17$
5574 reflections with $I > 2\sigma(I)$	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 1.2707P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.129$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.00 \text{ e \AA}^{-3}$
7607 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
446 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu1—N4	2.005 (2)	Cu1—N34	2.009 (2)
Cu1—N14	2.019 (2)	Cu1—F1	2.4009 (18)
Cu1—N24	2.002 (2)	Cu1—F11	2.5096 (18)
N4—Cu1—N34	90.48 (9)	N24—Cu1—F1	98.28 (9)
N24—Cu1—N4	89.92 (9)	N34—Cu1—F1	85.25 (9)
N24—Cu1—N14	88.80 (10)	N4—Cu1—F11	95.41 (8)
N34—Cu1—N14	90.83 (9)	N14—Cu1—F11	85.11 (8)
N4—Cu1—N14	178.60 (10)	N24—Cu1—F11	87.83 (8)
N24—Cu1—N34	176.46 (9)	N34—Cu1—F11	88.62 (8)
N4—Cu1—F1	88.66 (8)	F1—Cu1—F11	172.68 (7)
N14—Cu1—F1	90.97 (8)		

Since the ratio of the predicted transmission limits calculated based on the crystal size and absorption coefficient is relatively small (1.17), the X-ray data were not corrected for absorption. A multi-scan correction ($T_{\text{min}} = 0.895$ and $T_{\text{max}} = 0.936$) was tried, but did not significantly improve the intensity statistics (after correction, $R_{\text{int}} = 0.048$) or residual electron-density map (after correction, $\Delta\rho_{\text{max}} = 1.00 \text{ e \AA}^{-3}$ and $\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$). The 3-chloropropyl chain of one triazole ligand is disordered over two different conformations with refined occupancies of 0.857 (3) and 0.143 (3). The 1,2- and 1,3-distances of the partially occupied chains, and the displacement parameters of corresponding atoms within each chain, were restrained to be similar. All H atoms were constrained to idealized geometries and allowed to ride on their attached C atoms, with C—H = 0.95 or 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL2000 (Otwinowski & Minor, 1997); data reduction: HKL2000; program(s) used to solve structure: DIRDIF99 (Beurskens *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2002); software used to prepare material for publication: PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1102). Services for accessing these data are described at the back of the journal.

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