Bis(1-chloromethyldiazabicyclo[2.2.2]-octane-κN^4)bis(trifluoropentane-2,4-dionato)copper(II) bis(tetrafluoroborate)

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The title compound, (I), [Cu(trifacac)$_2$(DabcoCH$_2$Cl)](BF$_4$)$_2$ or [Cu(C$_5$H$_4$F$_3$O$_2$)$_2$(C$_7$H$_{14}$ClN$_2$)$_2$](BF$_4$)$_2$ (Dabco is diazabicyclo[2.2.2]octane and trifacac is trifluoroacetylacetonate) was synthesized from the reaction of Selectfluor [Selectfluor is 1-(chloromethyl)-4-fluoro-1,4-diazobicyclo[2.2.2]octane bis-(tetrafluoroborate)] and Cu(trifacac)$_2$. The central Cu atom is octahedrally coordinated by two N(CH$_2$CH$_2$)$_3$NCH$_2$Cl$^+$ and two trifacac ligands in a *trans* conformation. The Cu atom is located on a center of symmetry. The Cu—N and Cu—O distances are 2.5514 (19) and 1.9550 (15), 1.9592 (15) Å.
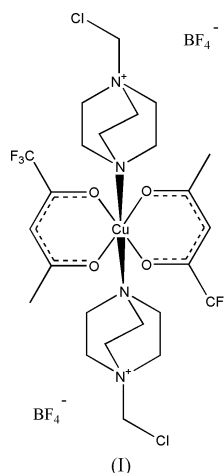
Comment

The title compound, (I) (Fig. 1), was synthesized by the reaction of Selectfluor with Cu(trifacac)$_2$ [Selectfluor is 1-(chloromethyl)-4-fluoro-1,4-diazobicyclo[2.2.2]octane bis-(tetrafluoroborate) and trifacac is trifluoroacetylacetonate]. In this case, Selectfluor did not act as a fluorinating reagent; fluorine was lost and the remainder of the ligand formed a donor complex with the Cu compound. The resultant complex consists of trifacac and DabcoCH$_2$Cl$^+$ ligands (Dabco is di-azabicyclo[2.2.2]octane), arranged in a *trans* configuration about the Cu atom. The Cu—O distances are essentially identical [1.9550 (15) and 1.9592 (15) Å] and the Cu(trifacac)$_2$ unit is planar, with an out-of-plane r.m.s. deviation of 0.0489 Å (all non-H atoms excluding F atoms). There is only a small deviation from ideal octahedral coordination, as seen by the angles O1—Cu—O2 [86.65 (6)°], N1—Cu1—O1 [91.92 (6)°] and N1—Cu1—O2 [94.63 (6)°]. The dihedral angle between N2—N1—Cu1—N1^i—N2^i [symmetry code: (i) $2-x$, $-y$, $1-z$] and the plane of the Cu(trifacac)$_2$ moiety (excluding H and F atoms) is 88.05 (3)°.

(I)

Although there are many structures in the Cambridge Structural Database (Allen & Kennard, 1993; Version 5.23 of
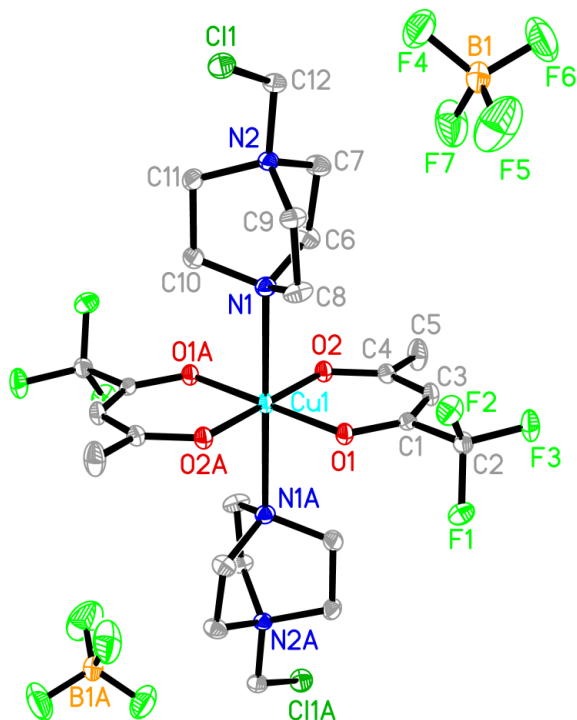
Figure 1
The molecular structure of (I). Atomic displacement ellipsoids are shown at the 30% probability level.

April 2002) with similar skeletons [*viz.* Cu(trifacac)$_2$ with *trans* nitrogen donors], only in four complexes is a Cu—N distance reported greater than 2.1 Å. [CSD refcode HOYZIE (Dong *et al.*, 1999); KOWFIL (Yun-Peng *et al.*, 1991); LECWEV (Kogane *et al.*, 1994); QOTMUH (Kwiatkowski *et al.*, 2001)]. These distances and angles are compared in Table 2; compound (I) displays the longest Cu—N distance to date. There is only one other compound which shares the same ligand configuration. This compound, [Zn(acac)$_2$(Dabco-CH$_2$Cl)]Cl$_2$ (Fronczek *et al.*, 1990), was also noted for having exceptionally long Zn—N distances. This can be attributed to the cationic DabcoCH$_2$Cl$^+$ ligand, which is a poorer electron donor than unsubstituted Dabco.

Distances for the closest approach of the counter ion, BF$_4^-$, to the complex are given in Table 1. These are in the range 2.43–2.55 Å (H···F), which are longer than accepted H···F intermolecular interactions (Desiraju & Steiner, 2001). There is a weak hydrogen bond between each Dabco and a neighboring acac moiety. This distance is also given in Table 1. This interaction links the Cu complexes into loosely associated two-dimensional sheets, separated by the BF$_4^-$ counter-ions. These sheets are parallel to (100) (see Fig. 2).

Experimental

Bis(1,1,1-trifluoroacetylacetonate)copper(II) (0.36 g, 1 mmol) was dissolved in dry acetonitrile (25 ml) and Selectfluor (0.71 g, 2 mmol) added (Selectfluor is a product of Air Products and is available from Aldrich Chemicals, Cat. No. 43,947–9). The solution was stirred at room temperature for 24 h under an inert atmosphere of N$_2$. The solvent was then concentrated under reduced pressure to *ca* 10 ml. The product crystallized as pale-green needles (yield 90%).
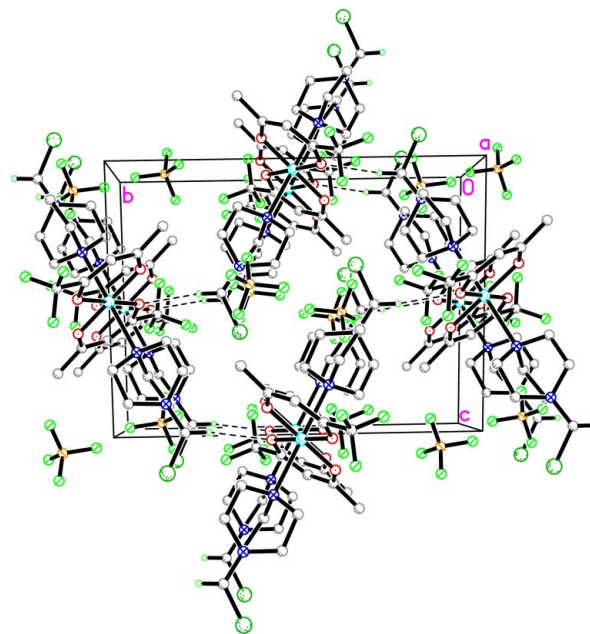

Figure 2
A ball-and-stick packing diagram of (I). Only H atoms involved in hydrogen bonding (dashed lines) are shown.

Crystal data

[Cu(C$_5$H$_4$F$_3$O$_2$)$_2$(C$_7$H$_{14}$ClN$_2$)$_2$]-(BF$_4$)$_2$	$D_x = 1.725$ Mg m^{-3}
$M_r = 866.63$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 993
$a = 10.0098\,(12)$ Å	reflections
$b = 15.1046\,(18)$ Å	$\theta = 2.3–28.2°$
$c = 11.5086\,(14)$ Å	$\mu = 0.93$ mm^{-1}
$\beta = 106.50\,(2)°$	$T = 203\,(2)$ K
$V = 1668.4\,(3)$ Å^3	Needle, pale green
$Z = 2$	$0.60 \times 0.25 \times 0.13$ mm

Data collection

Bruker–Siemens SMART 1K diffractometer	3984 independent reflections
	3155 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)	$\theta_{max} = 28.3°$
	$h = -13 \rightarrow 13$
$T_{min} = 0.605$, $T_{max} = 0.888$	$k = -18 \rightarrow 19$
12231 measured reflections	$l = -10 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.6096P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3984 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
233 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Table 1
C—H···F and hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···F4	0.98	2.55	3.362 (3)	140
C9—H9B···F7	0.98	2.43	3.296 (3)	147
C12—H12B···F7	0.98	2.46	3.312 (3)	146
C12—H12A···O1^i	0.98	2.54	3.512 (3)	170

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 2
A comparison of the Cu—N distances and angles in compound (I) and reported values in the CSD (Å). All N—Cu—N angles are exactly 180° as a consequence of crystallographic symmetry.

Refcode	Cu—N
(I)	2.5514 (19)
HOYZIE	2.389 (5)
KOWFIL	2.545 (4)
LECWEV	2.537 (10)
QOTMUH	2.445 (2)

H atoms were positioned geometrically and refined using a riding model, with U_{iso} constrained to $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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