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Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.033
 wR factor = 0.111
Data-to-parameter ratio = 12.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A copper(II)–oxalate compound resulting from the
fixation of carbon dioxide: μ -oxalato-bis[bis(1-benzyl-
1*H*-pyrazole)(trifluoromethanesulfonato)copper(II)]

Reductive coupling of adventitious CO_2 by Cu^{I} has afforded the title compound, μ -oxalato- $1\kappa^2\text{O}^1, \text{O}^2:2\kappa^2\text{O}^{1'}, \text{O}^{2'}$ -bis[bis(1-benzyl-1*H*-pyrazole- κN^2)(trifluoromethanesulfonato- κO)-copper(II)], $[\text{Cu}_2(\text{CF}_3\text{O}_3\text{S})_2(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_{10}\text{N}_2)_4]$, which contains centrosymmetric molecules in which the Cu^{II} ions, bridged by a planar oxalate ligand, exhibit a distorted square-pyramidal $\text{N}_2(\text{pyrazole})\text{O}_2(\text{oxalato})\text{O}(\text{trifluoromethanesulfonate})$ coordination geometry, with the trifluoromethanesulfonate ligand coordinated axially. The molecule exhibits five intramolecular $\text{C}-\text{H}\cdots\text{O}, \text{F}$ hydrogen bonds per asymmetric unit, which help to stabilize the molecule and to orient the benzyl and trifluoromethanesulfonate groups. Intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules to form two-dimensional layers.

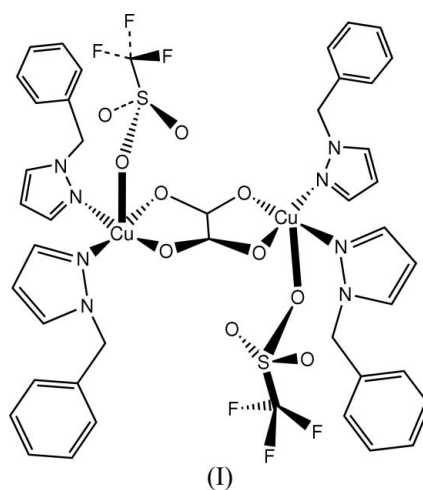
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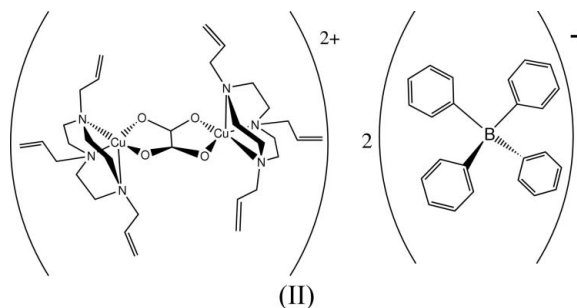
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Comment

As part of our continuing interest in the chemistry of Cu-containing complexes (Stibrany *et al.*, 2002, 2003, 2004), we attempted to prepare a tris(*N*-benzylpyrazole) complex of Cu^{I} and obtained instead the oxalate-containing title compound, (I), in which the oxalate ion appears to have been formed by the reductive coupling of adventitious CO_2 . Reductive coupling of CO_2 , induced by metal complexes, to afford oxalate is rare, and we are aware of only one such example, the salt μ -oxalato- $1\kappa^2\text{O}^1, \text{O}^2:2\kappa^2\text{O}^{1'}, \text{O}^{2'}$ -bis(triallyl-1,4,7-triazacyclononane)copper(II) bis(tetraphenylborate), (II), in which a Cu^{I} complex served as the reducing agent (Farrugia *et al.*, 2001). In that case also, the product was originally obtained serendipitously.





Crystals of (I) (Fig. 1) contain discrete neutral centrosymmetric molecules in which each Cu^{II} ion is five-coordinate and is bonded to two O atoms from a bridging oxalate group, the imine N atoms of two *N*-benzylpyrazole ligands, and one O atom from a trifluoromethanesulfonate anion. Five-coordinate copper(II) complexes typically have geometries ranging from trigonal-bipyramidal to square-pyramidal. Energetically, the limiting trigonal-bipyramidal and square-pyramidal forms are often almost equally favorable, with a low activation barrier to interconversion. In the present instance, the observed geometry is best described as distorted square-pyramidal, with atom O1 apical, as indicated by the geometric parameters in Table 1 and by the calculated value of the distortion parameter τ (Addison *et al.*, 1984) of 0.19, which is closer to the ideal value of $\tau = 0$ for a perfect square-pyramidal symmetry than to the ideal value of 1 for an ideal trigonal-bipyramidal geometry.

Structurally characterized examples of species with $\text{Cu}^{\text{II}}-\text{O}(\text{trifluoromethanesulfonate})$ bonds are uncommon. The Cambridge Structural Database (CSD, version 5.26; Allen, 2002) lists only a single example, CSD refcode RORFIN (van Albada *et al.*, 1997), a binuclear square-pyramidal dication (two per asymmetric unit), each of which contains a bridging

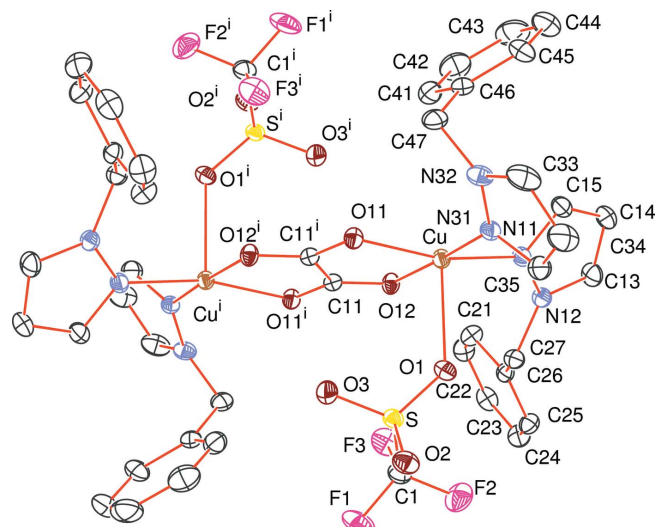


Figure 1
A view of (I), showing 25% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted. [Symmetry code: (i) $2 - x, 1 - y, -z$.]

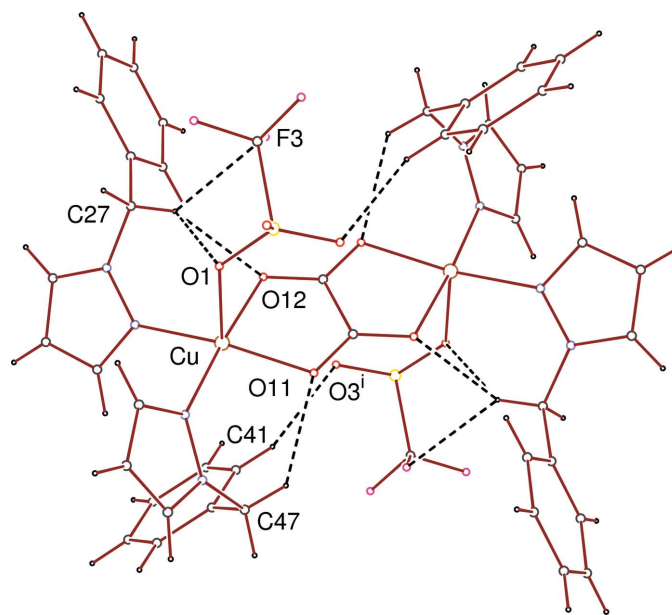


Figure 2
A view of (I), showing the intramolecular hydrogen-bonding scheme (dashed lines). [Symmetry code: (i) $2 - x, 1 - y, -z$.]

axially bonded trifluoromethanesulfonate ligand. Axial copper(II)–O bond lengths in these cations range from 2.408 (5) to 2.437 (6) Å, all significantly longer than the value of 2.3626 (17) Å for the corresponding bond in (I). The equatorial metal–ligand bond lengths in (I) agree well with those reported for other comparable systems. In particular, the Cu–O(oxalate) bond lengths in Table 1 lie within the range of 1.960 (2)–2.041 (3) Å reported for several distorted square-pyramidal Cu^{II} –oxalate complexes (refcodes FEYXUC, HOSTAK, IMIHAN, JOFKEU, QEJQOL, WURYEN and XUFZON), while the Cu–N(pyrazole) linkages are similarly within the range of 1.938 (5)–2.024 (3) Å observed for equatorial Cu–N(pyrazole) linkages in a variety of square-pyramidal complexes (refcodes BENDED, ESIKIA, FAYTOO02, PIBXIO, POWJAM, QOTJAK, REDLER, REDLER01 and RIHYAI).

Molecule (I) exhibits five intramolecular C–H···O,F hydrogen bonds per asymmetric unit (Table 2), one of which is trifurcated (Fig. 2). These hydrogen bonds, which involve the methylene C atoms of the benzyl fragments and a C atom of one of the phenyl rings, help to stabilize the molecule, while serving also to orient the benzyl and trifluoromethanesulfonate groups.

Two unique intermolecular C–H···O hydrogen bonds (Table 2) link the pyrazole and phenyl rings of one ligand to the O atoms of the oxalate and trifluoromethanesulfonate fragments, respectively, to form a two-dimensional network along the *a* and *b* unit-cell directions (Fig. 3). When translated along the *c* unit-cell direction, the resulting layers complete the structure, in which a variety of C–H···F,O and C–H··· π interactions complement the ubiquitous van der Waals interactions to complete the packing. There is little, if any, evidence of π – π interactions among the pyrazole and phenyl rings.

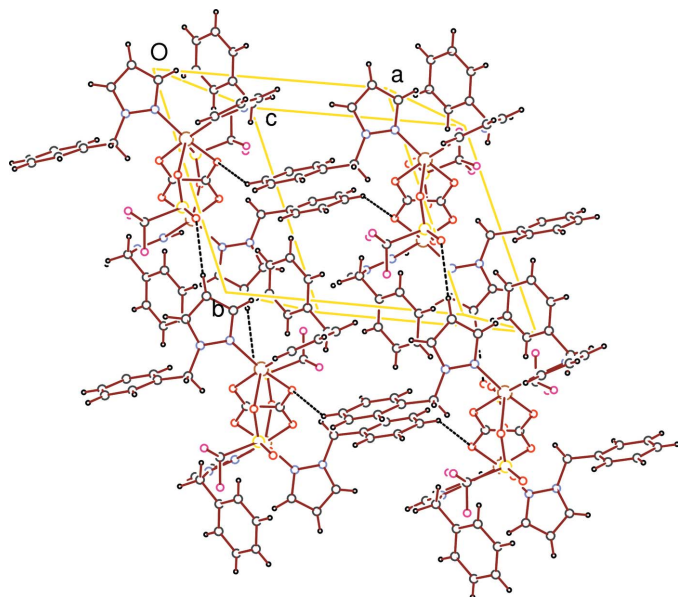


Figure 3
A view of the structure of (I) approximately normal to (001). Dashed lines indicate C—H...O hydrogen bonds.

Experimental

A colorless solution containing $\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4$ (trifluoromethanesulfonate) (154 mg, 0.41 mmol), *N*-benzylpyrazole (194 mg, 1.23 mmol), acetonitrile (8 ml) and triethyl orthoformate (1 ml) was prepared in a 50 ml flask. The flask was placed in a jar containing some liquid diethyl ether and diethyl ether vapor was diffused into the solution. Although the jar was closed, no special effort was made to exclude air. After approximately two weeks, blue rhomboids of (I) began to deposit.

Crystal data

$[\text{Cu}_2(\text{CF}_3\text{O}_3\text{S})_2(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_{10}\text{N}_2)_4]$	$Z = 1$
$M_r = 1146.05$	$D_x = 1.576 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.8432 (5) \text{ \AA}$	Cell parameters from 978 reflections
$b = 11.0190 (5) \text{ \AA}$	$\theta = 3.5\text{--}25.0^\circ$
$c = 11.4895 (5) \text{ \AA}$	$\mu = 1.06 \text{ mm}^{-1}$
$\alpha = 87.389 (4)^\circ$	$T = 298 (1) \text{ K}$
$\beta = 75.577 (4)^\circ$	Rhomboid, blue
$\gamma = 65.539 (4)^\circ$	$0.51 \times 0.41 \times 0.28 \text{ mm}$
$V = 1207.60 (11) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	4166 independent reflections
ω scans	3841 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$R_{\text{int}} = 0.018$
$T_{\text{min}} = 0.552$, $T_{\text{max}} = 0.744$	$\theta_{\text{max}} = 25.0^\circ$
12405 measured reflections	$h = -12 \rightarrow 12$
	$k = -12 \rightarrow 13$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2 + 0.5052P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
4166 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
325 parameters	
H-atom parameters constrained	

Table 1

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

Cu—O12	1.9771 (16)	Cu—N31	1.992 (2)
Cu—O11	1.9834 (16)	Cu—O1	2.3626 (17)
Cu—N11	1.990 (2)		
O12—Cu—O11	83.76 (6)	N11—Cu—N31	91.52 (8)
O12—Cu—N11	92.34 (8)	O12—Cu—O1	90.13 (7)
O11—Cu—N11	164.51 (8)	O11—Cu—O1	96.14 (7)
O12—Cu—N31	176.05 (7)	N11—Cu—O1	98.86 (8)
O11—Cu—N31	92.30 (7)	N31—Cu—O1	90.07 (7)

Table 2

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

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C27—H27A...F3	0.97	2.54	3.313 (3)	136
C27—H27A...O1	0.97	2.53	3.240 (4)	130
C27—H27A...O12	0.97	2.42	3.154 (3)	132
C41—H41...O3 ⁱ	0.93	2.57	3.327 (4)	139
C47—H47B...O11	0.97	2.36	3.109 (4)	133
C14—H14...O2 ⁱⁱ	0.93	2.53	3.454 (4)	172
C23—H23...O11 ⁱⁱⁱ	0.93	2.52	3.253 (4)	135

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

H atoms were included in the riding-model approximation, with $C\text{—}H = 0.93 \text{ \AA}$ (aromatic H) and 0.97 \AA (methylene H), and with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); 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 ORTEP32 (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Bruker, 2000).

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