O5—Co—N3^{i}	93.84 (7)	N2—C3—C2	122.6 (2)
O5^{i}—Co—N3^{i}	88.20 (7)	N2—C4—N1	125.7 (2)
N1^{i}—Co—N3^{i}	77.18 (7)	N2—C4—C5	118.8 (2)
N1—Co—N3^{i}	100.96 (6)	N1—C4—C5	115.5 (2)
N3^{i}—Co—N3	177.29 (10)	N4—C5—N3	126.0 (2)
C1—N1—C4	117.0 (2)	N4—C5—C4	117.8 (2)
C1—N1—Co	127.91 (14)	N3—C5—C4	116.2 (2)
C4—N1—Co	114.82 (14)	N3—C6—C7	121.2 (2)
C4—N2—C3	116.2 (2)	C8—C7—C6	116.8 (2)
C5—N3—C6	117.2 (2)	N4—C8—C7	123.4 (2)
C5—N3—Co	114.24 (13)		

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
O5—H5*A*···O6^{i}	0.79 (3)	1.91 (3)	174 (4)
O5—H5*B*···O2*A*^{ii}	0.77 (3)	2.13 (3)	161 (4)
O5—H5*B*···O2*B*^{ii}	0.77 (3)	2.13 (3)	137 (3)
O6—H6*A*···O3*A*^{iii}	0.83 (3)	2.19 (3)	162 (3)
O6—H6*A*···O4*B*^{iii}	0.83 (3)	2.26 (3)	156 (3)
O6—H6*B*···N2^{iv}	0.71 (3)	2.57 (3)	145 (4)
O6—H6*B*···N4^{iv}	0.71 (3)	2.43 (3)	147 (4)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-x, 1-y, -z$.

Several restraints were imposed on the model structure during refinement. The perchlorate anion is rotationally disordered about the O1—Cl bond. This feature was modeled as two tetrahedra (*A* and *B*) having a common O1—Cl bond, restrained to have a net occupancy of 1. Final occupancy factors for the *A* and *B* sets of O2, O3 and O4 atoms are 0.71 (1) and 0.29 (1), respectively. The disordered anion was also restrained to have tetrahedral geometry by fixing the Cl—O and O—O distances (20 restraints). Refinement of the four water H atoms was subject to a common H—O distance and displacement parameter (six restraints). The final distance parameter was 0.78 (2) Å and the displacement parameter was 0.071 (5) Å^2. H atoms bonded to C atoms were placed in calculated positions using a riding model with a fixed C—H distance of 0.93 Å. They were assigned isotropic displacement parameters of 1.2 times that of the parent C atom. The 244 parameters varied in the refinement included an extinction parameter and an overall scale factor. The largest peaks in the final electron-density difference map were associated with the disordered O atoms.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 2987–2989

[2,2′-Oxybis(1,1,1,3,3,3-hexafluoro-2-propanolato-*O*)](*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-*N*,*N*′)copper(II) Hemibenzene Solvate

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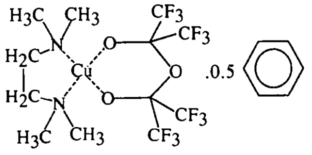
Abstract

The title compound, $[Cu(C_6F_{12}O_3)(C_6H_{16}N_2)].0.5C_6H_6$, forms a four-coordinate complex, with the Cu^{II} ion in a slightly distorted square-planar environment. The six-membered chelate ring and the co-ligand form a complex with approximate molecular C_2 symmetry. The benzene solvate molecule lies on a crystallographic inversion center.

Comment

Fluorinated *gem*-diols have been observed as an $[O—C(CF_3)_2—O]^{2-}$ dialkoxide, forming a four-membered chelate ring with the transition metal ions Cu^{II} and Ni^{II} (Bradford, Hynes, Payne & Willis, 1990), and Pt^{II} (Hynes, Willis & Payne, 1992). The condensed dialkoxide $[O—C(CF_3)_2—O—C(CF_3)_2—O]^{2-}$ has been shown to form a six-membered ring with Pt^{II} (Modinos & Woodward, 1975). In the title complex, $[(Me_2NCH_2CH_2NMe_2)Cu\{OC(CF_3)_2OC(CF_3)_2O\}].0.5C_6H_6$, (I), the dialkoxide forms a six-membered ring with the four-coordinate Cu^{II} ion, in a complex with a *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) co-ligand. A benzene solvate molecule is also present in an asymmetric unit which consists of one molecule of the complex and half a benzene molecule sited with its centroid on an inversion center.



(I)

The coordination of the Cu atom is almost square planar, with a maximum deviation from the least-squares plane of 0.013 Å. The six-membered condensed dialkoxide ring is twisted, but has approximate C_2 symmetry about the Cu···O3 axis, as does the complex as a whole. The Cu—O distances of 1.889 (2) and 1.894 (3) Å are within the range of values observed previously for four-coordinate Cu^{II} fluorinated alkoxides [1.895 (3) Å (Timmons *et al.*, 1981); 1.884 (3), 1.895 (3) and 1.910 (3) Å (Jeffries, Wilson & Girolami, 1992); 1.920 (11) Å (Loeb, Richardson & Willis, 1983); 1.937 (6) and 1.930 (6) Å (Hynes, Payne & Willis, 1990); 1.916 (5) and 1.969 (5) Å (Purdy, George & Callahan, 1991)], but significantly shorter than the values of 1.977 (3) and 1.999 (4) Å observed for five-coordinate Cu^{II} fluorinated alkoxides (Bradford *et al.*, 1990). The Cu—N distances of 2.021 (3) and 2.022 (3) Å are also near the values of 2.034 (4), 2.036 (4) and 2.064 (3) Å (Jeffries, Wilson & Girolami, 1992), and 2.030 (10) Å (Mitchell, Bernard & Wasson, 1970) observed in other four-coordinate TMEDA-Cu^{II} complexes. The conformation of the six-membered ring is similar to that found in the previously cited Pt^{II} complexes. The C—O distances adjacent to the metal ion are approximately 0.1 Å shorter than the C—O distances between the $C(CF_3)_2$ moieties due to the proximity to the electropositive metal atom. These values average 1.328 (2) and 1.436 (5) Å, respectively, in the present study and 1.31 (2) and 1.41 (2) Å in the Pt^{II} complexes. The C—F distances average 1.327 (6) Å, the F—F distances average 2.131 (8) Å and the F—C—F angles average 106.8°, which are slightly less than tetrahedral values. The N—C_{Me} distances range from 1.475 (5) to 1.481 (5) Å and the C—C_F distances range from 1.549 (6) to 1.556 (6) Å. The benzene solvate C—C distances range from 1.348 (9) to 1.368 (8) Å and average 1.36 (1) Å. There are two intermolecular contacts near van der Waals separations, but there are no intermolecular approaches less than van der Waals distances for the Cu complex.

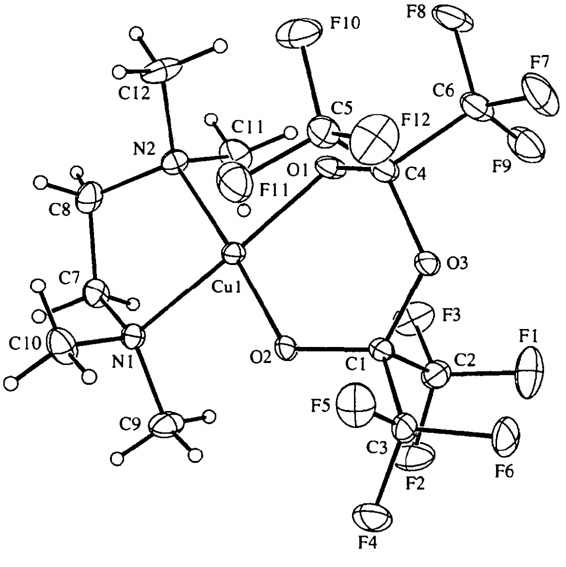


Fig. 1. Displacement ellipsoid plot of the title complex. The benzene solvate molecule has been omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level and H atoms are drawn with arbitrary radii.

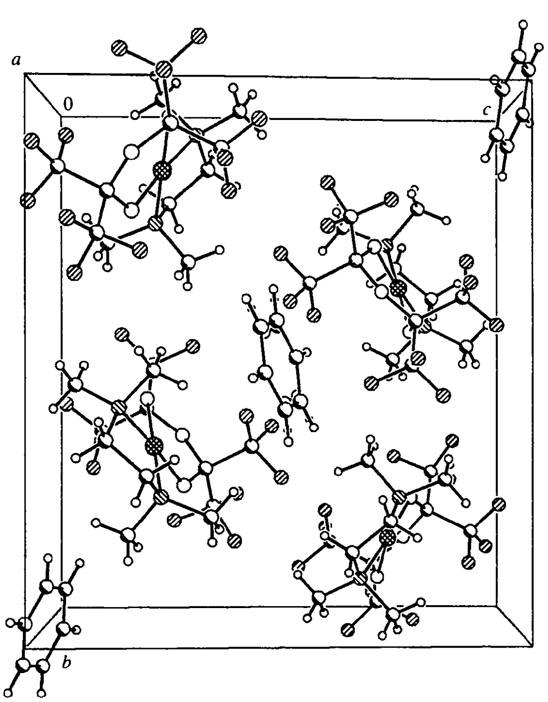


Fig. 2. Packing diagram of title complex viewed down the *a* axis.

Experimental

The synthesis of the title compound has been reported previously (Bradford *et al.*, 1990). It was synthesized here by an alternative method in which copper powder (0.163 g, 2.36 mmol) and an excess of hexafluoroisopropanol and TMEDA were stirred at 363 K under an oxygen atmosphere in a 100 ml bulb. The copper rapidly dissolved into a purple solution. Following solvent removal, the product was recrystallized by slow cooling and evaporation from a benzene/THF solution [isolated yield 1.01 g (69%)].

Crystal data

$[Cu(C_6F_{12}O_3)(C_6H_{16}N_2)].$-$0.5C_6H_6$
$M_r = 566.86$
Monoclinic
$P2_1/n$
$a = 10.020\,(3)$ Å
$b = 15.493\,(4)$ Å
$c = 13.851\,(5)$ Å
$\beta = 93.81\,(3)°$
$V = 2145.5\,(11)$ Å^3
$Z = 4$
$D_x = 1.755$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18–22°$
$\mu = 1.141$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.72 × 0.22 × 0.20 mm
Ruby

Data collection

Siemens *R3m/V* diffractometer
$\theta/2\theta$ scans
Absorption correction: face index numeric
$T_{\min} = 0.51$, $T_{\max} = 0.80$
5394 measured reflections
4944 independent reflections
3124 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.058$
$\theta_{\max} = 27.55°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 20$
$l = -18 \rightarrow 17$
3 standard reflections monitored every 97 reflections intensity decay: 2.0%

Refinement

Refinement on F^2
$R(F) = 0.052$
$wR(F^2) = 0.125$
$S = 1.03$
4943 reflections
298 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.6927P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	0.20727 (4)	0.84773 (3)	0.73942 (3)	0.02676 (13)
O1	0.0872 (3)	0.7714 (2)	0.7961 (2)	0.0370 (7)
O2	0.0758 (2)	0.9346 (2)	0.7200 (2)	0.0322 (6)
O3	−0.1048 (2)	0.8616 (2)	0.7868 (2)	0.0336 (6)
N1	0.3420 (3)	0.9212 (2)	0.6746 (2)	0.0327 (7)
N2	0.3560 (3)	0.7601 (2)	0.7597 (2)	0.0354 (8)
C1	−0.0538 (3)	0.9152 (2)	0.7133 (3)	0.0306 (8)
C2	−0.0942 (4)	0.8709 (3)	0.6149 (3)	0.0436 (11)
C3	−0.1351 (4)	0.9996 (3)	0.7242 (3)	0.0410 (10)
C4	−0.0188 (4)	0.8004 (3)	0.8386 (3)	0.0352 (9)
C5	0.0230 (4)	0.8433 (3)	0.9372 (3)	0.0465 (11)
C6	−0.1155 (5)	0.7241 (3)	0.8523 (4)	0.0488 (12)
C7	0.4558 (4)	0.8638 (3)	0.6541 (3)	0.0443 (11)
C8	0.4829 (4)	0.8015 (3)	0.7361 (4)	0.0481 (12)
C9	0.2887 (5)	0.9620 (3)	0.5839 (3)	0.0579 (14)
C10	0.3834 (5)	0.9888 (3)	0.7454 (4)	0.0575 (13)
C11	0.3208 (5)	0.6889 (3)	0.6913 (4)	0.0554 (13)
C12	0.3696 (5)	0.7245 (3)	0.8592 (3)	0.0600 (14)
F1	−0.2211 (3)	0.8457 (2)	0.6058 (2)	0.0820 (10)
F2	−0.0741 (3)	0.9228 (2)	0.5410 (2)	0.0723 (9)
F3	−0.0203 (3)	0.8016 (2)	0.6018 (2)	0.0647 (8)
F4	−0.1086 (3)	1.0575 (2)	0.6572 (2)	0.0639 (8)
F5	−0.1047 (3)	1.0352 (2)	0.8092 (2)	0.0610 (8)
F6	−0.2672 (2)	0.9872 (2)	0.7176 (2)	0.0648 (8)
F7	−0.2205 (3)	0.7448 (2)	0.9020 (2)	0.0722 (9)
F8	−0.0541 (3)	0.6585 (2)	0.8994 (2)	0.0658 (8)
F9	−0.1627 (3)	0.6938 (2)	0.7678 (2)	0.0707 (9)
F10	0.0765 (3)	0.7860 (2)	1.0002 (2)	0.0732 (9)
F11	0.1149 (3)	0.9033 (2)	0.9273 (2)	0.0684 (9)
F12	−0.0766 (3)	0.8804 (2)	0.9800 (2)	0.0768 (9)
C1*S*	0.5681 (7)	1.0661 (4)	0.9606 (4)	0.076 (2)
C2*S*	0.4428 (7)	1.0792 (4)	0.9916 (5)	0.075 (2)
C3*S*	0.3759 (5)	1.0139 (6)	1.0309 (4)	0.077 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—O2	1.889 (2)	O3—C4	1.440 (5)
Cu1—O1	1.894 (3)	N—$C_{\rm ave}$	1.480 (5)
Cu1—N1	2.021 (3)	N1—C7	1.488 (5)
Cu1—N2	2.022 (3)	N2—C8	1.480 (5)
O1—C4	1.327 (4)	C—$C_{\rm ave}$	1.54 (2)
O2—C1	1.330 (4)	C7—C8	1.501 (6)
O3—C1	1.433 (4)	C—$F_{\rm ave}$	1.327 (6)
O2—Cu1—O1	92.73 (11)	C1—O3—C4	120.4 (3)
O2—Cu1—N1	90.90 (12)	C7—N1—Cu1	106.9 (2)
O1—Cu1—N1	175.61 (12)	C8—N2—Cu1	108.3 (2)
O2—Cu1—N2	176.73 (12)	O2—C1—O3	118.3 (3)
O1—Cu1—N2	90.31 (12)	O1—C4—O3	118.2 (3)
N1—Cu1—N2	86.11 (13)	N1—C7—C8	110.0 (3)
C4—O1—Cu1	121.4 (2)	N2—C8—C7	109.4 (3)
C1—O2—Cu1	121.2 (2)		

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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