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Bis(cyclooctene)copper(I) Trifluoromethanesulfonate

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Abstract. $[Cu(C_8H_{14})_2]CF_3SO_3$, $M_r = 433{\cdot}01$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}340\,(1)$, $b = 16{\cdot}600\,(5)$, $c = 22{\cdot}370\,(5)$ Å, $V = 1983{\cdot}0\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}450$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 12{\cdot}4$ cm^{-1}, $F(000) = 904$, $T = 295$ K, final $R = 0{\cdot}0388$ for 1481 reflections $[I > 2{\cdot}5\sigma(I)]$. The structure consists of chains, parallel to the short *a* axis, of $Cu(cyclooctene)_2^+$ cations [Cu—(C=C) = 2·05 Å ave.] connected by bridging trifluoromethanesulfonate anions with one short [2·049 (4)] and one long [2·433 (4) Å] Cu—O contact.

Introduction. Copper(I) salts have been used extensively as catalysts for photochemical transformations of olefins (*e.g.* Kropp, 1979; Salomon, 1983; Moggi, Juris, Sandrini & Manfrin, 1981, 1984; Hennig, Rehorek & Archer, 1985); reactions observed include *cis*⇌*trans* isomerization, skeletal rearrangement, and di-and trimerizations. Although these latter reactions have been postulated to occur in the coordination sphere of the copper ion, implying the presence of $Cu(olefin)_2^+$ and $Cu(olefin)_3^+$ complexes under reaction conditions, the number of such complexes reported to date is very limited. In fact, the only compounds containing more than one C=C π bond coordinated to a single Cu atom that have been structurally characterized are Cu_2Cl_2(*trans*-cyclooctene)$_3$ (Ganis, Lepore & Martuscelli, 1970), [CuCl(1,5-cyclooctadiene)]$_2$ (Van den Hende & Baird, 1963) and possibly [CuCl(1,3,5,7-cyclooctatetraene)]$_n$ (Baenziger, Richards & Doyle, 1964). However, Evers (1979) obtained evidence for the formation of several $Cu(olefin)_n^+$ complexes in solution.

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The title compound is the first complex containing two molecules of an unstrained monoolefin coordinated to a single copper(I) ion to be characterized by X-ray diffraction analysis.

Experimental. Material obtained by slow crystallization from a solution of CuOTf(cyclooctene) (OTf $= CF_3SO_3$, trifluoromethanesulfonate, triflate) in neat cyclooctene.* Crystal of approximate dimensions $0·10 \times 0·25 \times 0·75$ mm, sealed under nitrogen in a Lindemann-glass capillary, mounted on an Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation. Lattice parameters and e.s.d.'s derived from the setting angles of 32 reflections ($11 < \theta < 12°$). Total of 2082 unique reflections measured in ω-scan mode ($0·91 < \theta < 25°$; $0 \leq h \leq 6$, $0 \leq k \leq 19$, $0 \leq l \leq 26$), of which 1481 were considered as observed [$I > 2·5\sigma(I)$]. Data were corrected for Lp and for a small linear decay during the data collection (4% after 33 h of X-ray exposure time), but not for absorption since ψ-scan data showed this effect to be small. Structure determined by standard Patterson and Fourier methods. All non-hydrogen atoms refined anisotropically, H atoms placed at calculated positions ($d_{CH} = 1·08$ Å) with fixed U values. The full-matrix least-squares refinement on F converged at $R = 0·0388$, $wR = 0·0356$ [$w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0·04$, $S = 1·21$, 226 independent parameters]. All peaks in the final difference Fourier map were inside the range $-0·3$ to $0·4$ e Å^{-3}. The atomic scattering factors used were those of Cromer & Mann (1968), corrected for anomalous dispersion (Cromer & Liberman, 1970).

Refinement of the opposite enantiomorph to determine the absolute structure resulted in an insignificantly higher R value. Programs used include *SHELX76* (structure refinement: Sheldrick, 1976), *PLATO* (geometry analysis) and *PLUTO* (plotting program) (Spek, 1982).

Table 1. *Final positional and equivalent isotropic thermal parameters* (Å^2)

	x	y	z	U_{eq}*
Cu	0·1387 (2)	0·16981 (4)	0·25023 (4)	0·0409 (3)
S	0·5758 (4)	0·2917 (1)	0·2231 (1)	0·0393 (6)
O(1)	0·7238 (8)	0·2192 (2)	0·2243 (2)	0·048 (2)
O(2)	0·664 (1)	0·3570 (2)	0·2580 (2)	0·066 (2)
O(3)	0·3088 (8)	0·2761 (2)	0·2275 (2)	0·044 (2)
C(1)	0·606 (2)	0·3264 (5)	0·1462 (3)	0·060 (3)
F(1)	0·8424 (9)	0·3461 (3)	0·1342 (2)	0·084 (2)
F(2)	0·535 (1)	0·2718 (3)	0·1073 (2)	0·087 (2)
F(3)	0·470 (1)	0·3924 (3)	0·1375 (2)	0·101 (2)
C(11)	0·136 (1)	0·0515 (4)	0·2074 (3)	0·041 (2)
C(12)	0·208 (1)	0·1081 (4)	0·1684 (3)	0·037 (3)
C(13)	0·051 (1)	0·1401 (4)	0·1170 (3)	0·046 (2)
C(14)	0·096 (2)	0·0911 (4)	0·0601 (3)	0·054 (3)
C(15)	0·067 (2)	0·0000 (4)	0·0685 (3)	0·058 (3)
C(16)	−0·170 (2)	−0·0298 (4)	0·0970 (3)	0·059 (3)
C(17)	−0·158 (2)	−0·0537 (4)	0·1632 (3)	0·053 (3)
C(18)	−0·124 (1)	0·0139 (4)	0·2083 (3)	0·044 (3)
C(21)	0·088 (1)	0·2027 (4)	0·3430 (3)	0·040 (3)
C(22)	0·004 (1)	0·1277 (4)	0·3364 (2)	0·043 (3)
C(23)	0·125 (2)	0·0541 (4)	0·3614 (3)	0·053 (3)
C(24)	0·030 (2)	0·0381 (4)	0·4253 (3)	0·070 (4)
C(25)	0·038 (2)	0·1068 (5)	0·4682 (3)	0·080 (4)
C(26)	0·281 (2)	0·1513 (5)	0·4756 (3)	0·086 (4)
C(27)	0·305 (2)	0·2311 (4)	0·4414 (3)	0·072 (3)
C(28)	0·327 (1)	0·2253 (4)	0·3736 (3)	0·052 (3)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Selected bond distances* (Å) *and bond and torsion angles* (°)

Cu–O(1^i)	2·433 (4)	C(16)–C(17)	1·53 (1)
Cu–O(3)	2·049 (4)	C(17)–C(18)	1·52 (1)
Cu–C(11)	2·185 (7)	C(18)–C(11)	1·52 (1)
Cu–C(12)	2·130 (7)	C(21)–C(22)	1·33 (1)
Cu–C(21)	2·163 (7)	C(22)–C(23)	1·49 (1)
Cu–C(22)	2·173 (5)	C(23)–C(24)	1·54 (1)
S–O(1)	1·440 (4)	C(24)–C(25)	1·49 (1)
S–O(2)	1·416 (4)	C(25)–C(26)	1·50 (1)
S–O (3)	1·452 (5)	C(26)–C(27)	1·54 (1)
C(11)–C(12)	1·34 (1)	C(27)–C(28)	1·52 (1)
C(12)–C(13)	1·52 (1)	C(28)–C(21)	1·50 (1)
C(13)–C(14)	1·53 (1)		
C(14)–C(15)	1·53 (1)		
C(15)–C(16)	1·50 (1)		

O(1^i)–Cu–O(3)	93·1 (1)	O(3)–Cu–C(12)	97·1 (2)
O(1^i)–Cu–C(11)	101·1 (2)	O(3)–Cu–C(21)	94·4 (2)
O(1^i)–Cu–C(12)	96·6 (2)	O(3)–Cu–C(22)	130·1 (2)
O(1^i)–Cu–C(21)	91·7 (2)	C(11)–Cu–C(12)	36·1 (2)
O(1^i)–Cu–C(22)	91·0 (2)	C(21)–Cu–C(22)	35·8 (2)
O(3)–Cu–C(11)	131·9 (2)		

C(18)–C(11)–C(12)–C(13)	−4 (1)	C(28)–C(21)–C(22)–C(23)	4 (1)
C(11)–C(12)–C(13)–C(14)	−90 (1)	C(21)–C(22)–C(23)–C(24)	88 (1)
C(12)–C(13)–C(14)–C(15)	52 (1)	C(22)–C(23)–C(24)–C(25)	−50 (1)
C(13)–C(14)–C(15)–C(16)	52 (1)	C(23)–C(24)–C(25)–C(26)	−53 (1)
C(14)–C(15)–C(16)–C(17)	−102 (1)	C(24)–C(25)–C(26)–C(27)	100 (1)
C(15)–C(16)–C(17)–C(18)	70 (1)	C(25)–C(26)–C(27)–C(28)	−70 (1)
C(16)–C(17)–C(18)–C(11)	−71 (1)	C(26)–C(27)–C(28)–C(21)	72 (1)
C(17)–C(18)–C(11)–C(12)	82 (1)	C(27)–C(28)–C(21)–C(22)	−83 (1)

Symmetry code: (i) $x - 1, y, z$.

Discussion. The final positional and equivalent isotropic thermal parameters are listed in Table 1.† Important bond lengths, bond angles and torsion angles are collected in Table 2. The title compound consists of a copper ion which is approximately trigonally surrounded by a triflate oxygen and the two cyclooctene π bonds. These molecules form infinite chains parallel to the short a axis *via* a weak axial coordination of the copper ion to an oxygen atom of a second triflate ion (related to the first by a unit translation along **a**). The chain structure is illustrated in Fig. 1. Overall, the coordination geometry around Cu is best described as trigonal pyramidal. The geometry of the staggered triflate anion is similar to those in CuOTf(cyclohexene) (Timmermans, Mackor, Spek & Kojić-Prodić, 1984),

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* The crystals easily lose cyclooctene, disintegrating to a white powder analyzing correctly for CuOTf(cyclooctene). They are only stable when wet with cyclooctene.

† Lists of anisotropic thermal parameters, H-atom parameters, bond distances, bond angles and torsion angles, structure factors, and a compilation of copper–olefin bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44258 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

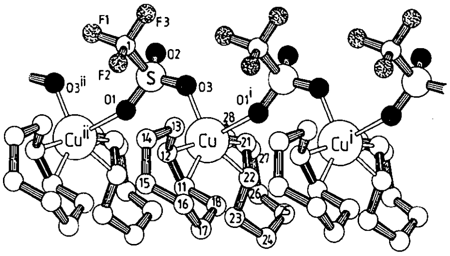

Fig. 1. *PLUTO* drawing showing three units of the chain structure of CuOTf(cyclooctene)$_2$ with the adopted numbering scheme.

with the longer S—O bonds corresponding to Cu—O interactions; bridging triflate anions have also been found in CuOTf(benzene)$_{1/2}$ (Dines & Bird, 1973). The cyclooctene ligands have a boat-twist conformation and are nearly each other's mirror images (*cf.* the torsion angles in Table 2).

The most interesting aspect of the present structure is the copper–olefin interaction. The distances from Cu to the midpoints of the two double bonds are nearly equal (2·05 Å ave.), although one of the two π bonds is coordinated somewhat asymmetrically (see Table 2). According to *ab initio* calculations (Merchan, Gonzalez-Luque, Nebot-Gil & Tomas, 1984) such a deformation from the ideal geometry costs very little energy; thus, it may simply be caused by packing forces here. Values for the Cu$^{\text{I}}$–olefin bond lengths reported to date have been deposited. They are seen to vary over a range of 1·88–2·2 Å, and the present complex fits in at the upper part of the range. As far as it is possible to generalize from this limited set of data, it appears that bis(olefin)copper(I) complexes have longer Cu–olefin bonds than mono(olefin) complexes. In accord with this, CuOTf(cyclooctene)$_2$ easily loses one molecule of cyclooctene, but the last molecule is retained tenaciously. Tris(olefin)copper(I) complexes are probably only isolable for very strongly coordinating olefins.

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Structures of Catalytically Related Species Involving Copper(II) Halides. IV. Bis(2,6-diamino-3,5-dichloropyridinium) Tetrachlorocuprate(II)

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Abstract. $2C_5H_6Cl_2N_3^+.CuCl_4^{2-}$, $M_r = 563·4$, monoclinic, $P2_1/c$, $a = 8·931$ (4), $b = 13·584$ (7), $c = 16·054$ (5) Å, $\beta = 92·77$ (3)°, $V = 1945$ (1) Å^3, $Z = 4$, $D_x = 1·92$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 22·6$ cm^{-1}, $F(000) = 1116$, $T = 295$ K, $R = 0·040$ for 2056 unique observed reflections with $F \geq 3\sigma(F)$. The