THE CRYSTAL AND MOLECULAR STRUCTURE OF COPPER(I) TRIFLUOROMETHANESULPHONATE CYCLOHEXENE COMPLEX

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Summary

The first crystal structure of a copper(I) trifluoromethanesulphonate (cyclo)olefin complex, viz. copper(I) triflate-cyclohexene, $CuOSO_2CF_3 \cdot C_6H_{10}$, is presented. The compound crystallises in the space group $P\bar{1}$ with a 10.288(1), b 10.412(1), c 11.059(1) Å, α 65.81(1), β 81.25(1), γ 70.45(1)° and $Z = 4$. The structure has been solved by Patterson and Fourier methods and refined to a final $R = 0.062$. The compound consists of tetrameric units which are interconnected by Cu–O–Cu bridges to give an infinite chain. The tetramer has S_i symmetry. Both Cu ions are four-coordinated with a geometry that is intermediate between trigonal pyramidal and tetrahedral. The copper ions in the tetramer are joined together by oxygen–sulphur–oxygen bridges of the triflate anion.

Introduction

In recent years copper(I) trifluoromethanesulphonate (triflate, OTf) has been used in a number of studies as a catalyst for the photoisomerisation and photodimerisation of (cyclo)alkenes and their derivatives [1]. The interest in its use arises from its superiority over cuprous halides. The very weak coordinating properties of the triflate anion do not interfere with the coordination of the (cyclo)alkene molecules to copper, and no dominating metal-anion clusters (like those found in cuprous halide complexes) occur in solution. Until now only one crystal structure of a cuprous triflate complex, viz. $(Cu^{I}OTf)_2 \cdot$ benzene, had been reported [2]. However, the structure of complexes of cuprous halide with *trans*-cyclooctene [3,4] and norbornadiene [5] have been established.

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The structure of the $Cu^IOTf \cdot$ cyclohexene complex has been studied because $Cu^IOTf \cdot$ (cyclo)olefin complexes can exist in solution in 1/1, 1/2 and 1/3 metal-to-ligand ratios, the three compounds being in dynamic equilibrium, and also because the coordination around copper ions by triflate anion and by cyclohexene can be arranged in several ways. It is likely that the coordination number and arrangement around copper will influence the photochemistry of the system in solution [6].

Experimental

White powder of $Cu^IOTf \cdot C_6H_{10}$ was prepared as previously described [7]. Colourless single crystals were prepared by slow crystallisation from hot toluene under nitrogen.

Data collection and structure determination

Intensities were collected, for a crystal mounted under nitrogen in a Lindemann glass capillary, on an Enraf–Nonius CAD-4F diffractometer in the $\omega/2\theta$ scan mode. Crystal data and details of the structure analysis are listed in Table 1.

TABLE 1

CRYSTAL DATA AND DETAILS OF THE STRUCTURE ANALYSIS

(a) Crystal data	
Formula	$C_7H_{10}CuF_3O_3S$
M_r	294.75
Crystal system	Triclinic
Space group	$P\bar{1}$
$a(\text{Å})$	10.288(1)
$b(\text{Å})$	10.412(1)
$c(\text{Å})$	11.059(1)
$\alpha(°)$	65.81(1)
$\beta(°)$	81.25(1)
$\gamma(°)$	70.45(1)
$U(\text{Å}^3)$	1018.2(2)
Z	4
D_X (g cm^{-3})	1.923
$F(000)$ electrons	592
$\mu(\text{Cu-}K_\alpha)$	49.99 cm^{-1}
(b) Data collection	
θ_{min}, $\theta_{max}(°)$	0.1, 70.0
$\omega/2\theta$ scan with parameters A and B	
in width $A + B \tan \theta$	$0.60 + 0.14$
Horizontal and vertical apertures (mm)	1.3, 4.0
Standard reflexions	$\bar{1}\,3\,0, \bar{2}\,1\,2, \bar{2}\,0\,\bar{2}$
Total data	3876
Total unique data	3864
Observed data $I > 2.5\sigma(I)$	2511
(c) Refinement	
No. of variables	273
g in $w^{-1} = \sigma^2(F_0) + g\,F_0^2$	0.0008
Final $R_F = \Sigma|\Delta F|/\Sigma|F_0|$	0.062
$R_{wF} = [\Sigma w|\Delta F|^2/\Sigma w|F_0|^2]^{1/2}$	0.077
(Shift/error)max.	0.308 for x of C(24)
Residual electron density min., max. (eÅ^{-3})	-0.65, 0.70

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares methods [8] minimising $\Sigma \ w(\Delta F)^2$. After the isotropic refinement ($R_F = 0.12$), an empirical absorption correction [9] was applied and further refinement in the anisotropic mode proceeded. The hydrogen atoms were introduced at calculated positions and refined in the riding mode on their carrier atoms. Convergence was reached at $R_F = 0.062$. Final refined parameters are given in Table 2. The scattering factors used were taken from ref. 10, 11, and 12.

Illustrations and geometrical calculations have been carried out with the programs of the Euclid package [13]. Calculations were done on either the in-house Eclipse S/230 minicomputer or on the Cyber-175 of the University of Utrecht.

Description and discussion of the crystal structure

The most important distances and bond angles, with their standard deviations, are given in Table 3.

The unit cell contains two crystallographically independent $Cu^I OTf \cdot C_6 H_{10}$ molecules (Fig. 1) which are joined into a tetramer $[Cu_4(CF_3SO_3)_4(C_6H_{10})_4]$ (through the operation of an inversion center) forming the basic structural unit (Fig. 2). Both copper ions are four-coordinate with three triflate groups and one π-bonding cyclohexene (Fig. 1). One triflate anion acts as a tridentate, bridging ligand (O(11), O(12), O(13)) coordinating to Cu(21), Cu(21B), and Cu(11), respectively. The other triflate anion interacts with O(23) and the symmetry-related O(23A) as a double O-bridge between Cu(11) and Cu(11A) (Fig. 2) at unequal distances (2.048(5), 2.587(6) Å); the atoms in this bridge are related through an inversion center, thus being strictly coplanar, with Cu(11)...Cu(11A) 3.740(2) Å. The O(22) atom is coordinated to Cu(21), but O(21) is not engaged in the coordination. Thus there is an infinite chain, along a with O(23) as the double bridge. The coordination around
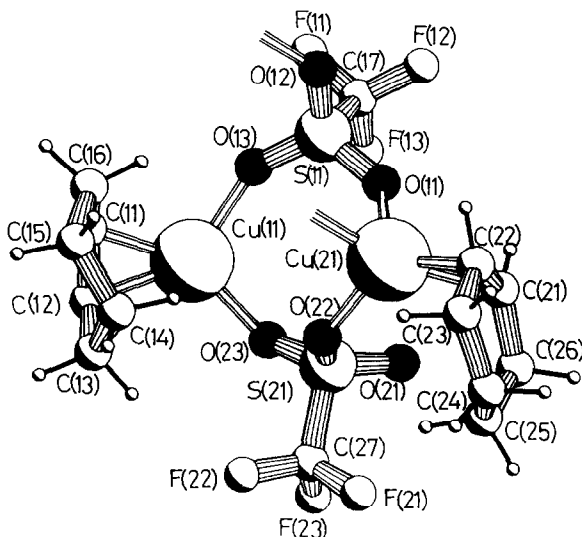
Fig. 1. The asymmetric unit of the structure of copper(I) triflate cyclohexene complex along with the adopted numbering scheme. Oxygen atoms are indicated as black spheres.

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS FOR THE COPPER(I) TRIFLATE CYCLOHEXENE COMPLEX

	x/a	y/b	z/c	$U_{1,1}$ or U	$U_{2,2}$	$U_{3,3}$	$U_{2,3}$	$U_{1,3}$	$U_{1,2}$
Cu(11)	0.1025(1)	0.0824(1)	0.0570(1)	0.0416(7)	0.0369(6)	0.0331(6)	−0.0160(5)	0.0046(5)	−0.0111(5)
Cu(21)	0.5072(1)	−0.2837(1)	0.1459(1)	0.0356(7)	0.0310(6)	0.0571(8)	−0.0151(6)	−0.0093(6)	−0.0052(5)
S(11)	0.3800(2)	0.0282(2)	−0.1389(2)	0.029(1)	0.0306(9)	0.0272(8)	−0.0116(7)	0.0012(7)	−0.0094(7)
S(21)	0.1863(2)	−0.2647(2)	0.1579(2)	0.029(1)	0.0298(9)	0.0350(9)	−0.0076(7)	−0.0076(8)	−0.0061(7)
F(11)	0.2849(6)	0.2037(5)	−0.3749(5)	0.079(3)	0.050(2)	0.045(2)	−0.005(2)	−0.014(2)	−0.008(2)
F(12)	0.4371(6)	0.0011(6)	−0.3659(5)	0.075(3)	0.083(3)	0.046(2)	−0.036(2)	0.009(2)	−0.014(2)
F(13)	0.2341(6)	0.0033(7)	−0.2948(5)	0.083(3)	0.101(3)	0.060(2)	−0.021(2)	−0.021(2)	−0.056(2)
F(21)	0.1197(6)	−0.4928(5)	0.3746(6)	0.071(3)	0.044(2)	0.072(3)	0.015(2)	−0.018(2)	−0.015(2)
F(22)	0.0516(6)	−0.2863(6)	0.3825(6)	0.067(3)	0.079(2)	0.068(2)	−0.032(2)	0.023(2)	−0.027(2)
F(23)	−0.0112(6)	−0.3791(6)	0.2697(6)	0.054(2)	0.090(3)	0.085(3)	−0.015(2)	−0.007(2)	−0.044(2)
O(11)	0.4270(6)	−0.1301(5)	−0.0739(5)	0.054(3)	0.031(2)	0.033(2)	−0.006(2)	−0.007(2)	−0.006(2)
O(12)	0.4860(5)	0.0983(5)	−0.1668(5)	0.035(2)	0.041(2)	0.038(2)	−0.18(2)	0.002(2)	−0.013(2)
O(13)	0.2537(6)	0.1024(6)	−0.0865(6)	0.038(2)	0.049(2)	0.050(2)	−0.020(2)	0.015(2)	−0.008(2)
O(21)	0.2199(6)	−0.3551(6)	0.0824(6)	0.052(3)	0.045(2)	0.050(2)	−0.026(2)	−0.012(2)	−0.001(2)
O(22)	0.2997(5)	−0.2541(6)	0.2120(5)	0.032(2)	0.050(2)	0.039(2)	−0.013(2)	−0.004(2)	−0.016(2)
O(23)	0.0839(5)	−0.1211(5)	0.0979(5)	0.035(2)	0.029(2)	0.043(2)	−0.005(2)	−0.012(2)	−0.005(2)
C(11)	0.0627(9)	0.2658(9)	0.1041(8)	0.051(3)	0.039(3)	0.038(3)	−0.014(2)	−0.010(3)	0.002(3)
C(12)	−0.0084(9)	0.1777(8)	0.1865(8)	0.048(3)	0.042(3)	0.034(3)	−0.016(2)	0.003(3)	−0.009(3)
C(13)	0.0364(9)	0.080(1)	0.3263(8)	0.046(3)	0.062(3)	0.036(3)	−0.017(2)	0.014(3)	−0.025(3)
C(14)	0.185(1)	0.064(1)	0.3455(9)	0.067(3)	0.073(3)	0.046(3)	−0.012(3)	−0.013(3)	−0.022(3)
C(15)	0.216(1)	0.207(1)	0.2884(9)	0.049(3)	0.081(3)	0.064(3)	−0.027(3)	−0.008(3)	−0.035(3)
C(16)	0.197(1)	0.2819(9)	0.1393(8)	0.063(3)	0.053(3)	0.043(3)	−0.009(2)	0.001(3)	−0.035(3)
C(17)	0.3320(9)	0.0599(9)	−0.3035(8)	0.045(3)	0.045(3)	0.038(3)	−0.012(2)	−0.006(3)	−0.017(3)
C(21)	0.6076(8)	−0.4927(8)	0.1416(7)	0.037(3)	0.037(3)	0.033(3)	−0.013(2)	−0.001(2)	−0.002(2)

C(22)	0.6892(8)	−0.4553(8)	0.2005(8)	0.040(3)	0.036(3)	0.0444(3)	−0.009(2)	−0.004(3)	−0.007(2)
C(23)	0.716(1)	−0.523(1)	0.3455(9)	0.066(3)	0.052(3)	0.055(3)	−0.006(3)	−0.022(3)	−0.022(3)
C(24)	0.658(1)	−0.648(1)	0.414(1)	0.094(3)	0.109(3)	0.59(3)	−0.010(3)	−0.022(3)	−0.046(3)
C(25)	0.538(1)	−0.645(1)	0.368(1)	0.083(3)	0.092(3)	0.072(3)	−0.003(3)	0.006(3)	−0.053(3)
C(26)	0.5340(9)	−0.6037(8)	0.2164(9)	0.053(3)	0.035(3)	0.060(3)	−0.018(2)	−0.012(3)	−0.012(2)
C(27)	0.0963(9)	−0.3609(9)	0.3039(8)	0.039(3)	0.042(3)	0.043(3)	−0.007(2)	0.002(3)	−0.018(2)
H(111)	0.0258(9)	0.3318(9)	0.0043(8)	0.092(4)					
H(121)	−0.1010(9)	0.2217(8)	0.1255(8)	0.092(4)					
H(131)	−0.0287(9)	0.128(1)	0.3927(8)	0.092(4)					
H(132)	0.0257(9)	−0.027(1)	0.3494(8)	0.092(4)					
H(141)	0.251(1)	−0.006(1)	0.2968(9)	0.092(4)					
H(142)	0.206(1)	0.013(1)	0.4503(9)	0.092(4)					
H(151)	0.149(1)	0.278(1)	0.3359(9)	0.092(4)					
H(152)	0.322(1)	0.188(1)	0.3082(9)	0.092(4)					
H(161)	0.187(1)	0.3976(9)	0.1070(8)	0.092(3)					
H(162)	0.285(1)	0.2304(9)	0.0900(8)	0.092(3)					
H(211)	0.5966(8)	−0.4388(8)	0.0353(7)	0.092(3)					
H(221)	0.7368(8)	−0.3714(8)	0.1386(8)	0.092(3)					
H(231)	0.826(1)	−0.561(1)	0.3598(9)	0.092(3)					
H(232)	0.667(1)	−0.441(1)	0.3875(9)	0.092(3)					
H(241)	0.638(1)	−0.659(1)	0.516(1)	0.092(3)					
H(242)	0.737(1)	−0.745(1)	0.409(1)	0.092(3)					
H(251)	0.521(1)	−0.752(1)	0.418(1)	0.092(3)					
H(252)	0.454(1)	−0.563(1)	0.392(1)	0.092(3)					
H(261)	0.4277(9)	−0.5580(8)	0.1862(9)	0.092(3)					
H(262)	0.5821(9)	−0.7017(8)	0.1950(9)	0.092(3)					

The temperature facture has the form $\exp(-T)$ where $T = 8\pi^2 U(\sin\theta/\lambda)^2$ for isotropic atoms; $T = 2\pi^2 \sum_{ij} h_i h_j U_{ij} a_i^{\star} a_j^{\star}$ for anisotropic atoms.

both Cu^I ions includes two short Cu–O bonds (in the range 2.043(6)–2.110(6) Å) and a long one (2.587(6) and 2.385(6) Å). The structure of a mixed-valence copper complex, containing substituted acetylacetonate and benzoate ligands, with Cu^I in a

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR THE NON-HYDROGEN ATOMS

Cu(11)–O(23)	2.048(5)	S(11)–C(11)	1.438(6)	C(11)–C(12)	1.33(1)
Cu(11)–O(23A)	2.587(6)	S(11)–O(13)	1.445(6)	C(11)–C(16)	1.57(1)
Cu(11)–C(11)	2.076(9)	S(21)–O(21)	1.429(7)	C(12)–C(13)	1.50(1)
Cu(11)–C(12)	2.060(9)	S(21)–O(27)	1 819(9)	C(13)–C(14)	1.52(1)
Cu(11)–O(13)	2.043(6)	S(21)–O(23)	1.460(6)	C(14)–C(15)	1.49(1)
Cu(21)–O(12B)	2.061(6)	S(21)–O(22)	1.443(6)	C(15)–C(16)	1.52(1)
Cu(21)–C(22)	2.070(8)	F(11)–C(17)	1.33(1)	C(21)–C(22)	1 37(1)
Cu(21)–O(11)	2.385(6)	F(12)–C(17)	1.30(1)	C(21)–C(26)	1.49(1)
Cu(21)–O(22)	2.110(5)	F(13)–C(17)	1.30(1)	C(22)–C(23)	1.49(1)
Cu(21)–C(21)	2.091(8)	F(21)–C(27)	1.33(1)	C(23)–C(24)	1.48(2)
S(11)–O(12)	1.436(6)	F(22)–C(27)	1.33(1)	C(24)–C(25)	1 39(2)
S(11)–C(17)	1.83(1)	F(23)–C(27)	1.31(1)	C(25)–C(26)	1.55(2)

O(13)–Cu(11)–O(23)	103.9(2)		Cu(11)–O(23)–Cu(11A)	107.1(2)
O(13)–Cu(11)–O(23A)	95.0(2)		Cu(11)–O(23)–S(21)	127.4(3)
O(13)–Cu(11)–C(11)	104.7(3)		Cu(11A)–O(23)–S(21)	121.4(3)
O(13)–Cu(11)–C(12)	141.9(3)		Cu(11)–C(11)–C(12)	70.6(5)
O(23)–Cu(11)–O(23A)	73.0(2)		Cu(11)–C(11)–C(16)	112.4(6)
O(23)–Cu(11)–C(11)	150.7(3)		C(12)–C(11)–C(16)	125.5(8)
O(23)–Cu(11)–C(12)	113.3(3)		Cu(11)–C(12)–C(11)	71.9(6)
O(23A)–Cu(11)–C(11)	110.9(3)		Cu(11)–C(12)–C(13)	110.6(6)
O(23A)–Cu(11)–C(12)	103.4(3)		C(11)–C(12)–C(13)	121.4(8)
C(11)–Cu(11)–C(12)	37.5(3)		C(12)–C(13)–C(14)	111.6(8)
O(11)–Cu(21)–O(12B)	88.3(2)		C(13)–C(14)–C(15)	113.0(8)
O(11)–Cu(21)–O(22)	88.7(2)		C(14)–C(15)–C(16)	112.0(9)
O(11)–Cu(21)–C(21)	105.2(3)		C(11)–C(16)–C(15)	109.4(8)
O(11)–Cu(21)–C(22)	127.0(3)		F(11)–C(17)–F(12)	108.9(7)
O(12B)–Cu(21)–O(22)	92.9(2)		F(11)–C(17)–F(13)	107.4(7)
O(12B)–Cu(21)–C(21)	150.0(3)		S(11)–C(17)–F(11)	110.2(6)
O(12B)–Cu(21)–C(22)	112.5(3)		F(12)–C(17)–F(13)	108.5(8)
O(22)–Cu(21)–C(21)	113.8(3)		S(11)–C(17)–F(12)	111.1(6)
O(22)–Cu(21)–C(22)	134.9(3)		S(11)–C(17)–F(13)	110.6(6)
C(21)–Cu(21)–C(22)	38.4(3)		Cu(21)–C(21)–C(22)	70.0(5)
O(11)–S(11)–O(12)	114.6(3)		Cu(21)–C(21)–C(26)	114.0(6)
O(11)–S(11)–O(13)	115.9(4)		C(22)–C(21)–C(26)	123.3(8)
O(11)–S(11)–C(17)	103.8(4)		Cu(21)–C(22)–C(21)	71.6(5)
O(12)–S(11)–O(13)	113.7(4)		Cu(21)–C(22)–C(23)	114.3(6)
O(12)–S(11)–C(17)	103.3(4)		C(21)–C(22)–C(23)	123.9(8)
O(13)–S(11)–C(17)	103.4(4)		C(22)–C(23)–C(24)	111.2(9)
O(21)–S(21)–O(22)	117.1(4)		C(23)–C(24)–C(25)	120(1)
O(21)–S(21)–O(23)	114.6(4)		C(24)–C(25)–C(26)	116(1)
O(21)–S(21)–C(27)	104.0(4)		C(21)–C(26)–C(25)	110.7(8)
O(22)–S(21)–C(23)	112.1(3)		F(21)–C(27)–F(22)	107.4(8)
O(22)–S(21)–C(27)	103.7(4)		F(21)–C(27)–F(23)	108.7(7)
O(23)–S(21)–C(27)	103.2(4)		S(21)–C(27)–F(21)	110.6(6)
Cu(21)–O(11)–S(11)	130.5(4)		F(22)–C(27)–F(23)	107.8(7)
Cu(21B)–O(12)–S(11)	132.4(4)		S(21)–C(27)–F(22)	111.5(6)
Cu(11)–O(13)–S(11)	146.8(4)		S(21)–C(27)–F(23)	110.7(7)
Cu(21)–O(22)–S(21)	129.4(4)			

distorted tetrahedral environment reveals a similarly long Cu–O distance of 2.524(7) Å [14]. However, the structure of the benzene complex of Cu^{I}OTf exhibits a Cu–O distance of 2.22 Å [2]. Such long distances are common for Cu^{II} octahedral species with tetragonal distortion.

The Cu^I–C(=C) distances in both coordination environments are the same within 3σ (ranging from 2.060(9) to 2.091(8) Å). They agree with the values found in the benzene complex of copper(I) triflate [2]. Both Cu^I ions are four-coordinate, with a geometry intermediate between trigonal pyramidal and tetrahedral. The distance of Cu to the basal plane through the oxygen atoms of two short Cu–O bonds and the center of the double bond is inversely related to the distance to the apical oxygen atom of the longer Cu–O bond (Cu(11): 0.102, 2.587 Å; Cu(21): 0.357, 2.385 Å). Bond angles O–Cu–O in the Cu(21) polyhedron are close to 90° (88.3(2), 88.7(2), 92.9(2)°), whereas in Cu(11) they are more scattered (73.0(2), 95.0(2), 103.9(4)°).

The C=C distances in both cyclohexene rings correspond to C(sp^2)–C(sp^2) hybridisation (1.33(1), 1.37(1) Å). However, other distances and bond angles of cyclohexene contributing to the Cu(21) coordination show greater deviations from the standard values (Table 3). Bond angles involving C(13), C(14), C(15), and C(16) are in the range 109.4(8)–113.0(8)°; those including C(23), C(24), C(25), and C(26) are in the range 110.7(8)–120(1)°. The significant deviations from the usual values for C(sp^3) show a C(24)–C(25) bond of 1.39(2) Å, with two large bond angles of 120(1) and 116(1)°. However, the relatively large anisotropic temperature factors of some of the ring atoms preclude definite conclusions. Aliphatic bond distances in the C(11) → C(16) cyclohexene ring range from 1.49(1) to 1.57(1) Å. This ring exhibits a symmetrical half-chair conformation, with C(14) and C(15) displaced from the plane of four atoms (Fig. 1). Ring-puckering analysis, according to Cremer and Pople [15], gives parameters θ 130(1), 52(2)°; φ 26(2), 218(3)°; ψ 0.47(1), 0.33(1) for C(11) →
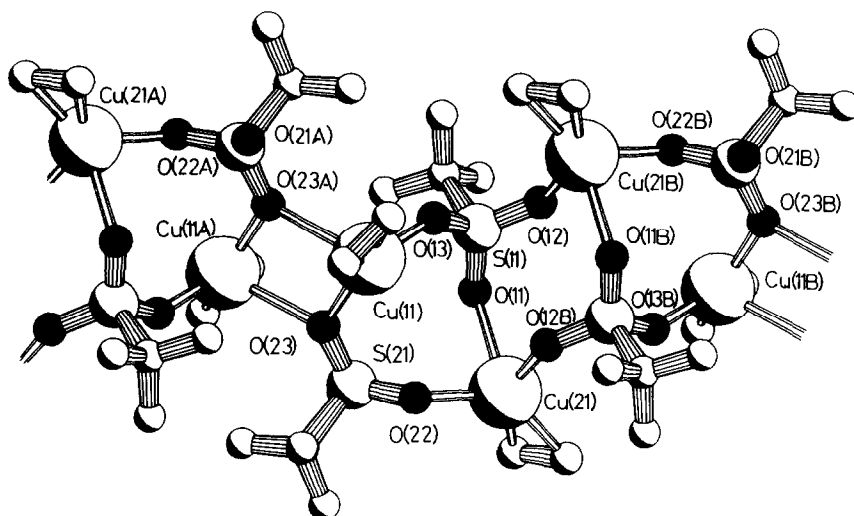

Fig. 2. Part of the infinite Cu^{I}OTf chain running in the a direction. The tetrameric structural unit consists of the units associated with Cu(11), Cu(21), Cu(21B) and Cu(11B). The cyclohexene ring is represented by the double bond only, for clarity. A designates the symmetry operation $-x, -y, -z$ and B the operation $1 - x, -y, -z$.

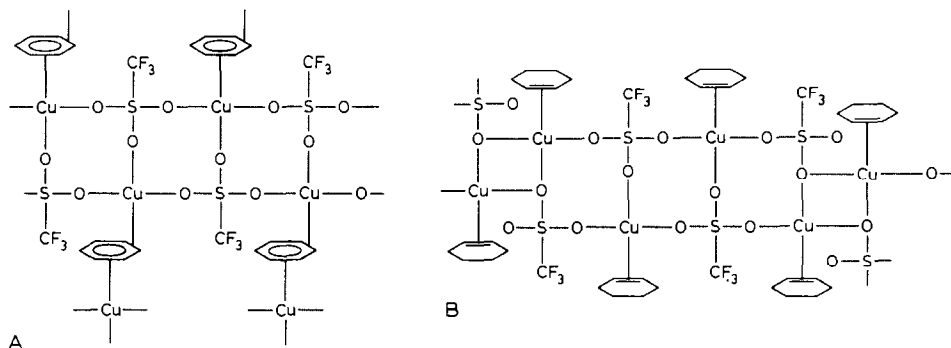Fig. 3. Schematic presentation of the chain structures of the complexes of copper(I) triflate with benzene (A) and cyclohexene (B).

C(16) and C(21) → C(26) rings, respectively. The C(21) → C(26) ring has a somewhat irregular half-chair conformation. The atoms C(21), C(22), and C(23) are coplanar, with the least-squares plane through the ring (deviations 0.03, 0.05, and 0.06 Å); C(24) and C(26) are shifted (0.21 and 0.10 Å) towards one side and C(25) (− 0.23 Å) towards the other one. This puckered part of the ring shows irregular bonding features. The geometries of both triflate groups are similar in spite of their somewhat different bonding properties. The S–O, C–F, and C–S bond lengths of both triflate anions are comparable within 3σ (Table 3). In the structure of a cubane-like Cu^{II} tetramer containing triflate anions [16], there are coordinated and uncoordinated triflate groups; the mean value of the S–O bond distances is 1.417(10) Å for two free anions and 1.430(8), 1.437(21) Å for two coordinated ones. In the title structure the S–O bonds have lengths in the range expected for coordinated species, ranging from 1.429(7) (for O(21)) to 1.460(6) Å (for O(23)). The C–F distances and angles are unaffected by the coordination of the triflate ion to the metal, as shown by comparison with the free anions [16]. Both anions are in an almost ideal staggered conformation with the values of the torsion angles in the intervals 58.1(7)–60.9(7)° for the ion containing S(11) and 57.1(7)–63.6(7)° for the one containing S(21).

Conclusion

The structure of the cyclohexene complex is in general consistent with that of the previously studied benzene complex [2] (Fig. 3). It is noteworthy that, despite the very poor coordinating properties of the triflate anion, its oxygens compete effectively for coordination to one or even two copper ions at the expense of another copper–olefin bond.

This study relates to our investigation of the mechanism of the copper-catalyzed photochemical cycloaddition of (cyclo)alkenes. The structure confirms our views on the bonding of the cyclohexene ligand.

Acknowledgement

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