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Bis(benzyldi-2-pyridylamine)-η^2,η'^2-(*s-trans*-isoprene)dicopper(I) bistrifluoromethanesulfonate. A stable Cu^I-diene complex

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Abstract

Addition of benzyldi-2-pyridylamine and isoprene to a solution of $[Cu(O_3SCF_3)]_2 \cdot C_6H_6$ in THF yields $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$, the title complex. This complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.721(4)$ Å, $b = 14.099(4)$ Å, $c = 14.179(4)$ Å, $\alpha = 80.01(2)°$, $\beta = 78.17(2)°$, $\gamma = 71.80(2)°$, $V = 2063.6$ Å^3, and $Z = 2$. The structure, which contains disordered triflate ligands, converged to an $R = 0.086$ and $R_w = 0.132$ for 2887 reflections of $I > 3\sigma(I_o)$. It exhibits the isoprene ligand in the *s-trans* configuration chelating η^2 to both Cu^I atoms.

1. Introduction

In addition to the proposed role of copper coordination at the ethylene binding site of biological systems [1], copper(I) compounds have been found to be efficient catalysts for photoinduced [2 + 2] [2] and [4 + 2] [3] cycloaddition reactions of monoolefins and dienes. Reduced oxide catalysts that contain Cu^I also find application in the selective hydrogenation of polyenes, such as the industrial hydrogenation of fatty oils [4]. Therefore, the synthesis, molecular structures, and bonding modes of copper(I)–olefin and –polyolefin complexes have been the subject of considerable research in recent years. Known monomeric η^2-ethylene complexes of Cu^I contain di-2-pyridylamine [5], bipyridine [6] and phenanthroline [6] ligands.

Several complexes between Cu^I and dienes are known [7]. The $[(1,5\text{-cyclooctadiene})CuCl]_2$ complex has been characterized crystallographically [8]. In this compound, the 1,5-COD ligand behaves as a bidentate chelate to complete a tetrahedral coordination sphere about Cu^I. A monomeric complex Cu(hexafluoroacetylacetonate)(1,5-COD) contains the COD ligand chelated to a single Cu^I with one weakly bound double bond (Cu–C 2.466(8) Å and 2.550(7) Å) and one normally ligated double bond (Cu–C 2.049(6) Å and 2.089(7) Å) [9]. Complexes of CuCl with dicyclopentadiene and 1,7-octadiene, where the diene functions as a bridging ligand, have been structurally characterized [10,11]. Little is known about the binding of linear polyenes to Cu^I. Recently the X-ray crystal structure of a polymeric complex between isoprene and copper(I) chloride $[Cu_2Cl_2(C_5H_8)]$ has been reported [12]. This compound is extremely unstable at room temperature, or in the air, and decomposes above −50°C. By using the benzyldi-2-pyridylamine ligand, we have been able to obtain a thermally stable dimeric 2 : 1 Cu–isoprene complex. Here we report its synthesis and molecular structure.

2. Experimental section

2.1. General

All work was conducted under dinitrogen and in dried solvents using standard Schlenk techniques. $[Cu(O_3SCF_3)]_2 \cdot C_6H_6$ was prepared using the method of Salomon and Kochi [7].

2.2. Synthesis of benzyldi-2-pyridylamine (1)

To a solution of 5.2 g (0.093 mol) of potassium hydroxide in 30 ml of DMSO, 2,2-dipyridylamine (3.42 g, 0.020 mol) was added with stirring. Stirring was continued for 45 min before 2.53 g (2.30 ml, 0.020 mol) of benzyl chloride was added dropwise. After 1 h the

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solution was diluted with 30 ml of water. Then the sticky yellow product was isolated by filtration, washed with water (3 × 10 ml), and dried under vacuum overnight. Ligand **1** recrystallizes from hot hexanes on cooling to 5°C as yellow crystals (2.5 g, 48%). Anal. Found: C, 78.1; H, 5.86; N, 16.1. $C_{17}H_{15}N_3$ calc.: C, 78.1; H, 5.79; N, 16.1%.

2.3. *Synthesis of bis(benzyldi-2-pyridylamine)-η^2,η'^2-(s-trans-isoprene)dicopper(I) (2)*

Addition of 1 ml of isoprene and 0.26 g of benzyldi-2-pyridylamine to a solution of $[Cu(O_3SCF_3)]_2 \cdot C_6H_6$ (0.26 g) in 10 ml of THF resulted in the precipitation of a pale yellow complex, which was washed with additional THF (2 × 4 ml) to yield 0.31 g (60%) of $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$ (**2**). ^1H NMR (CD_3OD): δ 8.24 (d, 4H); 7.92 (t, 4H); 7.24–7.51 (multiplet, 18H); 5.27 (s, 4H), for the coordinated benzyldi-2-pyridylamine; δ 5.93 (dd, 1H); 4.99 (s, 1H); 4.80 (s, 1H); 4.40 (multiplet, 2H); 1.84 (s, 3H), with vicinal *trans* and *cis* coupling of 16 and 10 Hz, respectively, for coordinated isoprene. Anal. Found: C, 50.49; H, 4.39; N, 8.13. $C_{41}H_{38}N_6O_6F_6S_2Cu_2$ calc.: C,

TABLE 1. Summary of crystal data, intensity collection and refinement for $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$

Formula	$C_{41}H_{38}N_6O_6F_6S_2Cu_2$
Formula weight	1016.0
Crystal color	yellow
Crystal size (mm)	0.2 × 0.2 × 0.4
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.721(4)
b (Å)	14.099(4)
c (Å)	14.179(4)
α (°)	80.01(2)
β (°)	78.17(2)
γ (°)	71.8(2)
Volume (Å^3)	2163.6(15)
Z	2
d_{calc} (g cm^{-3})	1.559
μ (mm^{-1})	1.155
Scan type	2θ
Scan speed (° min^{-1})	variable; 4.00–20.00
Scan range (°)	$3 \leq 2\theta \leq 45$
Unique reflections	6843
No. of reflections ($I > 3.0\sigma(I)$)	2887
No. of parameters	323
R	0.086
R_w	0.132
Largest residual peak (e Å^{-3})	0.87
GOF	0.80

TABLE 2. Atomic coordinates (×10^4) and isotropic temperature factors (Å^2 × 10^3) for $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$

	x	y	z	U_{eq} [a]
Cu(1)	−1679(2)	1629(1)	2837(1)	48(1)
Cu(2)	1359(2)	3348(1)	1784(1)	48(1)
N(1)	−2182(10)	393(8)	3055(8)	48(3)
N(2)	−2823(10)	766(8)	1524(9)	47(3)
N(3)	−2922(10)	2335(8)	1986(8)	45(3)
N(4)	1867(10)	4581(8)	1658(8)	43(3)
N(5)	2516(9)	4035(8)	3172(8)	41(3)
N(6)	2635(10)	2551(8)	2560(8)	43(3)
C(1)	−119(16)	1424(12)	3301(13)	71(5)
C(2)	−414(14)	2383(11)	2815(11)	55(4)
C(3)	38(13)	2633(11)	1807(11)	53(4)
C(4)	−224(15)	3609(12)	1354(13)	68(4)
C(5)	508(18)	1796(14)	1167(14)	59(5)
C(6)	−3720(34)	3211(24)	5435(29)	142(22)
C(7)	3665(20)	3312(19)	−1551(19)	74(12)
C(8)	−2697(12)	128(10)	2431(10)	44(3)
C(9)	−3127(15)	−708(12)	2626(12)	64(4)
C(10)	−3004(15)	−1281(12)	3479(12)	64(4)
C(11)	−2477(15)	−1031(13)	4153(13)	71(5)
C(12)	−2054(14)	−220(12)	3913(12)	61(4)
C(13)	−2962(15)	277(13)	728(11)	65(5)
C(15)	−2368(11)	1006(9)	−1997(7)	87(6)
C(16)	−1253	1214	−2137	83(5)
C(17)	−698	1164	−1341	86(6)
C(18)	−1258	907	−406	65(4)
C(19)	−2373	699	−266	53(4)
C(14)	−2928	749	−1062	69(5)
C(20)	−3350(12)	1800(10)	1499(10)	44(3)
C(21)	−4282(13)	2324(11)	946(10)	51(4)
C(22)	−4789(12)	3317(10)	958(10)	47(3)
C(23)	−4353(13)	3836(11)	1461(11)	54(4)
C(24)	−3419(12)	3316(10)	1958(10)	45(3)
C(25)	2377(11)	4766(9)	2337(9)	36(3)
C(26)	2845(12)	5576(10)	2221(10)	43(3)
C(27)	2649(13)	6290(11)	1416(11)	52(4)
C(28)	2055(14)	6133(11)	725(12)	57(4)
C(29)	1721(13)	5279(11)	862(11)	54(4)
C(30)	2484(12)	4430(10)	4074(10)	47(3)
C(32)	791(9)	3603(8)	4818(6)	67(4)
C(33)	52	3268	5626	72(5)
C(34)	216	3332	6558	80(5)
C(35)	1118	3730	6682	89(6)
C(36)	1857	4064	5874	64(4)
C(31)	1693	4001	4942	48(3)
C(37)	3035(11)	3010(9)	3140(9)	33(3)
C(38)	3975(12)	2423(10)	3692(10)	50(4)
C(39)	4384(13)	1422(11)	3668(10)	49(4)
C(40)	3987(14)	959(12)	3114(11)	57(4)
C(41)	3101(13)	1556(11)	2549(11)	52(4)
S(1)	−3215(5)	2041(5)	5202(4)	69(3)
O(1)	−3191(12)	2212(11)	4170(8)	68(6)
O(2)	−2036(14)	1698(14)	5512(10)	94(9)
O(3)	−4070(17)	1546(15)	5777(14)	118(11)
F(1)	−3111(23)	3836(14)	5045(17)	173(15)
F(2)	−4918(17)	3659(13)	5346(14)	139(10)
F(3)	−3849(17)	3270(17)	6469(15)	155(12)
S(2)	2928(6)	2554(6)	−581(4)	69(3)
O(4)	2710(13)	3027(12)	261(9)	73(7)
O(5)	3947(22)	1548(14)	−531(19)	141(14)

TABLE 2 (continued)

	x	y	z	U_{eq} [a]
O(6)	1961(13)	2462(13)	−976(10)	88(9)
F(4)	4647(14)	3356(13)	−1300(9)	101(8)
F(5)	3912(17)	2929(17)	−2347(11)	142(12)
F(6)	2980(22)	4204(16)	−1700(18)	176(14)
S(2′)	2337(33)	3116(26)	−705(25)	94(10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

48.47; H, 3.77; N, 8.27%. Crystals suitable for X-ray diffraction studies were obtained by dissolving **2** in the minimum amount of methanol and cooling to 5°C.

2.4. X-Ray structure determination

All X-ray data were collected with the use of a Nicolet R$\bar{3}$m/V automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined from 25 machine centered reflections with 15° < 2θ < 30°. Intensities of three check reflections were monitored after every 197 reflections during data collection. No absorption correction was applied. All calculations were carried out on a Microvax II computer with the SHELXTL PLUS program package. Disorder was observed in the weakly bound triflate counterions. Two sites were observed for S(2) of 0.79 and 0.21 occupancy. Only the major species was refined for S(1). The six largest features in the final difference Fourier map (0.71 to 0.87 e Å^{-3}) were clustered near the disordered triflate counterions.

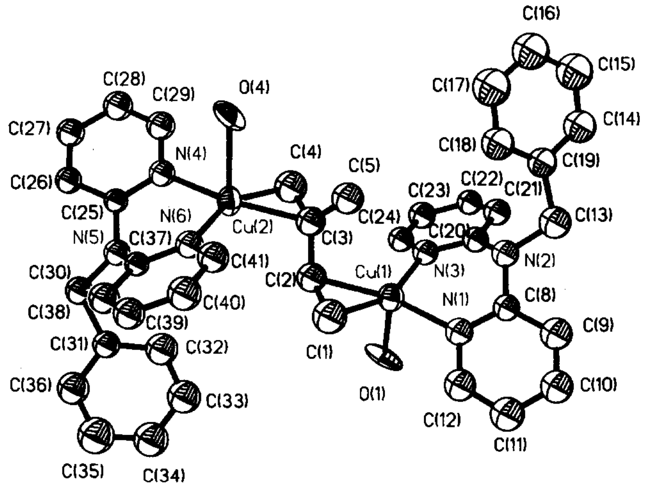

Fig. 1. Molecular structure of $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$ (50% thermal ellipsoids). Only the weakly bound oxygen of each O_3SCF_3 group is shown.

3. Results and discussion

The crystal and intensity data for **2** from an X-ray structure determination are given in Table 1. Final atomic positional parameters for nonhydrogen atoms of complex **2** are shown in Table 2. The molecular structure of **2** (Fig. 1) shows that the nearly planar isoprene fragment (mean deviation of 0.053 Å from diene plane) adopts the *s-trans* conformation. Each Cu^I atom binds η^2 to a localized double bond on opposite faces of the diene. This resembles the structure found for bridging butadiene in polymeric $[Cu_2Cl_2(C_5H_8)]$ [12] and in η^2,η'^2-butadiene-bis[η^2-butadiene(2,2′-bipyridyl)nickel(0)] [13]. The Cu-C distances (Cu(1)-C(1) = 1.99 ± 0.02 Å, Cu(1)-C(2) = 2.07 ± 0.02 Å, Cu(2)-C(3) = 2.09 ± 0.02 Å, and Cu(2)-C(4) = 1.98 ± 0.02 Å) are similar to that found in the $[Cu_2Cl_2(C_5H_8)]$ complex [12]. The approximate coplanar geometry of the carbon and nitrogen donor atoms about each Cu^I center also resembles that found in related olefin complexes [5,6]. Each Cu atom is dis-

TABLE 3. Bond lengths (Å) for $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$

Cu(1)–N(1)	1.965(13)	Cu(1)–N(3)	1.991(11)
Cu(1)–C(1)	1.990(20)	Cu(1)–C(2)	2.070(19)
Cu(1)–O(1)	2.376(11)	Cu(2)–N(4)	1.976(12)
Cu(2)–N(6)	1.976(11)	Cu(2)–C(3)	2.088(18)
Cu(2)–C(4)	1.978(19)	Cu(2)–O(4)	2.421(12)
N(1)–C(8)	1.327(22)	N(1)–C(12)	1.371(18)
N(2)–C(8)	1.442(17)	N(2)–C(13)	1.481(23)
N(2)–C(20)	1.392(17)	N(3)–C(20)	1.362(22)
N(3)–C(24)	1.320(16)	N(4)–C(25)	1.331(20)
N(4)–C(29)	1.364(17)	N(5)–C(25)	1.428(15)
N(5)–C(30)	1.472(19)	N(5)–C(37)	1.386(15)
N(6)–C(37)	1.358(20)	N(6)–C(41)	1.339(17)
C(1)–C(2)	1.381(21)	C(2)–C(3)	1.442(21)
C(3)–C(4)	1.383(21)	C(3)–C(5)	1.510(25)
C(6)–S(1)	1.636(34)	C(6)–F(1)	1.287(46)
C(6)–F(2)	1.370(41)	C(6)–F(3)	1.457(47)
C(7)–S(2)	1.832(26)	C(7)–F(4)	1.295(33)
C(7)–F(5)	1.276(34)	C(7)–F(6)	1.272(30)
C(7)–S(2′)	1.823(42)	C(8)–C(9)	1.385(24)
C(9)–C(10)	1.341(23)	C(10)–C(11)	1.383(30)
C(11)–C(12)	1.348(26)	C(13)–C(19)	1.544(18)
C(20)–C(21)	1.415(20)	C(21)–C(22)	1.341(19)
C(22)–C(23)	1.367(25)	C(23)–C(24)	1.367(20)
C(25)–C(26)	1.386(21)	C(26)–C(27)	1.391(19)
C(27)–C(28)	1.396(26)	C(28)–C(29)	1.350(24)
C(30)–C(31)	1.538(16)	C(37)–C(38)	1.439(18)
C(38)–C(39)	1.345(20)	C(39)–C(40)	1.333(26)
C(40)–C(41)	1.410(20)	S(1)–O(1)	1.436(13)
S(1)–O(2)	1.447(17)	S(1)–O(3)	1.435(22)
S(2)–O(4)	1.408(16)	S(2)–O(5)	1.544(20)
S(2)–O(6)	1.411(20)	S(2)–S(2′)	0.893(32)
O(4)–S(2′)	1.495(42)	O(6)–S(2′)	1.280(48)
F(6)–S(2′)	2.109(42)		

TABLE 4. Bond angles (°) for $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$

N(1)–Cu(1)–N(3)	92.4(5)	N(1)–Cu(1)–C(1)	112.4(6)
N(3)–Cu(1)–C(1)	152.7(6)	N(1)–Cu(1)–C(2)	151.6(5)
N(3)–Cu(1)–C(2)	113.9(5)	C(1)–Cu(1)–C(2)	39.7(6)
N(1)–Cu(1)–O(1)	88.3(5)	N(3)–Cu(1)–O(1)	87.3(4)
C(1)–Cu(1)–O(1)	103.9(6)	C(2)–Cu(1)–O(1)	102.8(6)
N(4)–Cu(2)–N(6)	93.1(5)	N(4)–Cu(2)–C(3)	151.0(5)
N(6)–Cu(2)–C(3)	113.0(5)	N(4)–Cu(2)–C(4)	112.5(6)
N(6)–Cu(2)–C(4)	152.1(6)	C(3)–Cu(2)–C(4)	39.6(6)
N(4)–Cu(2)–O(4)	85.7(5)	N(6)–Cu(2)–O(4)	92.8(4)
C(3)–Cu(2)–O(4)	104.6(6)	C(4)–Cu(2)–O(4)	99.7(6)
Cu(1)–N(1)–C(8)	123.8(9)	Cu(1)–N(1)–C(12)	119.3(12)
C(8)–N(1)–C(12)	116.8(14)	C(8)–N(2)–C(13)	114.8(12)
C(8)–N(2)–C(20)	121.3(11)	C(13)–N(2)–C(20)	117.2(11)
Cu(1)–N(3)–C(20)	120.3(8)	Cu(1)–N(3)–C(24)	120.2(11)
C(20)–N(3)–C(24)	119.2(12)	Cu(2)–N(4)–C(25)	121.9(8)
Cu(2)–N(4)–C(29)	121.2(11)	C(25)–N(4)–C(29)	116.9(13)
C(25)–N(5)–C(30)	115.1(11)	C(25)–N(5)–C(37)	124.6(11)
C(30)–N(5)–C(37)	117.1(10)	Cu(2)–N(6)–C(37)	119.9(8)
Cu(2)–N(6)–C(41)	121.5(11)	C(37)–N(6)–C(41)	118.6(12)
Cu(1)–C(1)–C(2)	73.3(11)	Cu(1)–C(2)–C(1)	67.0(11)
Cu(1)–C(2)–C(3)	106.3(13)	C(1)–C(2)–C(3)	123.9(13)
Cu(2)–C(3)–C(2)	106.4(12)	Cu(2)–C(3)–C(4)	65.9(11)
C(2)–C(3)–C(4)	122.6(13)	Cu(2)–C(3)–C(5)	111.4(11)
C(2)–C(3)–C(5)	117.8(14)	C(4)–C(3)–C(5)	117.4(14)
Cu(2)–C(4)–C(3)	74.5(10)	S(1)–C(6)–F(1)	120.2(25)
S(1)–C(6)–F(2)	114.0(31)	F(1)–C(6)–F(2)	108.5(25)
S(1)–C(6)–F(3)	111.0(22)	F(1)–C(6)–F(3)	103.0(34)
F(2)–C(6)–F(3)	97.1(24)	S(2)–C(7)–F(4)	108.8(17)
S(2)–C(7)–F(5)	110.4(22)	F(4)–C(7)–F(5)	110.6(19)
S(2)–C(7)–F(6)	111.8(17)	F(4)–C(7)–F(6)	108.3(26)
F(5)–C(7)–F(6)	107.0(24)	S(2)–C(7)–S(2′)	28.3(11)
F(4)–C(7)–S(2′)	124.8(23)	F(5)–C(7)–S(2′)	116.7(26)
F(6)–C(7)–S(2′)	83.9(18)	N(1)–C(8)–N(2)	116.9(13)
N(1)–C(8)–C(9)	123.0(13)	N(2)–C(8)–C(9)	120.0(15)
C(8)–C(9)–C(10)	118.5(18)	C(9)–C(10)–C(11)	120.5(18)
C(10)–C(11)–C(12)	118.2(16)	N(1)–C(12)–C(11)	122.8(18)
N(2)–C(13)–C(19)	111.3(14)	C(13)–C(19)–C(18)	122.7(19)
C(13)–C(19)–C(14)	116.8(9)	N(2)–C(20)–N(3)	119.3(12)
N(2)–C(20)–C(21)	122.0(15)	N(3)–C(20)–C(21)	118.7(12)
C(20)–C(21)–C(22)	120.3(16)	C(21)–C(22)–C(23)	119.8(14)
C(22)–C(23)–C(24)	118.5(13)	N(3)–C(24)–C(23)	123.4(15)
N(4)–C(25)–N(5)	116.4(12)	N(4)–C(25)–C(26)	122.7(12)
N(5)–C(25)–C(26)	120.7(13)	C(25)–C(26)–C(27)	118.7(15)
C(26)–C(27)–C(28)	118.8(15)	C(27)–C(28)–C(29)	118.0(14)
N(4)–C(29)–C(28)	124.4(16)	N(5)–C(30)–C(31)	112.0(12)
C(30–C(31)–C(32)	121.9(8)	C(30)–C(31)–C(36)	118.1(8)
N(5)–C(37)–N(6)	118.1(11)	N(5)–C(37)–C(38)	122.5(13)
N(6)–C(37)–C(38)	119.3(11)	C(37)–C(38)–C(39)	119.1(15)
C(38)–C(39)–C(40)	122.1(14)	C(39)–C(40)–C(41)	117.7(14)
N(6)–C(41)–C(40)	123.0(16)	C(6)–S(1)–C(1)	98.7(16)
C(6)–S(1)–O(2)	103.0(18)	O(1)–S(1)–O(2)	115.4(8)
C(6)–S(1)–O(3)	106.1(16)	O(1)–S(1)–O(3)	117.6(12)
O(2)–S(1)–O(3)	113.3(11)	Cu(1)–O(1)–S(1)	133.1(7)
C(7)–S(2)–O(4)	105.9(13)	C(7)–S(2)–O(5)	101.0(11)
O(4)–S(2)–O(5)	111.6(13)	C(7)–S(2)–O(6)	103.7(11)
O(4)–S(2)–O(6)	121.2(10)	O(5)–S(2)–O(6)	110.9(14)
C(7)–S(2)–S(2′)	75.3(24)	O(4)–S(2)–S(2′)	77.5(26)
O(5)–S(2)–S(2′)	170.9(28)	O(6)–S(2)–S(2′)	62.9(30)
Cu(2)–O(4)–S(2)	144.1(11)	Cu(2)–O(4)–S(2′)	126.3(15)
S(2)–O(4)–S(2′)	35.7(13)	S(2)–O(6)–S(2′)	38.4(16)
C(7)–F(6)–S(2′)	59.2(16)	C(7)–S(2′)–S(2)	76.5(23)
C(7)–S(2′)–O(4)	102.7(25)	S(2)–S(2′)–O(4)	66.9(24)
C(7)–S(2′)–O(6)	110.2(24)	S(2)–S(2′)–O(6)	78.8(29)
O(4)–S(2′)–O(6)	124.4(26)	C(7)–S(2′)–F(6)	36.9(11)
S(2)–S(2′)–F(6)	112.8(29)	O(4)–S(2′)–F(6)	111.2(26)
O(6)–S(2′)–F(6)	122.3(25)		

TABLE 4 (continued)

placed from the mean olefin–dipyridyl coordination plane by 0.12–0.13 Å toward the triflate counterion, so the complete coordination shell about Cu can be viewed as square pyramidal. This differs from the tetrahedral Cu^I coordination in $[Cu_2Cl_2(C_5H_8)]$.

Bond lengths within the isoprene ligand (C(1)–C(2) = 1.38 ± 0.02 Å, C(2)–C(3) = 1.44 ± 0.02 Å, C(3)–C(4) = 1.38 ± 0.02 Å) are consistent with a localized double bond binding to each Cu atom. This has also been observed for $[Cu_2Cl_2(C_5H_8)]$ [12]. The Cu-C distances suggest that steric factors favor binding the terminal carbons (C(1) and C(4) of the diene lie closer to the metal than the internal C(2) and C(3) atoms). The O(1) and O(4) oxygens of the two triflate counterions associate weakly along one of the open axial coordination positions at each copper. The Cu(1)–O(1) and Cu(2)–O(4) distances of 2.38(1) Å and 2.42(1) Å, respectively, exceed the normal range of 2.0–2.1 Å found [14] for metal–oxygen bond lengths in first row transition metal complexes that contain O_3SCF_3-. This is consistent with the role of triflate being a weakly associated counterion, and is reflected in its disordered conformation in the crystal lattice.

The structural results suggest alternative intermediates for the catalytic hydrogenation of isoprene by reduced oxides of $CuAl_2O_4$ and $CuCr_2O_x$. Bidentate coordination of isoprene to a single Cu^I center was favored in the mechanism [15], but monodentate or bridging geometries also need to be considered.

4. Supplementary material available

Tables of thermal parameters, positional parameters for hydrogen atoms, bond lengths and bond angles for $Cu_2[(C_6H_5CH_2)N(C_5H_4N)_2]_2(\mu\text{-}C_5H_8)(O_3SCF_3)_2$ (11 pages) and a listing of observed and calculated structure factors (25 pages) are available from the authors.

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