METAL-ORGANIC COMPOUNDS

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Structure of the Copper Tripodal Schiff Base Complex {Tris[4-(2-thienyl)-3-aza-*κN*-3-butenyl]amine-*κN*}copper(I) Tetrafluoroborate

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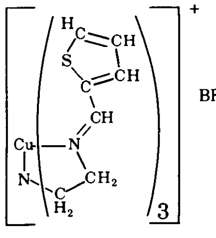
Abstract

The copper Schiff base complex {tris[4-(2-thienyl)-3-aza-*κN*-3-butenyl]amine-*κN*}copper(I) tetrafluoroborate, $[Cu\{N(C_7H_8NS)_3\}]^+.BF_4^-$ (I), crystallizes with the cation residing in a general position and two disordered tetrafluoroborate anions residing on twofold axes. The cation has approximate threefold symmetry and the copper(I) geometry is distorted trigonal pyramidal with coordination from the apical tertiary amine N atom and the three azomethine N atoms but not from the S atoms of the three thiophene moieties. The principal bond lengths are Cu—N_{apical} 2.300 (5) Å and mean Cu—$N_{equatorial}$ 1.994 (4) Å, with a mean Cu···S contact of 3.270 (2) Å.

Comment

The Schiff base ligand tris[4-(2-thienyl)-3-aza-3-butenyl]amine (S_3tren) has been analyzed previously by crystallography, primarily because of its potential use as a heptadentate tripodal ligand (Alyea, Liu, Li, Xu & You, 1989). This ligand has also been used in metal complexation studies with copper(I) and copper(II) salts and two related copper(I) crystal structures have been reported (Alyea, Ferguson, Jennings & Xu, 1990; Alyea, Ferguson, Jennings, Li, Xu, You & Liu, 1990).



(I)

The structure determination of the title compound (I) was undertaken to establish the overall molecular conformation in the solid state and compare it with previous structure determinations. The cation lies in a general position and disordered tetrafluoroborate anions reside on twofold axes.

The copper(I) geometry is distorted trigonal pyramidal with coordination to the Cu atom from the apical tertiary amine N(4) atom and the three azomethine N(1), N(2) and N(3) atoms of the tripodal Schiff base ligand. There is no coordination from the S(1), S(2) and S(3) atoms of the three thiophene moieties. The principal bond lengths include Cu—N_{apical} 2.300 (5), Cu—$N_{equatorial}$ 1.977 (4), 1.992 (4) and 2.012 (5) Å and three Cu···S separations of 3.246 (2), 3.300 (2) and 3.263 (2) Å. The approximate threefold symmetry can be evidenced by the N_{apical}—C_{sp^3}—C_{sp^3}—$N_{equatorial}$ torsion angles, −55.8 (4), −58.8 (4) and −54.7 (4)°, and also by the interplanar angles between the plane through the three equatorial N(1), N(2) and N(3) atoms and the thiophene planes, 64.3 (3), 61.7 (3) and 60.7 (3)°. A comparison of the copper dimensions of this complex with those of two related $[Cu(S_3tren)]^+$ structures is given in Table 3. The molecular geometry of the cation is similar in all three Cu^I derivatives. In all three structures, the Cu—N_{apical} distances are significantly different, but the counterion does not interact with the Cu or apical N atoms in any of the examples.

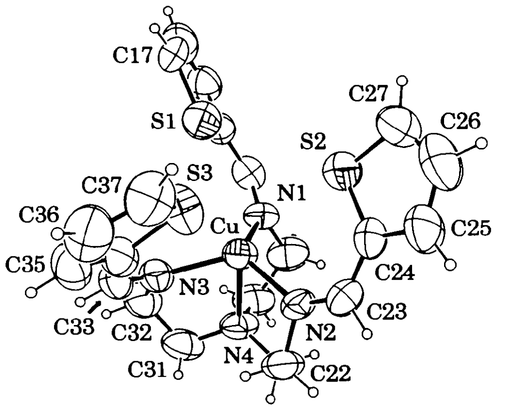


Fig. 1. A view of the cation in (I) showing the general conformation and numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity, H atoms are drawn as small spheres of arbitrary size.

Experimental

Crystal data

$[Cu(C_{21}H_{24}N_4S_3)][BF_4]$
M_r = 578.97
Orthorhombic

Cell parameters from 25 reflections
θ = 9.0 - 18.0°

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Pbcn
$a = 14.840\ (1)$ Å
$b = 19.592\ (1)$ Å
$c = 17.716\ (1)$ Å
$V = 5151\ (1)$ Å^3
$Z = 8$
$D_x = 1.49$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

$\mu = 1.14$ mm^{-1}
$T = 293$ K
Block
$0.30 \times 0.25 \times 0.20$ mm
Orange
Crystal source: recrystallized from acetone

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.718$, $T_{\max} = 0.766$
5313 measured reflections
5313 independent reflections

1857 observed reflections [$I_{\rm net} > 3.0\sigma(I_{\rm net})$]
$\theta_{\max} = 27.0°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity variation: $<1\%$

Refinement

Refinement on F
$R = 0.040$
$wR = 0.047$
$S = 1.30$
1857 reflections
341 parameters
H atoms riding, C—H 0.95 Å
$w = 1/[\sigma^2(F) + 0.0006F^2]$

$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
Cu	0.18341 (5)	0.18869 (3)	0.12864 (4)	0.0624 (4)
S(1)	0.12831 (12)	0.30464 (9)	0.00619 (11)	0.0880 (12)
S(2)	−0.01836 (12)	0.16134 (9)	0.05648 (12)	0.0903 (12)
S(3)	0.19997 (12)	0.13855 (9)	−0.04645 (12)	0.0910 (12)
N(1)	0.1321 (3)	0.26978 (21)	0.1793 (3)	0.067 (3)
N(2)	0.1395 (3)	0.09500 (21)	0.1521 (3)	0.065 (3)
N(3)	0.3114 (3)	0.19387 (23)	0.0917 (3)	0.071 (3)
N(4)	0.2552 (3)	0.17686 (22)	0.2429 (3)	0.074 (3)
C(11)	0.2227 (5)	0.2346 (3)	0.2864 (4)	0.093 (5)
C(12)	0.1293 (5)	0.2556 (3)	0.2611 (4)	0.091 (5)
C(13)	0.1157 (4)	0.3315 (3)	0.1594 (4)	0.070 (4)
C(14)	0.1168 (4)	0.3554 (3)	0.0825 (4)	0.067 (4)
C(15)	0.1031 (4)	0.4240 (3)	0.0596 (4)	0.084 (5)
C(16)	0.1013 (5)	0.4295 (3)	−0.0173 (5)	0.116 (6)
C(17)	0.1142 (4)	0.3707 (4)	−0.0545 (4)	0.096 (5)
C(21)	0.2244 (4)	0.1100 (3)	0.2689 (4)	0.089 (5)
C(22)	0.2080 (4)	0.0635 (3)	0.2023 (4)	0.088 (5)
C(23)	0.0720 (4)	0.0591 (3)	0.1347 (4)	0.075 (4)
C(24)	−0.0030 (4)	0.0808 (3)	0.0885 (3)	0.070 (4)
C(25)	−0.0718 (4)	0.0389 (3)	0.0660 (4)	0.101 (5)
C(26)	−0.1355 (5)	0.0737 (4)	0.0227 (4)	0.111 (6)
C(27)	−0.1155 (4)	0.1387 (4)	0.0123 (4)	0.105 (5)
C(31)	0.3518 (4)	0.1805 (3)	0.2247 (4)	0.090 (5)
C(32)	0.3667 (4)	0.2225 (3)	0.1535 (4)	0.088 (5)
C(33)	0.3539 (4)	0.1685 (3)	0.0346 (4)	0.081 (4)
C(34)	0.3131 (4)	0.1390 (3)	−0.0310 (4)	0.074 (4)
C(35)	0.3578 (4)	0.1068 (3)	−0.0894 (4)	0.085 (5)
C(36)	0.2994 (5)	0.0830 (3)	−0.1436 (4)	0.101 (5)
C(37)	0.2145 (5)	0.0964 (3)	−0.1293 (4)	0.095 (5)
B(1)	0.0000	0.5120 (5)	0.2500	0.085 (8)
F(11)	0.0000	0.4441 (3)	0.2500	0.164 (6)
F(12)	0.0037 (8)	0.5461 (5)	0.1891 (5)	0.155 (8)
F(13)	0.0905 (6)	0.5090 (5)	0.2209 (6)	0.157 (8)
F(14)	−0.0510 (7)	0.5391 (4)	0.1973 (5)	0.149 (7)
B(21)	0.5000	0.3207 (13)	0.2500	0.111 (20)
B(22)	0.5000	0.3738 (7)	0.2500	0.077 (14)
F(21)	0.5000	0.4310 (4)	0.2500	0.317 (15)
F(22)	0.4602 (6)	0.3244 (4)	0.2893 (6)	0.148 (9)
F(23)	0.4075 (6)	0.3883 (5)	0.2173 (6)	0.145 (7)
F(24)	0.4966 (9)	0.3722 (7)	0.3243 (8)	0.230 (12)

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

Cu—N(1)	1.977 (4)	Cu—N(3)	2.012 (5)
Cu—N(2)	1.992 (4)	Cu—N(4)	2.300 (5)
N(1)—Cu—N(2)	121.34 (19)	Cu—N(2)—C(22)	106.5 (3)
N(1)—Cu—N(3)	118.08 (19)	Cu—N(2)—C(23)	136.3 (4)
N(1)—Cu—N(4)	81.93 (18)	Cu—N(3)—C(32)	107.5 (4)
N(2)—Cu—N(3)	115.05 (19)	Cu—N(3)—C(33)	134.2 (4)
N(2)—Cu—N(4)	82.64 (17)	Cu—N(4)—C(11)	115.3 (5)
N(3)—Cu—N(4)	81.63 (19)	Cu—N(4)—C(21)	113.7 (5)
Cu—N(1)—C(12)	107.8 (3)	Cu—N(4)—C(31)	114.7 (4)
Cu—N(1)—C(13)	134.9 (4)		
N(4)—Cu—N(1)—C(12)	−28.7 (3)	N(4)—Cu—N(2)—C(23)	154.0 (4)
N(4)—Cu—N(1)—C(13)	138.3 (4)	N(4)—Cu—N(3)—C(32)	−28.8 (3)
N(4)—Cu—N(2)—C(22)	−26.6 (3)	N(4)—Cu—N(3)—C(33)	137.8 (4)

Table 3. *A comparison of the mean dimensions* (Å) *for three related tripodal Schiff base structures*

Structure	Cu—N$_{\rm ap}$	Cu—N$_{\rm eq}$	Cu···S
$[\mathrm{Cu(S_3tren)}]^+[\mathrm{BF_4}]^-$ [a]	2.300 (5)	1.994 (4)	3.270 (2)
$[\mathrm{Cu(S_3tren)}]^+[\mathrm{I_3}]^-$ [b]	2.275 (3)	2.004 (3)	3.238 (1)
$[\mathrm{Cu(S_3tren)}]^+[\mathrm{BPh_4}]^-$ [c]	2.232 (2)	2.010 (2)	3.344 (1)

References: (*a*) this work; (*b*) Alyea, Ferguson, Jennings & Xu (1990); (*c*) Alyea, Ferguson, Jennings, Li, Xu, You & Liu (1990).

An orange crystal of the title compound was isolated from the attempted reaction between $[\mathrm{Cu(S_3tren)}]^+.[\mathrm{BF_4}]^-$ and quinuclidine in acetone. The ω-scan width was $(0.6 + 0.35\tan\theta)°$ with a θ scan rate of 5.79° min^{-1} and background counts for 5 s on each side of every scan. The systematic absences ($0kl$ absent if $k = 2n + 1$, $h0l$ absent if $l = 2n + 1$, $hk0$ absent if $h + k = 2n + 1$) determine the centrosymmetric space group *Pbcn* (No. 60) uniquely. The H atoms attached to the C atoms were clearly visible in difference maps at an intermediate stage of the refinement; they were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. The $\mathrm{BF_4^-}$ ion containing B(1) lies on a twofold axis and has its F atoms disordered; each F site was assigned an occupancy of 0.5. The other $\mathrm{BF_4^-}$ ion also lies about a twofold axis but has its B atom disordered over two sites [B(21) and B(22)] with occupancies of 0.5; the F atoms are also disordered with site occupancies of 0.5. Such disorder is not uncommon in structures containing the small symmetrical $\mathrm{BF_4^-}$ ion. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71482 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1057]

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Hydrogen-Bonding Patterns in Ferrocene Derivatives: Structures of 1,1′-Diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol and 1,1′-(1,1′-Ferrocenediyl)diethanol

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Abstract

Racemic 1,1′-diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(Ph)MeOH}$_2$] (I), crystallizes as hydrogen-bonded dimeric aggregates with the Fe atoms on twofold crystallographic axes and the four O atoms defining a folded trapezium with O···O distances of 2.784 (2) (×2), 2.877 (3) and 2.795 (4) Å. The four hydroxyl H atoms are disordered equally over two orientations such that there are two half-occupancy H-atom sites between each hydrogen-bonded O-atom pair. Racemic 1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(H)MeOH}$_2$] (II), crystallizes as hydrogen-bonded centrosymmetric dimers, with O···O distances of 2.778 (2) and 2.764 (2) Å and ordered hydroxyl H atoms. In (I), the dimers are formed from either two *RR* or two *SS* molecules, while in (II) the dimers each contain one *RR* and one *SS* molecule.

Comment

We are currently studying the molecular structures and hydrogen-bonding patterns in the crystal lattices of ferrocene-alcohol derivatives. The diol, ferrocene-1,1′-diylbis(diphenylmethanol), [Fe{(C_5H_4)C(Ph)$_2$OH}$_2$] (III) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*), crystallizes with the asymmetric unit comprising two independent half molecules lying on crystallographic twofold axes; these molecules form dimeric aggregates held together by a hydrogen-bonded motif with graph set $R^4_4(8)$ (Etter, MacDonald & Bernstein, 1990), in which the hydroxyl H atoms are all disordered equally over two sites.

The monoalcohols 1,1′-bis(ferrocenyl)-2,2′-dimethylpropan-1-ol, [(C_5H_5)Fe(C_5H_4)]$_2$C(CMe_3)OH (Sharma, Cervantes-Lee & Pannell, 1992), and ferrocenyl(diphenyl)methanol, [(C_5H_5)Fe(C_5H_4)]CPh_2OH (IV) (Ferguson, Gallagher, Glidewell & Zakaria, 1993), crystallize as hydrogen-bonded dimeric aggregates with a hydrogen-bonded motif characterized by the graph set $R^2_2(4)$. However, in racemic 1-ferrocenyl-1-phenylethanol, [(C_5H_5)-Fe(C_5H_4)]CPhMeOH (V), where the steric demands about the central C atom are considerably less, there is no O—H···O hydrogen bonding in the crystal structure (Ferguson, Gallagher, Glidewell & Zakaria, 1993).

The extent and nature of the hydrogen bonding in ferrocenyl monoalcohols of the type [(C_5H_5)Fe(C_5H_4)]-C*R′R″*OH is clearly not a function solely of the steric demands about the central C atom, as appears to be the case in, for example, the series $(Ph)_x(PhCH_2)_{3-x}COH$ (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992; Ferguson, Gallagher, Glidewell & Zakaria, 1994). Hence, in order to assess further the effects on the hydrogen-bonding patterns in the crystal structures of ferrocenediols by the changes in substituents at the central C atom, we have determined the structures of 1,1′-diphenyl-1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(Ph)-MeOH}$_2$] (I), and 1,1′-(1,1′-ferrocenediyl)diethanol, [Fe{(C_5H_4)C(H)MeOH}$_2$] (II).

[Fe{(C_5H_4)C(Ph)MeOH}$_2$] (I) crystallizes in the centrosymmetric space group *C*2/*c* with two independent half molecules in the asymmetric unit; both Fe atoms lie on a crystallographic twofold axis. The molecules are hydrogen bonded to form a dimeric structural motif with graph set $R^4_2(8)$ (Fig. 1). The O atoms form a flattened trapezium with hydrogen-bonded O···O distances 2.784 (2) (×2), 2.877 (3) and 2.795 (4) Å. Difference maps showed that within the dimeric aggregate, the hydroxyl H atoms are each disordered equally over two sites, while directed towards the two neighbouring hydroxyl O atoms, as shown

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