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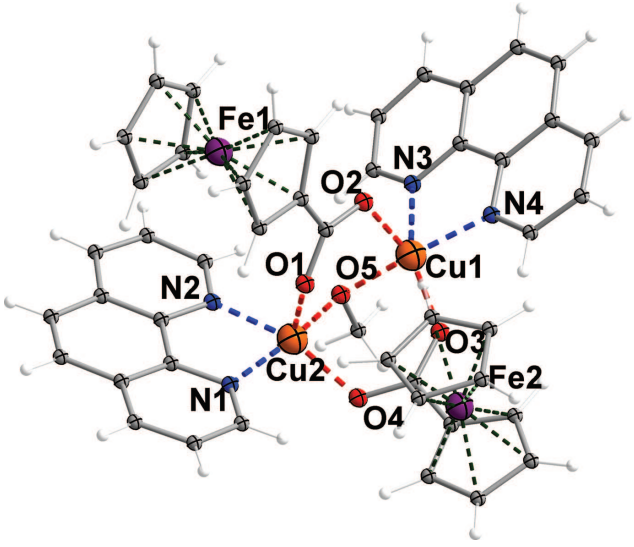
Crystal structure of bis(μ$_2$-ferrocenecarboxylato-κ^2*O*:*O*′)-bis(1,10-phenanthroline-κ^2*N*,*N*′)-(μ$_2$-*methanolato*-κ^2*O*,*O*)dicopper(II) tetrafluoroborate – acetonitrile (1/1), $C_{49}H_{40}BCu_2F_4Fe_2N_5O_5$



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Abstract

$C_{49}H_{40}BCu_2F_4Fe_2N_5O_5$, triclinic, $P\bar{1}$ (no. 2), $a = 11.526(2)$ Å, $b = 12.902(2)$ Å, $c = 15.469(3)$ Å, $\alpha = 95.632(2)°$, $\beta = 107.789(2)°$, $\gamma = 96.251(2)°$, $V = 2156.3(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0443$, $wR_{ref}(F^2) = 0.1198$, $T = 100(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Blue-green block
Size:	0.21 × 0.20 × 0.19 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	17.1 cm^{-1}
Diffractometer, scan mode:	Bruker CCD, *φ* and *ω*
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	15093, 7571, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5704
$N(param)_{refined}$:	637
Programs:	SHELX [1], DIAMOND [2], Bruker programs [3]

Parts of the title crystal structure are shown using a ball-and-stick scheme in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Blue-green crystals of $[Cu(II)_2(FcCOO)_2(phen)_2(CH_3O)]BF_4 \cdot CH_3CN$ were prepared by treating ferrocenecarboxylic acid (FcCOOH) with $Cu(CH_3CN)_4BF_4$ in methanol in molar ratio 1:1. To the resulting solution, equivalent amounts of triethylamine and 1,10-phenantroline (phen) was added. The brown suspension was sealed in a vial that was heated and kept at 343 K for 20 h. Then the solution was cooled to room temperature and filtered, slow evaporation afforded blue-green block crystals of title complex.

Experimental details

All hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms. The acetonitrile molecule shows a positional disorder.

Comment

Heterometallic complexes have attracted great attention in catalysis [4], magnetic materials [5], sensing [6], medical usage [7], etc. metalloligands are the best building blocks

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
B1	0.6060(6)	0.4603(4)	0.6830(4)	0.0358(14)
Cu1	−0.02525(4)	0.17999(4)	0.39136(3)	0.01835(14)
Cu2	−0.02780(4)	0.09554(4)	0.19203(3)	0.01927(14)
Fe2	−0.36557(5)	−0.15626(4)	0.26782(4)	0.01788(15)
Fe1	−0.35154(5)	0.36527(5)	0.08624(4)	0.01868(16)
O1	−0.1984(3)	0.1446(2)	0.18177(19)	0.0276(7)
O2	−0.1781(3)	0.2560(2)	0.30717(18)	0.0234(7)
O3	−0.0881(3)	0.0299(2)	0.37014(18)	0.0220(7)
O4	−0.0700(3)	−0.0375(2)	0.23497(18)	0.0215(6)
O5	0.0727(3)	0.1671(2)	0.31094(17)	0.0214(6)
N1	−0.1151(3)	0.0307(3)	0.0588(2)	0.0221(8)
N2	0.0438(3)	0.2055(3)	0.1291(2)	0.0223(8)
N3	0.0791(3)	0.3172(3)	0.4637(2)	0.0200(8)
N4	−0.1007(3)	0.1950(3)	0.4935(2)	0.0205(8)
N5[a]	−0.5445(8)	0.0991(7)	0.4620(6)	0.087(3)
N5A[b]	−0.6635(17)	0.1209(15)	0.3943(13)	0.082(7)
C1	−0.1991(4)	−0.0546(3)	0.0271(3)	0.0276(10)
H1A	−0.2137	−0.0999	0.0687	0.033*
C2	−0.2674(4)	−0.0796(4)	−0.0671(3)	0.0306(11)
H2A	−0.3271	−0.1411	−0.0880	0.037*
C3	−0.2476(4)	−0.0155(4)	−0.1281(3)	0.0296(11)
H3A	−0.2934	−0.0321	−0.1914	0.035*
C4	−0.1593(4)	0.0745(3)	−0.0964(3)	0.0249(10)
C5	−0.1286(4)	0.1470(4)	−0.1536(3)	0.0284(11)
H5A	−0.1689	0.1335	−0.2180	0.034*
C6	−0.0440(4)	0.2338(4)	−0.1182(3)	0.0301(11)
H6A	−0.0254	0.2795	−0.1582	0.036*
C7	0.0183(4)	0.2585(4)	−0.0215(3)	0.0282(11)
C8	0.1031(4)	0.3494(4)	0.0205(3)	0.0310(11)
H8A	0.1230	0.3998	−0.0155	0.037*
C9	0.1574(4)	0.3651(4)	0.1142(3)	0.0305(11)
H9A	0.2159	0.4259	0.1432	0.037*
C10	0.1255(4)	0.2907(3)	0.1667(3)	0.0268(10)
H10A	0.1639	0.3020	0.2313	0.032*
C11	−0.0090(4)	0.1881(3)	0.0360(3)	0.0196(9)
C12	−0.0955(4)	0.0953(3)	−0.0015(3)	0.0202(9)
C13	0.1709(4)	0.3753(3)	0.4490(3)	0.0236(10)
H13A	0.1990	0.3504	0.4002	0.028*
C14	0.2290(4)	0.4720(3)	0.5021(3)	0.0269(10)
H14A	0.2968	0.5100	0.4906	0.032*
C15	0.1876(4)	0.5112(4)	0.5704(3)	0.0309(11)
H15A	0.2238	0.5781	0.6053	0.037*
C16	0.0901(4)	0.4508(3)	0.5885(3)	0.0241(10)
C17	0.0380(4)	0.4842(4)	0.6581(3)	0.0295(11)
H17A	0.0683	0.5515	0.6938	0.035*
C18	−0.0535(4)	0.4217(3)	0.6736(3)	0.0296(11)
H18A	−0.0845	0.4450	0.7213	0.036*
C19	−0.1044(4)	0.3213(3)	0.6201(3)	0.0241(10)
C20	−0.1996(4)	0.2519(4)	0.6309(3)	0.0296(11)
H20A	−0.2354	0.2708	0.6769	0.035*
C21	−0.2416(4)	0.1572(4)	0.5758(3)	0.0313(11)
H21A	−0.3051	0.1095	0.5839	0.038*
C22	−0.1891(4)	0.1312(3)	0.5067(3)	0.0260(10)
H22A	−0.2186	0.0654	0.4683	0.031*
C23	−0.0569(4)	0.2882(3)	0.5498(3)	0.0198(9)
C24	0.0395(4)	0.3532(3)	0.5341(3)	0.0215(9)
C25	−0.4173(4)	0.2109(3)	0.0797(3)	0.0245(10)
H25A	−0.3990	0.1504	0.0428	0.029*
C26	−0.5161(4)	0.2691(3)	0.0489(3)	0.0289(11)
H26A	−0.5796	0.2567	−0.0133	0.035*
C27	−0.5093(4)	0.3479(4)	0.1224(3)	0.0273(10)
H27A	−0.5665	0.4012	0.1206	0.033*
C28	−0.4049(4)	0.3385(3)	0.1984(3)	0.0236(10)
H28A	−0.3761	0.3841	0.2592	0.028*
C29	−0.3473(4)	0.2541(3)	0.1716(3)	0.0202(9)
C30	−0.2314(4)	0.2168(3)	0.2259(3)	0.0175(9)
C31	−0.1732(4)	0.4161(3)	0.0966(3)	0.0242(10)
H31A	−0.0988	0.3903	0.1359	0.029*
C32	−0.2423(4)	0.3737(4)	0.0042(3)	0.0264(10)
H32A	−0.2250	0.3128	−0.0327	0.032*
C33	−0.3400(4)	0.4328(3)	−0.0259(3)	0.0251(10)
H33A	−0.4040	0.4208	−0.0878	0.030*
C34	−0.3320(4)	0.5108(3)	0.0475(3)	0.0214(9)
H34A	−0.3896	0.5637	0.0461	0.026*
C35	−0.2292(4)	0.5011(3)	0.1233(3)	0.0215(9)
H35A	−0.2010	0.5460	0.1845	0.026*
C36	−0.2229(4)	−0.1664(3)	0.3820(3)	0.0221(9)
H36A	−0.2014	−0.1214	0.4427	0.027*
C37	−0.3036(4)	−0.2632(3)	0.3540(3)	0.0254(10)
H37A	−0.3492	−0.2983	0.3914	0.030*
C38	−0.3084(4)	−0.3019(3)	0.2637(3)	0.0256(10)
H38A	−0.3588	−0.3685	0.2262	0.031*
C39	−0.2319(4)	−0.2286(3)	0.2348(3)	0.0226(9)
H39A	−0.2183	−0.2348	0.1738	0.027*
C40	−0.1787(4)	−0.1435(3)	0.3082(3)	0.0191(9)
C41	−0.1071(4)	−0.0430(3)	0.3045(3)	0.0175(9)
C42	−0.5282(4)	−0.1585(4)	0.1660(3)	0.0411(13)
H42A	−0.5651	−0.2135	0.1112	0.049*
C43	−0.4483(4)	−0.0661(4)	0.1715(3)	0.0345(12)
H43A	−0.4176	−0.0438	0.1213	0.041*
C44	−0.4189(4)	−0.0103(4)	0.2601(3)	0.0329(11)
H44A	−0.3634	0.0585	0.2838	0.039*
C45	−0.4810(5)	−0.0675(4)	0.3095(3)	0.0389(12)
H45A	−0.4777	−0.0466	0.3743	0.047*
C46	−0.5479(4)	−0.1594(4)	0.2519(4)	0.0443(14)
H46A	−0.6013	−0.2154	0.2684	0.053*
C47	0.1791(5)	0.1234(5)	0.3500(4)	0.0591(17)
H47A	0.2251	0.1637	0.4101	0.089*
H47B	0.2306	0.1257	0.3100	0.089*
H47C	0.1562	0.0502	0.3573	0.089*
C48[a]	−0.5099(10)	0.1810(8)	0.4407(8)	0.068(3)
C48A[b]	−0.581(2)	0.1862(16)	0.3960(18)	0.064(6)
C49[a]	−0.478(2)	0.264(2)	0.397(2)	0.059(3)
H49A[a]	−0.3991	0.2578	0.3870	0.089*
H49B[a]	−0.4722	0.3313	0.4345	0.089*
H49C[a]	−0.5421	0.2616	0.3371	0.089*
C49A[b]	−0.474(4)	0.257(5)	0.408(5)	0.059(3)
H49D[b]	−0.4311	0.2789	0.4733	0.089*
H49E[b]	−0.4972	0.3193	0.3784	0.089*
H49F[b]	−0.4199	0.2233	0.3796	0.089*
F1	0.5053(3)	0.4827(3)	0.7045(3)	0.0878(14)
F2	0.6804(3)	0.4135(2)	0.7527(2)	0.0635(10)
F3	0.5736(3)	0.3913(2)	0.6026(2)	0.0543(8)
F4	0.6735(3)	0.5536(2)	0.67552(19)	0.0501(8)

[a]Occupancy: 0.683(11); [b]Occupancy: 0.317(11).

for the construction of heterometallic complexes [8]. Since its discovery, ferrocene has proven to be a versatile backbone for various ligands because of its rich chemistry, stability and redox properties [9]. Ferrocenecarboxylic acid is the mono-carboxylated ferrocene [10] and widely used in the modification of electrode for biosensors and electrocatalytic oxidation [11–13]. As a versatile functionalized ligand, ferrocenecarboxylate is widely used for the construction of heterometallic complexes with other metals. Among them, most of heterodimetallic complexes, such as mononuclear complexes [14–16], polymers [17], clusters [18], and MOFs [19] are reported in the last few years.

The title complex is a dinuclear copper(II) complex with two ferrocenecarboxylato ligands, two 1,10-phenanthroline ligands and one methanolato ligand. Each Cu(II) adopts square pyramid configuration by two nitrogen atoms of the phen ligand, one oxygen atom from the methanolate and the other two from each ferrocenecarboxylato ligand. The phen ligand coordinates in bidentate fashion with an average d(Cu—N) = 2.036(3) Å [range from 2.026(3) Å to 2.043(3) Å]. Each ferrocenecarboxylato ligand bridges two copper ions (*cf.* the figure) with Cu1—O2 = 2.233(3) Å, Cu1—O3 = 1.951(3) Å, Cu2—O1 = 2.095(3) Å, Cu2—O4 = 1.966(3) Å, respectively. The methanolato ligand bridges two copper ions with Cu1—O5 = 1.926(3) Å, Cu2—O5 = 1.926(3) Å, respectively. Those distances are in a reasonable range [20].

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