Crystal structure of *catena*-poly[(1,4-diazabicyclo[2.2.2]octane)tetrakis(2-thiopheneacetato)dicopper(II)], $\text{Cu}_2(\text{C}_6\text{H}_{12}\text{N}_2)(\text{C}_6\text{H}_5\text{O}_2\text{S})_4$

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Abstract

$\text{C}_{30}\text{H}_{32}\text{Cu}_2\text{N}_2\text{O}_8\text{S}_4$, monoclinic, $P12_1/n1$ (no. 14), $a = 9.7712(9)$ Å, $b = 10.734(1)$ Å, $c = 15.457(2)$ Å, $\beta = 98.136(2)^\circ$, $V = 1604.9$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.061$, $wR_{\text{ref}}(F^2) = 0.191$, $T = 298$ K.

Source of material

The complex was synthesized by layer-method using three-layer solutions in a slender tube. The upper layer solution was 5 ml of CH_3OH containing 0.06 M 1,4-diazabicyclo[2.2.2]octane. The bottom layer solution was 5 ml of DMF solution containing 0.03 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.06 M 2-thiopheneacetic acid. The intermediate layer was 5 ml of $\text{CH}_3\text{OH}/\text{DMF}$ (v/v 1:1) mixed solvent. After standing for two weeks, green block-shaped crystals were obtained and collected by suction filtration.

Experimental details

The carbon-bonded H atoms were generated geometrically ($d(\text{C}_{\text{aromatic}}-\text{H}) = 0.93$ Å, $d(\text{C}_{\text{sp}^3}-\text{H}) = 0.97$ Å, $U_{\text{iso}} = 1.2 U_{\text{eq}}$). These were included in the refinement in the riding model approximation. The 1,4-diazabicyclo[2.2.2]octane ligand is in disorder created by the inversion center and considered over two sites. The small U values of C4 may be caused by a little part of disordered sulfur atoms which occupy the C4 position.

Discussion

Thiophene derivatives show biological activities and have been used in pharmaceutical and clinical purpose [1]. Recently, thiophenecarboxylate complexes have received increasing attention, but only seven 2-thiopheneacetate (tpa) complexes have been structurally characterized [1–4]. Two copper complexes of them have a dinuclear $[\text{Cu}_2(\text{COO})_4]$ unit, which has been widely reported in copper(II) carboxylates due to interests in exchange-coupling interactions and special bioactive and biocatalytic functions in the past decades. Herein we present a new 1D 2-thiopheneacetate copper(II) complex containing a dinuclear $[\text{Cu}_2(\text{COO})_4]$ motif.

The complex is a one-dimensional chain containing a dinuclear $[\text{Cu}_2(\text{COO})_4]$ unit, in which each copper(II) atom is coordinated by four oxygen donors of four carboxylate groups from four 2-thiopheneacetate ligands acting in a *syn,syn* bridging mode. The apical position of the copper(II) coordination polyhedron (along the Cu–Cu direction) is occupied by nitrogen atom from the 1,4-diazabicyclo[2.2.2]octane (dbco) ligand. Each dbco bridges two dinuclear $[\text{Cu}_2(\text{COO})_4]$ units and extends the structure into a one-dimensional chain. In the dinuclear $[\text{Cu}_2(\text{COO})_4]$ motif, the Cu–O distances are similar to those of the complex $[\text{Cu}(\text{tpa})_2(\text{DMF})]_2$ [3], but is very different from the complex $[\text{Cu}_2(\text{tpa})_4]_n$ [1]. The Cu–N distance in the title complex is significant longer than Cu–O bond distances due to the apical coordination of the dbco ligand. The Cu–Cu distance in the dimeric units depends on the bridging and apical ligands. The separation of 2.699(1) Å in the title complex is longer than those of $[\text{Cu}(\text{tpa})_2(\text{DMF})]_2$ and $[\text{Cu}_2(\text{tpa})_4]_n$ or dinuclear copper acetates, indicating the dbco linker results in a weaker Cu...Cu interaction. As a consequence of such interaction, the O–C–O angles in the Cu–O–C–O–Cu rings are greater than those of $[\text{Cu}_2(\text{tpa})_4]_n$ and $[\text{Cu}(\text{tpa})_2(\text{DMF})]_2$.

Table 1. Data collection and handling.

Crystal:	green block, size 0.12 × 0.15 × 0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	16.39 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/ϕ
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	7941, 2816
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2122
$N(\text{param})_{\text{refined}}$:	236
Programs:	SHELXS-97 [5], SHELXL-97 [6], ORTEP-3 [7], WinGX [8]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ	x	y	z	U _{iso}
H(2A)	4e		0.6242	0.2258	1.2426	0.044
H(2B)	4e		0.4705	0.1951	1.2539	0.044
H(4)	4e		0.7091	-0.0832	1.2345	0.022
H(5)	4e		0.7436	-0.1983	1.3811	0.070
H(6)	4e		0.6695	-0.0887	1.4975	0.060
H(8A)	4e		0.3986	0.3081	0.8164	0.061
H(8B)	4e		0.3794	0.3748	0.9034	0.061
H(10)	4e		0.5068	0.5807	0.9212	0.050
H(11)	4e		0.7059	0.6845	0.8715	0.078
H(12)	4e		0.8296	0.5518	0.7878	0.094
H(3E)	4e	0.5	0.8604	0.0605	0.8764	0.050

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(3F)	4e	0.5	0.8672	-0.0847	0.8867	0.05
H(4E)	4e	0.5	0.9181	0.1227	1.1000	0.05
H(4F)	4e	0.5	0.9012	0.1887	1.0086	0.05
H(5E)	4e	0.5	0.8855	-0.1772	1.0269	0.05
H(5F)	4e	0.5	0.9136	-0.0929	1.1104	0.05
H(3E')	4e	0.5	0.8933	0.1875	0.9807	0.05
H(3F')	4e	0.5	0.8648	0.1115	0.8932	0.05
H(4E')	4e	0.5	0.9166	-0.0720	1.1187	0.05
H(4F')	4e	0.5	0.9128	0.0743	1.1210	0.05
H(5E')	4e	0.5	0.8617	-0.1136	0.8992	0.05
H(5F')	4e	0.5	0.8783	-0.1814	0.9900	0.05

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu(1)	4e		0.63731(6)	0.00727(5)	0.99762(4)	0.0146(4)	0.0319(5)	0.0342(5)	-0.0005(3)	0.0057(3)	0.0035(3)
S(1)	4e		0.5902(2)	0.0790(2)	1.4117(1)	0.077(2)	0.076(2)	0.067(1)	-0.005(1)	0.020(1)	-0.002(1)
S(2)	4e		0.6923(2)	0.3796(2)	0.8067(2)	0.074(1)	0.071(1)	0.086(2)	0.010(1)	0.041(1)	0.005(1)
O(1)	4e		0.6380(4)	0.0923(4)	1.1109(2)	0.024(2)	0.050(3)	0.035(2)	-0.007(2)	0.010(2)	-0.003(2)
O(2)	4e		0.5901(4)	-0.0757(4)	0.8830(2)	0.022(2)	0.055(3)	0.041(2)	-0.001(2)	0.006(2)	-0.010(2)
O(3)	4e		0.5987(4)	0.1701(4)	0.9391(3)	0.023(2)	0.039(2)	0.060(3)	-0.001(2)	0.004(2)	0.017(2)
O(4)	4e		0.6262(4)	-0.1547(4)	1.0566(3)	0.027(2)	0.038(2)	0.059(3)	0.001(2)	0.008(2)	0.014(2)
C(1)	4e		0.5317(6)	0.1069(5)	1.1479(4)	0.039(4)	0.030(3)	0.034(3)	0.001(3)	0.006(3)	0.005(2)
C(2)	4e		0.5558(6)	0.1598(5)	1.2395(4)	0.039(3)	0.034(3)	0.039(3)	0.000(3)	0.012(3)	-0.002(2)
C(3)	4e		0.6059(5)	0.0582(5)	1.3045(3)	0.023(3)	0.053(4)	0.032(3)	-0.011(3)	0.004(2)	-0.003(3)
C(4)	4e		0.6817(5)	-0.0569(4)	1.2868(3)	0.034(3)	0.012(2)	0.008(2)	-0.002(2)	-0.006(2)	0.003(2)
C(5)	4e		0.7029(7)	-0.1199(6)	1.3736(4)	0.051(4)	0.054(4)	0.070(5)	0.007(3)	0.015(4)	0.015(4)
C(6)	4e		0.6604(7)	-0.0579(6)	1.4407(4)	0.045(4)	0.064(4)	0.039(4)	-0.005(3)	0.007(3)	0.012(3)
C(7)	4e		0.4773(6)	0.2080(5)	0.9236(3)	0.029(3)	0.034(3)	0.034(3)	-0.004(2)	0.002(2)	0.002(2)
C(8)	4e		0.4454(6)	0.3295(6)	0.8741(5)	0.035(4)	0.043(4)	0.073(5)	0.004(3)	-0.003(3)	0.016(3)
C(9)	4e		0.5587(5)	0.4173(5)	0.8620(4)	0.029(3)	0.041(3)	0.041(3)	0.001(3)	0.003(2)	0.011(3)
C(10)	4e		0.5679(6)	0.5420(5)	0.8887(4)	0.031(3)	0.038(3)	0.057(4)	0.006(3)	0.010(3)	0.014(3)
C(11)	4e		0.6826(7)	0.6016(7)	0.8597(5)	0.047(4)	0.043(4)	0.098(6)	-0.007(3)	-0.011(4)	0.011(4)
C(12)	4e		0.7539(8)	0.5260(7)	0.8135(6)	0.039(4)	0.088(6)	0.110(7)	-0.005(4)	0.019(5)	0.052(5)
N(1)	4e	0.5	0.8663(4)	0.0042(4)	1.0002(3)	0.016(3)	0.030(3)	0.039(3)	-0.001(2)	0.005(2)	0.000(2)
C(13)	4e	0.5	0.904(1)	-0.0068(8)	0.9124(9)	0.022(9)	0.23(5)	0.06(1)	0.01(1)	0.008(8)	-0.03(2)
C(14)	4e	0.5	0.939(1)	0.115(1)	1.0413(6)	0.019(8)	0.08(1)	0.16(3)	0.003(8)	0.03(1)	-0.05(2)
C(15)	4e	0.5	0.928(2)	-0.099(1)	1.0498(6)	0.026(8)	0.09(2)	0.18(4)	0.003(9)	0.02(1)	0.09(2)
N(1')	4e	0.5	0.8663(4)	0.0042(4)	1.0002(3)	0.016(3)	0.030(3)	0.039(3)	-0.001(2)	0.005(2)	0.000(2)
C(13')	4e	0.5	0.913(1)	0.1092(9)	0.9525(6)	0.013(7)	0.05(1)	0.16(3)	0.014(7)	0.02(1)	0.06(2)
C(14')	4e	0.5	0.940(2)	0.0032(8)	1.0892(8)	0.022(8)	0.16(3)	0.046(9)	-0.01(1)	0.015(6)	-0.01(1)
C(15')	4e	0.5	0.908(1)	-0.109(1)	0.9587(6)	0.013(6)	0.048(9)	0.11(2)	-0.009(6)	0.013(8)	-0.03(1)

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