Crystal structure of *catena*-bis[2,2′-(1,3-propanedithio)-bis(1,3,4-thiadiazole)]bis(2,4,6-trinitrophenolate)copper(II), $Cu(C_7H_8N_4S_4)_2(C_6H_2N_3O_7)_2$

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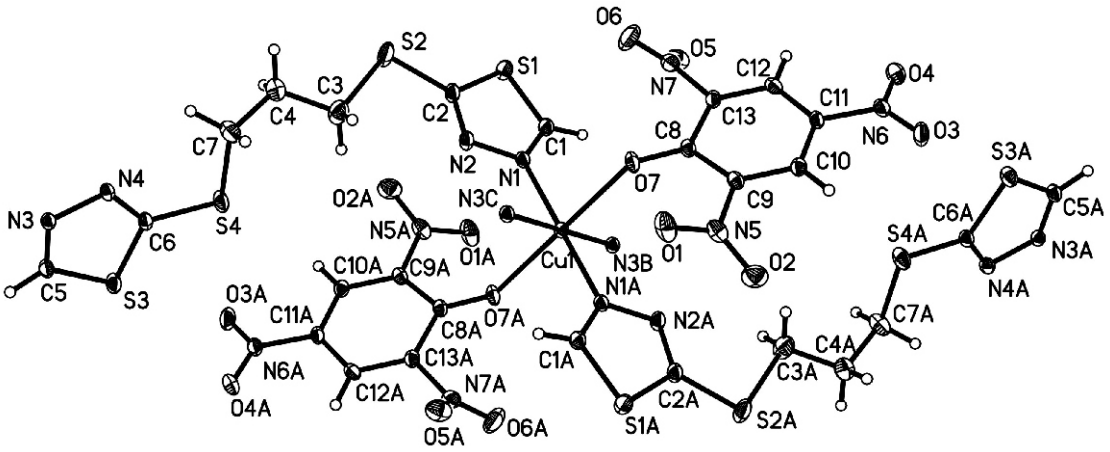

Abstract

$C_{26}H_{20}CuN_{14}O_{14}S_8$, triclinic, $P\bar{1}$ (no. 2), a = 8.709(1) Å, b = 11.492(2) Å, c = 11.845(2) Å, α = 65.594(2)°, β = 70.588(2)°, γ = 73.989(2)°, V = 1004.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.096, T = 291 K.

Source of material

The reaction of 2,2′-(1,3-propanedithio)bis(1,3,4-thiadiazole) (0.1 mmol) with copper dipicrate tetrahydrate (0.1 mmol) in MeOH (10 mL) for a few minutes afforded a light blue solid, which was filtered, washed with acetone, and dried in air. The single crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into the acetonitrile solution of the solid.

Discussion

In recent years, the rational design of coordination polymers based on multitopic or flexible bridging ligands as linkers and metal centers as connectors represents one of the most rapidly developing fields owing to their potential as functional materials in, e. g., electronic, magnetic, optical, catalytic applications [1-3]. In particular, the uses of flexible ligands in such studies have attracted remarkable attention because the flexibility and conformation restrainability of such ligands offer the possibility for the construction of diverse frameworks. Among the diverse flexible ligands, flexible bisthiadiazole alkanes, like 2,2′-(1,2-propanedithio)bis(1,3,4-thiadiazole), bearing alkyl spacers are a good choice of *N*-donor ligand, and the flexible nature of spacers allows the ligands to bend and rotate when coordinating to metal centers so as to conform to the coordination of metal ions [4-9].

In the title crystal structure, the asymmetric unit consists of half a Cu^{2+} ion, one thiadiazole ligand, and one 2,4,6-trinitrophenolate (picrate) ligand. The Cu^{2+} ion has a slightly distorted octahedral coordination (CuN_4O_2), in which four nitrogen atoms from four thiadiazole ligands occupy the equatorial plane, and two oxygen atoms from two picrate ligands occupy the axial positions. All Cu—O and Cu—N bond distances are within the range expected for such coordination bonds [8-9]. Obviously, only the N atoms of the thiadiazole ligands coordinate to Cu^{2+} ion. The thiadiazole ligands adopts a *N*,*N*′-bidentate bridging mode in *trans* configuration and bridge the copper atoms into a one dimensional chain, with the bridging distance d(Cu1—CuA) = 12.64(1) Å. The chains are further connected by C–H···O and C–H···N hydrogen bonds to generate a three-dimensional supramolecular structure. The centroid separation and dihedral angle of thiadiazole rings are 9.4638(3) Å and 68.46(8)°, respectively. The picrate ligand adopts monodentate coordination mode and serves to complete the coordination sphere of the Cu^{2+} ion.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.19 × 0.26 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.43 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7518, 3714
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3096
$N(param)_{refined}$:	286
Programs:	SHELXS-97, SHELXL-97, SHELXTL [10]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	0.1345	1.1229	0.4945	0.046
H(3A)	2*i*	0.2023	0.6499	0.9115	0.075
H(3B)	2*i*	0.2641	0.7176	0.9761	0.075
H(4A)	2*i*	0.0198	0.5601	1.1008	0.075
H(4B)	2*i*	0.0690	0.6337	1.1661	0.075
H(5)	2*i*	0.4955	–0.0816	1.2912	0.043
H(7A)	2*i*	0.2033	0.4269	1.2334	0.066
H(7B)	2*i*	0.3396	0.5104	1.1363	0.066
H(10)	2*i*	0.7186	1.5406	0.2613	0.040
H(12)	2*i*	0.2226	1.5988	0.3597	0.042

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	1*f*	½	1	½	0.0248(3)	0.0275(3)	0.0263(3)	–0.0011(2)	–0.0096(2)	–0.0043(2)
S(1)	2*i*	–0.0413(1)	1.03231(9)	0.69528(8)	0.0293(4)	0.0484(5)	0.0469(5)	0.0057(4)	–0.0061(4)	0.0048(4)
S(2)	2*i*	–0.0027(1)	0.8255(1)	0.94680(9)	0.0432(5)	0.0599(6)	0.0469(5)	–0.0085(4)	–0.0051(4)	0.0154(4)
S(3)	2*i*	0.4266(1)	0.09154(7)	1.11444(7)	0.0694(6)	0.0299(4)	0.0294(4)	–0.0048(4)	–0.0182(4)	–0.0069(3)
S(4)	2*i*	0.3020(1)	0.37605(8)	1.04862(8)	0.0814(7)	0.0296(4)	0.0352(4)	0.0011(4)	–0.0280(4)	–0.0038(3)
O(1)	2*i*	0.7934(3)	1.2120(2)	0.4934(3)	0.064(2)	0.049(2)	0.082(2)	0.002(1)	–0.049(2)	0.002(1)
O(2)	2*i*	0.9007(3)	1.3263(3)	0.2985(3)	0.039(1)	0.071(2)	0.080(2)	–0.003(1)	–0.012(1)	–0.031(2)
O(3)	2*i*	0.6029(3)	1.7648(2)	0.1651(2)	0.078(2)	0.035(1)	0.046(1)	–0.024(1)	–0.007(1)	–0.004(1)
O(4)	2*i*	0.3394(3)	1.7885(2)	0.1928(3)	0.072(2)	0.034(1)	0.061(2)	0.013(1)	–0.009(1)	0.002(1)
O(5)	2*i*	0.0668(3)	1.3871(3)	0.4626(3)	0.042(1)	0.066(2)	0.086(2)	–0.009(1)	–0.012(1)	–0.039(2)
O(6)	2*i*	0.1517(4)	1.3157(3)	0.6334(3)	0.074(2)	0.085(2)	0.045(2)	–0.029(2)	0.008(1)	–0.004(2)
O(7)	2*i*	0.4712(3)	1.2042(2)	0.5154(2)	0.058(1)	0.022(1)	0.039(1)	–0.008(1)	–0.017(1)	–0.0016(9)
N(1)	2*i*	0.2667(3)	0.9883(2)	0.6072(2)	0.030(1)	0.025(1)	0.033(1)	–0.002(1)	–0.010(1)	–0.005(1)
N(2)	2*i*	0.2387(3)	0.9011(2)	0.7319(2)	0.030(1)	0.032(1)	0.038(1)	–0.006(1)	–0.010(1)	0.001(1)
N(3)	2*i*	0.4252(3)	0.0748(2)	1.3340(2)	0.028(1)	0.027(1)	0.029(1)	–0.003(1)	–0.010(1)	–0.005(1)
N(4)	2*i*	0.3697(3)	0.2052(2)	1.2744(2)	0.037(1)	0.027(1)	0.031(1)	0.001(1)	–0.014(1)	–0.005(1)
N(5)	2*i*	0.7829(4)	1.3003(3)	0.3922(3)	0.045(2)	0.037(2)	0.062(2)	–0.002(1)	–0.027(2)	–0.018(1)
N(6)	2*i*	0.4710(4)	1.7226(2)	0.2141(2)	0.067(2)	0.027(1)	0.029(1)	–0.002(1)	–0.008(1)	–0.009(1)
N(7)	2*i*	0.1708(3)	1.3696(3)	0.5185(3)	0.042(2)	0.037(2)	0.055(2)	–0.007(1)	–0.003(1)	–0.019(1)
C(1)	2*i*	0.1342(4)	1.0607(3)	0.5755(3)	0.033(2)	0.033(2)	0.036(2)	0.000(1)	–0.009(1)	–0.003(1)
C(2)	2*i*	0.0833(4)	0.9152(3)	0.7893(3)	0.034(2)	0.032(2)	0.040(2)	–0.004(1)	–0.010(1)	0.001(1)
C(3)	2*i*	0.1696(5)	0.6878(4)	0.9772(4)	0.046(2)	0.067(3)	0.051(2)	–0.005(2)	–0.015(2)	–0.000(2)
C(4)	2*i*	0.1107(5)	0.5919(4)	1.1030(4)	0.068(3)	0.046(2)	0.058(2)	–0.003(2)	–0.014(2)	–0.010(2)
C(5)	2*i*	0.4577(4)	0.0071(3)	1.2631(3)	0.046(2)	0.025(2)	0.032(2)	–0.004(1)	–0.014(1)	–0.005(1)
C(6)	2*i*	0.3646(4)	0.2269(3)	1.1580(3)	0.040(2)	0.026(2)	0.030(2)	–0.003(1)	–0.011(1)	–0.005(1)
C(7)	2*i*	0.2432(5)	0.4783(3)	1.1441(4)	0.073(3)	0.039(2)	0.059(2)	0.004(2)	–0.031(2)	–0.020(2)
C(8)	2*i*	0.4750(4)	1.3221(3)	0.4542(3)	0.042(2)	0.026(2)	0.028(1)	–0.005(1)	–0.013(1)	–0.006(1)
C(9)	2*i*	0.6222(4)	1.3802(3)	0.3832(3)	0.038(2)	0.027(2)	0.034(2)	–0.001(1)	–0.016(1)	–0.010(1)
C(10)	2*i*	0.6201(4)	1.5085(3)	0.3068(3)	0.040(2)	0.030(2)	0.031(2)	–0.011(1)	–0.008(1)	–0.009(1)
C(11)	2*i*	0.4713(4)	1.5894(3)	0.2980(3)	0.050(2)	0.022(1)	0.025(1)	–0.006(1)	–0.011(1)	–0.005(1)
C(12)	2*i*	0.3227(4)	1.5439(3)	0.3662(3)	0.042(2)	0.028(2)	0.035(2)	0.004(1)	–0.015(1)	–0.013(1)
C(13)	2*i*	0.3276(4)	1.4166(3)	0.4430(3)	0.039(2)	0.028(2)	0.031(2)	–0.009(1)	–0.008(1)	–0.008(1)

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