Crystal structure of *catena*-bis[2,2′-(methylenedithio)bis(1,3,4-thiadiazole)]bis(2,4,6-trinitrophenolate)copper(II) — methanol (1:1), $Cu(C_5H_4S_4N_4)_2(C_6H_2N_3O_7)_2 \cdot CH_3OH$

Shi-Hui Li[I], Yong Li[II] and Pu-Zhou Hu[*,I]

[I] Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China
[II] Henan Institute of Education, Department of Chemistry, Zhengzhou 450014, Henan, P. R. China

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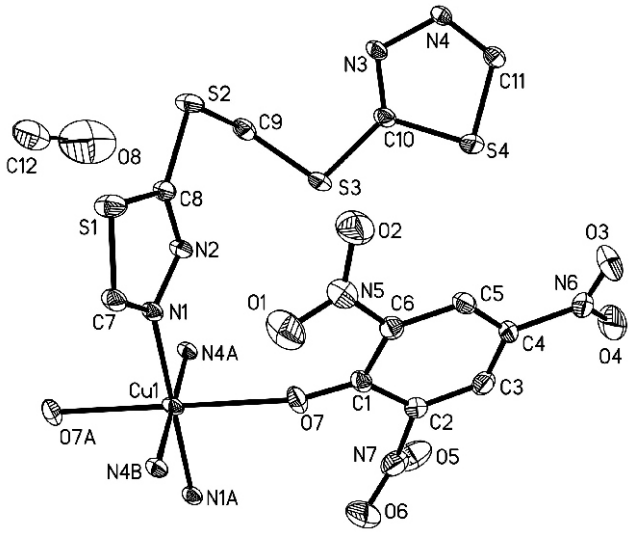

Abstract

$C_{46}H_{32}Cu_2N_{28}O_{30}S_{16}$, monoclinic, *C*12/*c*1 (no. 15), $a = 23.767(3)$ Å, $b = 9.102(1)$ Å, $c = 19.558(3)$ Å, $\beta = 113.365(2)°$, $V = 3884.1$ Å^3, $Z = 2$, $R_{gt(F)} = 0.043$, $wR_{ref(F^2)} = 0.110$, $T = 296$ K.

Source of material

The reaction of 2,2′-(methylenedithio)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

The construction of metal-organic frameworks (MOFs) has become an exciting and expanding approach to novel materials. The interest is stimulated not only by the MOFs' structural diversities but also by their extensive potential applications in such areas as separation, molecular recognition, ion exchange, gas sorption and storage, nonlinear optics, magnetics and catalysis [1-3]. In constructing MOFs, flexible ligands are usually selected because they may act as bridging to extend the architecture to chains, layers and 3D networks [4,5]. Among the diverse flexible ligands, flexible bisthiadiazole alkanes, like 2,2′-(methylenedithio)-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 [6-8].

The asymmetric unit of the title crystal structure consists of half a Cu^{2+} ion, one 2,2′-(methylenedithio)bis(1,3,4-thiadiazole) ligand, one 2,4,6-trinitrophenolate (picrate) ligand, and half a methanol molecule. The Cu^{2+} ion, occupying a crystallographic inversion centre, is six-coordinated by four nitrogen atoms from four thiadiazole ligands occupying the equatorial plane and two oxygen atoms from two picrate ligands occupying the axial positions, in a slightly distorted octahedral manner. All bond distances *d*(Cu—O) and *d*(Cu—N) are within the range expected for such coordination bonds [7,8]. 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 for bridging the Cu^{2+} ions *via* translation symmetry into a two-dimensional layer, with the bridged distance *d*(Cu—Cu) = 10.786(1) Å. The centroid separation and dihedral angle of thiadiazole rings are 6.5070(6) Å and 70.765(5)°, respectively. The region between the layers is taken up by methanol molecules. The C–H···O and C–H···N hydrogen bonds connect the layers to generate a three-dimensional supramolecular structure. 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 0.07 × 0.21 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.78 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13998, 3605
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2556
$N(param)_{refined}$:	286
Programs:	SHELXS-97, SHELXL-97, SHELXTL [9]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(8)	8*f*	0.50	0.0774	0.7954	0.2468	0.268
H(12A)	8*f*	0.50	0.0473	0.9650	0.2906	0.208
H(12B)	8*f*	0.50	–0.0132	0.8726	0.2583	0.208
H(12C)	8*f*	0.50	–0.0025	1.0010	0.2114	0.208
H(3A)	8*f*		0.4910	0.6855	0.4198	0.072
H(5A)	8*f*		0.4352	1.1042	0.3857	0.067
H(7)	8*f*		0.2011	1.0647	0.5166	0.058
H(9A)	8*f*		0.1578	0.8714	0.2226	0.057
H(9B)	8*f*		0.1663	0.9667	0.1608	0.057
H(11)	8*f*		0.3714	1.1349	0.1125	0.049

* Correspondence author (e-mail: luoyangmdh@126.com)

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(8)	8*f*	0.50	0.0452(6)	0.825(1)	0.2146(8)	0.169(8)	0.146(8)	0.189(8)	–0.060(6)	0.039(6)	0.013(6)
C(12)	8*f*	0.50	0.0169(8)	0.924(2)	0.246(1)	0.113(9)	0.172(9)	0.127(8)	–0.053(7)	0.045(7)	0.040(7)
Cu(1)	4*c*		¼	¾	½	0.0481(4)	0.0324(3)	0.0221(3)	0.0042(3)	0.0171(3)	–0.0004(3)
S(1)	8*f*		0.16523(6)	1.1880(1)	0.40246(6)	0.0900(9)	0.0466(7)	0.0429(6)	0.0283(6)	0.0269(6)	0.0048(5)
S(2)	8*f*		0.14995(6)	1.1167(1)	0.24582(6)	0.0740(8)	0.0474(6)	0.0345(6)	0.0103(6)	0.0200(5)	0.0117(5)
S(3)	8*f*		0.25931(6)	0.9301(2)	0.25763(6)	0.0636(8)	0.090(1)	0.0444(6)	0.0186(7)	0.0318(6)	0.0327(6)
S(4)	8*f*		0.36095(5)	1.0164(1)	0.21291(6)	0.0517(7)	0.0685(8)	0.0358(6)	0.0088(6)	0.0168(5)	0.0131(5)
O(1)	8*f*		0.3319(2)	1.1042(4)	0.4863(2)	0.158(4)	0.081(3)	0.099(3)	0.018(3)	0.085(3)	–0.011(2)
O(2)	8*f*		0.3403(2)	1.2007(5)	0.3922(3)	0.132(4)	0.079(3)	0.129(4)	0.028(3)	0.071(3)	0.041(3)
O(3)	8*f*		0.5180(2)	1.0544(7)	0.3463(3)	0.086(3)	0.214(6)	0.126(4)	–0.022(4)	0.060(3)	0.067(4)
O(4)	8*f*		0.5363(2)	0.8213(8)	0.3470(3)	0.109(4)	0.278(8)	0.179(6)	0.100(5)	0.118(4)	0.116(5)
O(5)	8*f*		0.4301(2)	0.4826(5)	0.4561(3)	0.096(3)	0.068(3)	0.113(4)	0.010(2)	–0.007(3)	–0.004(3)
O(6)	8*f*		0.4287(2)	0.5865(5)	0.5549(3)	0.123(4)	0.114(4)	0.097(3)	0.019(3)	0.052(3)	0.056(3)
O(7)	8*f*		0.3427(1)	0.8082(3)	0.4863(2)	0.056(2)	0.068(2)	0.051(2)	–0.007(2)	0.037(2)	–0.002(2)
N(1)	8*f*		0.2098(1)	0.9337(3)	0.4420(2)	0.046(2)	0.038(2)	0.026(2)	0.006(2)	0.019(1)	0.001(1)
N(2)	8*f*		0.1970(2)	0.9411(3)	0.3666(2)	0.051(2)	0.034(2)	0.030(2)	0.003(2)	0.019(2)	0.005(1)
N(3)	8*f*		0.2490(2)	1.0800(3)	0.1323(2)	0.049(2)	0.043(2)	0.029(2)	0.001(2)	0.022(2)	0.004(1)
N(4)	8*f*		0.2845(1)	1.1329(3)	0.0958(2)	0.045(2)	0.034(2)	0.027(2)	–0.002(1)	0.018(2)	–0.001(1)
N(5)	8*f*		0.3528(2)	1.1049(4)	0.4386(2)	0.077(3)	0.048(2)	0.060(3)	–0.008(2)	0.030(2)	–0.005(2)
N(6)	8*f*		0.5115(2)	0.9270(9)	0.3617(3)	0.042(3)	0.196(7)	0.071(3)	0.022(4)	0.028(2)	0.057(4)
N(7)	8*f*		0.4277(2)	0.5915(5)	0.4924(3)	0.055(3)	0.067(3)	0.074(3)	0.006(2)	0.013(2)	0.012(3)
C(1)	8*f*		0.3827(2)	0.8411(5)	0.4630(2)	0.043(2)	0.054(3)	0.028(2)	–0.006(2)	0.017(2)	–0.006(2)
C(2)	8*f*		0.4266(2)	0.7347(5)	0.4579(2)	0.043(2)	0.060(3)	0.041(2)	0.004(2)	0.015(2)	0.008(2)
C(3)	8*f*		0.4661(2)	0.7605(6)	0.4243(2)	0.040(2)	0.094(4)	0.045(3)	0.016(3)	0.015(2)	0.004(3)
C(4)	8*f*		0.4688(2)	0.8986(7)	0.3971(2)	0.035(2)	0.108(4)	0.040(3)	0.001(3)	0.018(2)	0.021(3)
C(5)	8*f*		0.4321(2)	1.0107(6)	0.4029(2)	0.044(3)	0.080(3)	0.037(2)	–0.015(2)	0.010(2)	0.015(2)
C(6)	8*f*		0.3906(2)	0.9827(5)	0.4347(2)	0.043(2)	0.050(3)	0.037(2)	–0.004(2)	0.013(2)	–0.003(2)
C(7)	8*f*		0.1954(2)	1.0533(5)	0.4671(2)	0.068(3)	0.053(3)	0.033(2)	0.018(2)	0.029(2)	0.004(2)
C(8)	8*f*		0.1729(2)	1.0669(4)	0.3389(2)	0.046(2)	0.036(2)	0.034(2)	0.003(2)	0.017(2)	0.004(2)
C(9)	8*f*		0.1780(2)	0.9580(5)	0.2141(2)	0.058(3)	0.057(3)	0.031(2)	–0.006(2)	0.022(2)	–0.000(2)
C(10)	8*f*		0.2835(2)	1.0166(4)	0.1944(2)	0.051(2)	0.047(2)	0.029(2)	0.006(2)	0.021(2)	0.004(2)
C(11)	8*f*		0.3424(2)	1.1067(4)	0.1307(2)	0.048(3)	0.047(2)	0.031(2)	–0.001(2)	0.020(2)	–0.000(2)

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