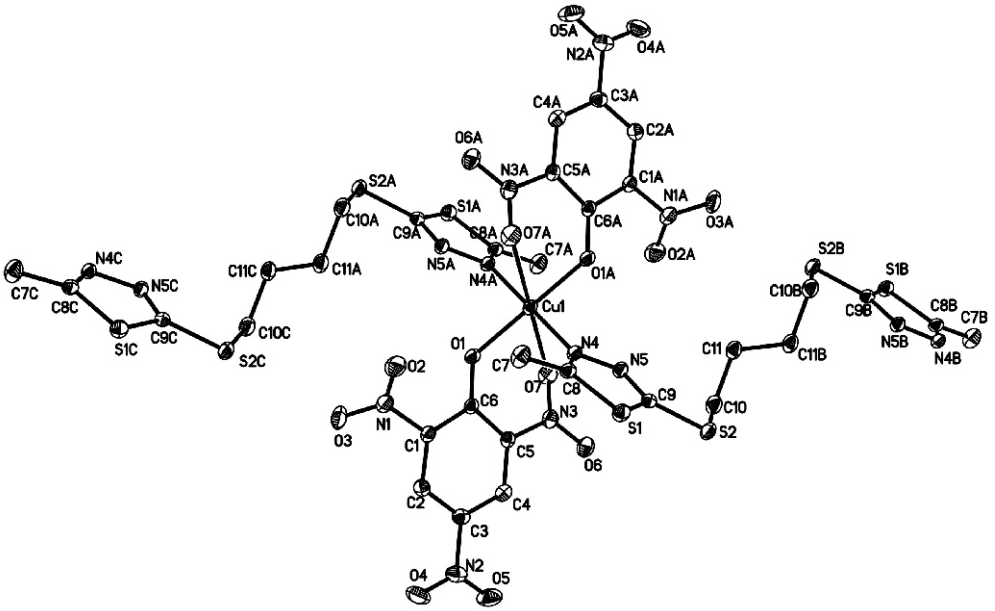
Crystal structure of *catena*-{2,2′-[butylene-1,4-dithio]bis(5-methyl-1,3,4-thiadiazole)}bis(2,4,6-trinitrophenolate)copper(II), $Cu(C_{10}H_{14}S_4N_4)(C_6H_2N_3O_7)_2$

Jian-Ge Wang[I], Hui-Ju Zhang[II] and Pu-Zhou Hu[*,I]

[I] Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China
[II] Henan Polytechnic University, Department of Chemistry and Physics, Jiaozuo 454000, Henan, P. R. China

Received June 4, 2011, accepted and available on-line September 6, 2011; CCDC no. 1267/3597



Abstract

$C_{22}H_{18}CuN_{10}O_{14}S_4$, triclinic, $P\bar{1}$ (no. 2), a = 8.518(3) Å, b = 9.978(4) Å, c = 10.444(4) Å, α = 108.853(4)°, β = 98.761(4)°, γ = 103.085(4)°, V = 793.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.081, T = 291 K.

Source of material

The reaction of 2,2′-[butylene-1,4-dithio]bis(5-methyl-1,3,4-thiadiazole) (0.1 mmol) with $Cu(Pic)_2 \cdot 4H_2O$ (0.1 mmol) in MeOH (10 mL) for a few minutes afforded a light blue solid. It 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

Metal-organic frameworks (MOFs) are continuously studied because of their intriguing structural architectures and topologies, as well as their potential applications as functional materials in the fields of nonlinear optics, magnetism, molecular separation, catalysis, luminescence, and gas sorption [1,2]. In principle, the most effective approach for the construction of MOFs is to rationally modify the building blocks and to control the assembled motifs for required products via selecting appropriate organic ligands [3-5].

The flexible bisthiadiazole alkanes, as 2,2′-[butylene-1,4-dithio]-bis(5-methyl-1,3,4-thiadiazole), bearing alkyl spacer $(-CH_2-)_4$, are good candidates for *N*-donor linkers [6,7]. The flexible nature of the $(-CH_2-)_4$ spacer allows the molecules to bend and rotate freely when binding to metal centers and adjust to the coordinative ability of metal ions.

The asymmetric unit of the title crystal structure consists of a half Cu^{2+} ion, a half 2,2′-[butylene-1,4-dithio]bis(5-methyl-1,3,4-thiadiazole) ligand, and one 2,4,6-trinitrophenolate (picrate) ligand. Each Cu^{2+} ion is six-coordinated with a $\{CuN_2O_4\}$ distorted octahedral environment. Four oxygen atoms from two picrate ligands occupy the equatorial plane (d(Cu1—O1) = 1.931(2) Å and d(Cu1—O7) = 2.5789(7) Å). Nitrogen atoms from two thiadiazole ligands occupy the apical sites (d(Cu1—N4) = 1.995(2) Å). All Cu—O and Cu—N bond distances are within the range expected for such bonds [6,7]. Obviously, only the N atoms of the thiadiazole ligands coordinate to Cu^{2+} ion. The thiadiazole ligands adopt a *N*,*N*-bidentate bridging mode in *trans* configuration for bridging the Cu^{2+} ions *via* translation symmetry into one-dimensional chains, with the bridged distance d(Cu—Cu) = 12.176(3) Å. These chains are further interconnected with neighbouring molecules by weak intermolecular N–O···π interactions and C–H···O hydrogen bonds to generate a three-dimensional network. The centroid separation of thiadiazole rings is 9.401(3) Å. The picrate ligand adopts bidentate-chelating coordination mode and serves to complete the coordination sphere of the Cu^{2+} ion.

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

Table 1. Data collection and handling.

Crystal:	light blue block, size 0.06 × 0.20 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.36 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5920, 2911
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2323
$N(param)_{refined}$:	233
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	–0.2796	0.4214	0.0893	0.051
H(4)	2*i*	0.1787	0.6853	0.3022	0.050
H(7A)	2*i*	–0.3235	0.9250	0.0760	0.088
H(7B)	2*i*	–0.3773	1.0475	0.1818	0.088
H(7C)	2*i*	–0.3713	0.9027	0.2085	0.088
H(10A)	2*i*	0.5547	1.3165	0.5663	0.062
H(10B)	2*i*	0.4442	1.2071	0.4193	0.062
H(11A)	2*i*	0.3804	1.4073	0.3741	0.058
H(11B)	2*i*	0.5706	1.4225	0.3963	0.058

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*a*	0	1	0	0.0303(2)	0.0454(3)	0.0271(2)	0.0014(2)	0.0051(2)	0.0157(2)
S(1)	2*i*	–0.08636(9)	1.12173(8)	0.43111(7)	0.0480(4)	0.0525(4)	0.0344(4)	0.0072(3)	0.0153(3)	0.0176(3)
S(2)	2*i*	0.27692(9)	1.26983(8)	0.57036(7)	0.0534(4)	0.0535(4)	0.0310(4)	–0.0034(3)	0.0003(3)	0.0147(3)
O(1)	2*i*	–0.0887(2)	0.7931(2)	–0.0306(2)	0.049(1)	0.049(1)	0.032(1)	–0.0003(9)	0.0032(8)	0.0186(9)
O(2)	2*i*	–0.4152(3)	0.6437(3)	–0.0884(2)	0.045(1)	0.084(2)	0.076(2)	0.011(1)	–0.003(1)	0.038(1)
O(3)	2*i*	–0.4141(3)	0.4174(3)	–0.1471(2)	0.068(2)	0.065(2)	0.051(1)	–0.009(1)	–0.009(1)	0.005(1)
O(4)	2*i*	–0.1609(3)	0.3498(3)	0.2737(3)	0.092(2)	0.067(2)	0.100(2)	0.019(1)	0.023(2)	0.056(2)
O(5)	2*i*	0.0923(3)	0.4826(3)	0.3791(3)	0.083(2)	0.103(2)	0.085(2)	0.039(2)	0.006(2)	0.061(2)
O(6)	2*i*	0.3314(2)	0.9050(2)	0.2859(2)	0.042(1)	0.069(1)	0.062(1)	0.003(1)	–0.008(1)	0.022(1)
O(7)	2*i*	0.2456(2)	0.9131(2)	0.0840(2)	0.046(1)	0.078(2)	0.056(1)	0.002(1)	0.016(1)	0.030(1)
N(1)	2*i*	–0.3528(3)	0.5492(3)	–0.0765(2)	0.040(1)	0.062(2)	0.039(1)	0.000(1)	0.008(1)	0.020(1)
N(2)	2*i*	–0.0381(4)	0.4514(3)	0.2937(3)	0.071(2)	0.059(2)	0.062(2)	0.029(2)	0.022(2)	0.034(1)
N(3)	2*i*	0.2272(3)	0.8628(3)	0.1760(3)	0.036(1)	0.051(1)	0.047(1)	0.010(1)	0.010(1)	0.013(1)
N(4)	2*i*	–0.0166(2)	1.0640(2)	0.1979(2)	0.033(1)	0.043(1)	0.030(1)	0.0034(9)	0.0051(9)	0.0150(9)
N(5)	2*i*	0.1349(2)	1.1397(2)	0.2938(2)	0.035(1)	0.043(1)	0.032(1)	0.0026(9)	0.0044(9)	0.014(1)
C(1)	2*i*	–0.1996(3)	0.5929(3)	0.0310(3)	0.035(1)	0.043(2)	0.031(1)	0.006(1)	0.008(1)	0.011(1)
C(2)	2*i*	–0.1914(3)	0.5046(3)	0.1066(3)	0.043(2)	0.042(2)	0.041(2)	0.010(1)	0.015(1)	0.015(1)
C(3)	2*i*	–0.0491(3)	0.5421(3)	0.2093(3)	0.050(2)	0.044(2)	0.042(2)	0.021(1)	0.017(1)	0.019(1)
C(4)	2*i*	0.0835(3)	0.6617(3)	0.2326(3)	0.040(2)	0.051(2)	0.036(1)	0.020(1)	0.009(1)	0.013(1)
C(5)	2*i*	0.0748(3)	0.7467(3)	0.1523(3)	0.035(1)	0.040(1)	0.033(1)	0.009(1)	0.010(1)	0.010(1)
C(6)	2*i*	–0.0693(3)	0.7201(3)	0.0477(2)	0.038(1)	0.040(1)	0.027(1)	0.007(1)	0.010(1)	0.010(1)
C(7)	2*i*	–0.3194(3)	0.9740(4)	0.1727(3)	0.037(2)	0.078(2)	0.050(2)	0.001(2)	0.010(1)	0.020(2)
C(8)	2*i*	–0.1436(3)	1.0465(3)	0.2527(3)	0.039(1)	0.041(1)	0.034(1)	0.007(1)	0.010(1)	0.018(1)
C(9)	2*i*	0.1177(3)	1.1769(3)	0.4202(3)	0.042(1)	0.037(1)	0.035(1)	0.004(1)	0.007(1)	0.018(1)
C(10)	2*i*	0.4555(3)	1.2981(3)	0.4959(3)	0.041(2)	0.054(2)	0.048(2)	0.006(1)	–0.001(1)	0.014(1)
C(11)	2*i*	0.4804(3)	1.4238(3)	0.4428(3)	0.040(2)	0.053(2)	0.039(2)	–0.002(1)	0.006(1)	0.013(1)

References

1. Zhang, J.; Wu, T.; Feng, P. Y.; Bu, X. H.: In Situ Synthesis of Tetradentate Dye for Construction of Three-Dimensional Homochiral Phosphor. Chem. Mater. **20** (2008) 5457-5459.
2. Zhang, X. L.; Chen, X. M.: Supramolecular Architectures and Helical Water Chains in Cocrystals of Melamine and Aromatic Carboxylic acids. Cryst. Growth Des. **5** (2005) 617-622.
3. Ma, L. F.; Wang, L. Y.; Huo, X. K.; Wang, Y. Y.; Fan, Y. T.; Wang, J. G.; Chen, S. H.: Chain, Pillar, Layer, and Different Pores: A *N*-[(3-Carboxyphenyl)-sulfonyl]glycine Ligand as a Versatile Building Block for the Construction of Coordination Polymers. Cryst. Growth Des. **8** (2008) 620-628.
4. Yang, G. P.; Zhou, J. H.; Wang, Y. Y.; Liu, P.; Shi, C. C.; Fu, A.Y.; Shi, Q. Z.: An unusual 1D ladder-like silver(I) coordination polymer involving novel 1D → 3D five-folded interpenetrated and [3 + 2] catenaned features generated by Ag···O interactions. CrystEngComm **13** (2011) 33-35.
5. Yang, G. P.; Wang, Y. Y.; Zhang, W. H.; Fu, A. Y.; Liu, R. T.; Lermontovaab, E. K.; Shi, Q. Z.: A series of Zn(II) coordination complexes derived from isomeric phenylenediacetic acid and dipyridyl ligands: syntheses, crystal structures, and characterizations. CrystEngComm **12** (2010) 1509-1517.
6. Hu, P. Z.; Wang, J. G.; Ma, L. F.; Qin, J. H.; Zhao, B. T.; Wang, L. Y.: Probing the frameworks of polymeric of silver(I) nitrate complexes with flexible bisthiadiazole alkanes by tuning the ligand spacers. J. Mol. Struct. **876** (2008) 225-233.
7. Song, J. L.; Dong, Z. C.; Zeng, H. Y.; Zhou, W. B.; Naka, T.; Wei, Q.; Mao, J. G.; Guo, G. C.; Huang, J. S.: $[Cu(H_4C_3N_2S)Cl_2]_n$, an Unprecedented Diazole-Bridged One-Dimensional Copper Halide: Synthesis, Structure, and Magnetic Properties. Inorg. Chem. **42** (2003) 2136-2140.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.