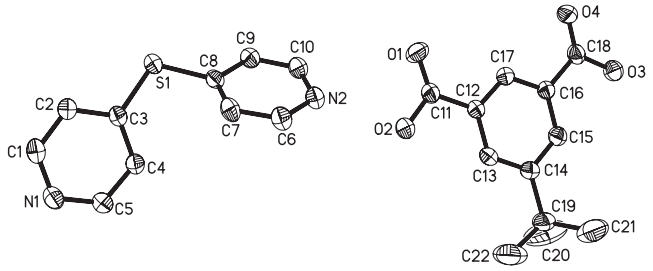
© by Oldenbourg Wissenschaftsverlag, München

Crystal structure of 4,4′-dipyridyl sulfide —5-*tert*-butyl-benzene-1,3-dicarboxylic acid, $C_{10}H_8N_2S \cdot C_{12}H_{14}O_4$

Xiao-Ling Li[*,I] and Miao-Ling Huang[II]

[I] LuoYang Normal University, College of Chemistry and Chemical Engineering, Luoyang, Henan 471022, P. R. China
[II] Quanzhou Normal University, College of Chemistry and Chemical Engineering, Quanzhou, Fujian 362000, P. R. China

Received July 10, 2008, accepted and available on-line October 16, 2008; CCDC no. 1267/2415



Abstract

$C_{22}H_{22}N_2O_4S$, monoclinic, $P12_1/n1$ (no. 14), a = 6.8652(8) Å, b = 27.424(3) Å, c = 11.450(1) Å, β = 96.397(2)°, V = 2142.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.169, T = 291 K.

Source of material

5-*Tert*-butyl-benzene-1,3-dicarboxylic acid (22.35 mg, 0.1 mmol), 4,4′-dipyridyl sulfide (18.81 mg, 0.1 mmol) and NaOH (8.15 mg, 0.2 mmol) were added to a H_2O solution (15 ml) in a Teflon-lined stainless steel reactor. The mixture was heated at 473 K for 3 days, and then slowly cooled down to room temperature for crystallization of the colorless crystals of the title compound. Elemental analysis — found: C, 64.37 %; H, 5.40 %, N, 6.82 %, calculated for $C_{22}H_{22}N_2O_4S$: C, 64.31 %; H, 5.48 %; N, 6.75 %.

Discussion

The design and synthesis of supramolecular coordination polymeric networks, especially those constructed by hydrogen bonding and intermolecular weak interactions have been a field of rapid growth due to their special physical properties and potential application in functional materials [1-10]. Of particular interest are compounds capable of forming very strong hydrogen bonds. In contrast to the large and increasing amount of work on the synthesis with ligands containing O or N donors, there have been fewer reports of studies based on organothiolate ligands. Two kinds of organothiolate ligands, thiolatopyridine and thiolatocarboxylate, have been explored to construct structures with luminescent or magnetic properties. 4,4′-Dipyridyl sulfide (dps) possesses non-rigid backbone from a magic angle (C–S–C) bent around the sulfur atom and exhibits special adaptability for coordination requirements [11-12]. Although dps has been exploited to produce a number of new coordination polymers there is few reports forming supramolecular reported.

The crystal structure of the title compound comprises a 4,4′-dipyridyl sulfide molecule and a 5-*tert*-butyl isophthalic acid molecule per asymmetric unit. Both of the carboxylate groups of the acid are protonated. There exist intermolecular hydrogen bonds between carboxylate oxygen atoms and nitrogen atoms of bps (d(O···N): 2.676 and 2.690 Å, and ∠O–H–N are 170.6° and 177.5°, respectively). Then, an extended one-dimensional chain structure along [010] is formed. Here in the complex the hydrogen bonds play an important role in forming by self-assembly and stabilizing the supramolecular structure.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.14 × 0.21 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.81 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15927, 3990
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2531
$N(param)_{refined}$:	267
Programs:	SHELXS-97 [13], SHELXL-97 [14], SHELXTL [15]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.8491	0.1113	0.8143	0.106
H(3)	4*e*	1.8205	0.1380	0.4290	0.106
H(1)	4*e*	–0.0225	0.0440	1.4505	0.084
H(2A)	4*e*	0.2328	–0.0008	1.3927	0.076
H(4)	4*e*	0.4088	0.1192	1.2360	0.066
H(5)	4*e*	0.1437	0.1590	1.2944	0.072
H(6)	4*e*	0.4539	0.0918	0.8915	0.072
H(7)	4*e*	0.3484	0.0638	1.0617	0.069
H(9)	4*e*	0.9003	0.0259	1.1711	0.070
H(10)	4*e*	0.9863	0.0534	0.9951	0.074
H(13)	4*e*	1.0176	0.1995	0.6692	0.065
H(15)	4*e*	1.4835	0.2133	0.4924	0.066
H(17)	4*e*	1.3921	0.0878	0.6556	0.061
H(20A)	4*e*	1.4509	0.2930	0.5599	0.258
H(20B)	4*e*	1.3397	0.3014	0.6706	0.258
H(20C)	4*e*	1.2922	0.3342	0.5589	0.258
H(21A)	4*e*	1.1094	0.3050	0.3877	0.206
H(21B)	4*e*	1.0431	0.2503	0.3778	0.206
H(21C)	4*e*	1.2647	0.2639	0.3763	0.206
H(22A)	4*e*	0.9976	0.2849	0.6656	0.246
H(22B)	4*e*	0.8877	0.2557	0.5605	0.246
H(22C)	4*e*	0.9354	0.3111	0.5456	0.246

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

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}
S(1)	4*e*	0.5521(1)	0.01887(3)	1.27220(8)	0.0737(6)	0.0628(6)	0.0671(6)	0.0181(5)	0.0341(5)	0.0105(4)
O(1)	4*e*	1.1174(4)	0.0681(1)	0.7801(3)	0.075(2)	0.071(2)	0.115(2)	0.024(1)	0.041(2)	0.043(2)
O(2)	4*e*	0.9071(4)	0.12955(9)	0.7732(2)	0.069(2)	0.071(2)	0.079(2)	0.016(1)	0.038(1)	0.016(1)
O(3)	4*e*	1.7302(3)	0.15297(9)	0.4539(2)	0.060(2)	0.074(2)	0.084(2)	0.010(1)	0.034(1)	0.012(1)
O(4)	4*e*	1.6859(4)	0.08238(9)	0.5439(2)	0.074(2)	0.063(2)	0.085(2)	0.021(1)	0.033(1)	0.011(1)
N(1)	4*e*	0.0342(4)	0.1055(1)	1.3770(2)	0.058(2)	0.069(2)	0.062(2)	0.007(2)	0.019(1)	–0.003(2)
N(2)	4*e*	0.7313(4)	0.0767(1)	0.9277(2)	0.059(2)	0.065(2)	0.057(2)	0.001(1)	0.021(2)	–0.001(1)
C(1)	4*e*	0.0645(5)	0.0591(2)	1.4054(3)	0.066(2)	0.075(3)	0.074(2)	–0.001(2)	0.033(2)	0.006(2)
C(2)	4*e*	0.2186(5)	0.0319(1)	1.3715(3)	0.070(2)	0.056(2)	0.070(2)	0.005(2)	0.030(2)	0.009(2)
C(3)	4*e*	0.3505(5)	0.0539(1)	1.3060(3)	0.056(2)	0.053(2)	0.048(2)	0.002(2)	0.017(2)	–0.002(2)
C(4)	4*e*	0.3216(5)	0.1027(1)	1.2785(3)	0.061(2)	0.051(2)	0.056(2)	–0.001(2)	0.020(2)	–0.000(2)
C(5)	4*e*	0.1623(5)	0.1264(1)	1.3148(3)	0.064(2)	0.057(2)	0.061(2)	0.008(2)	0.017(2)	0.000(2)
C(6)	4*e*	0.5453(5)	0.0786(1)	0.9489(3)	0.055(2)	0.074(2)	0.051(2)	0.003(2)	0.009(2)	–0.003(2)
C(7)	4*e*	0.4806(5)	0.0620(1)	1.0513(3)	0.043(2)	0.072(2)	0.058(2)	–0.006(2)	0.014(2)	–0.010(2)
C(8)	4*e*	0.6131(5)	0.0428(1)	1.1380(3)	0.053(2)	0.044(2)	0.055(2)	0.000(1)	0.018(2)	–0.006(1)
C(9)	4*e*	0.8061(5)	0.0394(1)	1.1158(3)	0.054(2)	0.061(2)	0.061(2)	0.008(2)	0.015(2)	0.004(2)
C(10)	4*e*	0.8563(5)	0.0564(1)	1.0098(3)	0.049(2)	0.067(2)	0.071(2)	0.005(2)	0.023(2)	0.004(2)
C(11)	4*e*	1.0680(5)	0.1082(1)	0.7469(3)	0.054(2)	0.064(2)	0.054(2)	0.010(2)	0.017(2)	0.006(2)
C(12)	4*e*	1.1852(4)	0.1389(1)	0.6737(3)	0.051(2)	0.051(2)	0.048(2)	0.008(1)	0.014(2)	0.003(1)
C(13)	4*e*	1.1303(5)	0.1866(1)	0.6431(3)	0.057(2)	0.052(2)	0.057(2)	0.010(2)	0.019(2)	–0.002(2)
C(14)	4*e*	1.2394(5)	0.2152(1)	0.5748(3)	0.067(2)	0.046(2)	0.061(2)	0.006(2)	0.017(2)	0.001(2)
C(15)	4*e*	1.4071(5)	0.1947(1)	0.5376(3)	0.059(2)	0.050(2)	0.059(2)	–0.003(2)	0.018(2)	0.001(2)
C(16)	4*e*	1.4635(4)	0.1473(1)	0.5660(3)	0.050(2)	0.053(2)	0.047(2)	0.005(1)	0.010(1)	0.003(1)
C(17)	4*e*	1.3535(5)	0.1195(1)	0.6350(3)	0.056(2)	0.051(2)	0.048(2)	0.008(2)	0.011(2)	0.004(1)
C(18)	4*e*	1.6381(5)	0.1240(1)	0.5217(3)	0.050(2)	0.065(2)	0.053(2)	0.003(2)	0.013(2)	–0.001(2)
C(19)	4*e*	1.1772(6)	0.2675(1)	0.5400(4)	0.089(3)	0.046(2)	0.092(3)	0.009(2)	0.027(2)	0.007(2)
C(20)	4*e*	1.328(1)	0.3020(2)	0.5863(7)	0.192(5)	0.063(3)	0.239(6)	–0.015(3)	–0.077(5)	0.015(4)
C(21)	4*e*	1.146(1)	0.2721(2)	0.4086(5)	0.199(6)	0.091(3)	0.118(4)	0.049(4)	–0.001(4)	0.022(3)
C(22)	4*e*	0.981(1)	0.2810(2)	0.5818(7)	0.180(5)	0.089(4)	0.240(6)	0.061(4)	0.098(5)	0.044(4)

References

1. Yue, Q.; Yang, J.; Li, G. H.; Li, G. D.; Xu,W.; Chen, J. S.; Wang, S. N.: Three-dimensional 3d-4f heterometallic coordination polymers: synthesis, structures, andmagnetic properties. Inorg. Chem. **44** (2005) 5241-5246.
2. Cai, J. W.; Chen, C. H.; Feng, X. L.; Liao, C. Z.; Chen, X. M.: A novel supramolecular synthon for H-bonded coordination networks: syntheses and structures of extended two-dimensional cadmium(II) arenedisulfonates. J. Chem. Soc., Dalton. Trans. (2001) 2370-2375.
3. Du, M.; Zou, R. Q.; Zhong, R. Q.; Xu, Q.: Metal-regulated assemblies of CuII, NiII, and ZnII complexes with isoquinoline-3-carboxylate displaying diverse supramolecular networks. Inorg. Chim. Acta **360** (2007) 3442-3447.
4. Ma, L. F.; Huo, X. K.; Wang, L. Y.; Wang, J. G.; Fan, Y. T.: Three new 2-D metal-organic frameworks containing 1-D metal chains bridged by *N*-benzesulfonylglutamic acid: Syntheses, crystal structures and properties. J. Solid State Chem. **180** (2007) 1648-1657.
5. 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.
6. Du, M.; Jiang, X. J.; Zhao, X. J.: Molecular Tectonics of Mixed- Ligand Metal-Organic Frameworks: Positional Isomeric Effect, Metal-Directed Assembly, and Structural Diversification. Inorg. Chem. **46** (2007) 3984-3995.
7. Fan, S. R.; Zhu, L. G.: Influence of the Reaction Conditions on the Self-assembly of Lead(II) 5-Sulfosalicylate Coordination Polymers with Chelating Amine Ligands. Inorg. Chem. **45** (2006) 7935-7942.
8. Ma, L. F.; Wang, Y. Y.; Wang, L. Y.; Liu, J. Q.; Wu, Y. P.; Wang, J. G.; Shi, Q. Z.: Two Novel Flexible Multidentate Ligands for Crystal Engineering: Syntheses, Structures, and Properties of CuII, MnII Complexes with *N*-[(3-Carboxyphenyl)-sulfonyl]glycine and *N,N′*-(1,3-Phenylenedisulfonyl)bis(glycine). Eur. J. Inorg. Chem. **5** (2008) 693-703.
9. Li, D. S.; Zhou, C. H.; Wang, Y. Y.; Fu, F.; Wu, Y. P.; Qi, G. C.; Shi, Q. Z.: Novel Hydrogen-bonded Three-dimensional Supramolecular Architectures Containing 2D Honeycomb Networks or 2D Grids. Chinese J. Chem. **24** (2006) 1352-1358.
10. Ma, L. F.; Wang, L. Y.; Wang, J. G.; Wang, Y. F.; Feng, X.: Two Novel Three-Dimensional Lead(II) Coordination Polymers Involving 16-Membered Rings: $[Pb_2(Bs\text{-}glu)_2(bipy)_2]$ and $[Pb_2(Bs\text{-}glu)_2(phen)_2]$. Z. Anorg. Allg. Chem. **632** (2006) 487-490.
11. Muthu, S.; Zheng, N.; Vittal, J. J.: Photoluminescent coordination polymers of d^{10} metals with 4,4′-dipyridylsulfide (dps). Inorg. Chim. Acta. **358** (2005) 595-605.
12. Zheng, N.; Vittal, J. J.: Interpenetrating versus Noninterpenetrating (4,4) Nets: Influence of the Size of the Metal and Counter Ions. Cryst. Growth Des. **1** (2001) 195-197.
13. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
14. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
15. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.