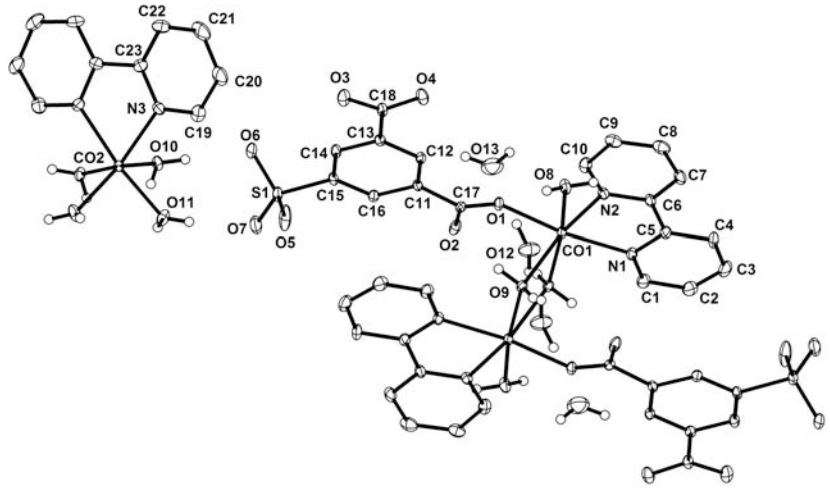
Crystal structure of tetraaqua(2,2′-bipyridyl-*N*,*N*′)cobalt(II) di-μ-aqua-bis[aqua(2,2′-bipyridyl-*N*,*N*′)-(5-sulfoisophthalato)cobalt(II)] tetrahydrate, $Co(H_2O)_4(C_{10}H_8N_2) \cdot Co_2(H_2O)_4(C_{10}H_8N_2)_2(C_8H_3SO_7)_2 \cdot 4H_2O$

Zhaoxun Lian*, Ning Zhao, Jiamin Zhang, Yongqing Gu, Xiabo Li and Bo Tang

Henan Institute of Science and Technology, School of Chemistry and Chemical Engineering, Xinxiang 453003, P. R. China

Received March 22, 2009, accepted and available on-line April 19, 2009; CCDC no. 1267/2601



Abstract

$C_{46}H_{54}Co_3N_6O_{26}S_2$, monoclinic, *C*12/*c*1 (no. 15), a = 19.411(4) Å, b = 9.037(2) Å, c = 31.626(7) Å, β = 96.442(3)°, V = 5512.7 Å^3, Z = 4, $R_{gf}(F)$ = 0.076, $wR_{ref}(F^2)$ = 0.248, T = 298 K.

Source of material

A mixture of 5-sulfoisophthalic acid monosodium salt (SIP, 0.027 g, 0.1 mmol), $Co(CH_3COO)_2$ (0.018 g, 0.1 mmol), 2,2′-bipyridine (2,2′-bipy, 0.016 g, 0.1 mmol) and H_2O (10 mL) was stirred for about 30 min. The resulting solution was sealed in a Teflon-lined stainless autoclave and heated to 393 K for 3 days. The bottle was cooled to ambient temperature spontaneously. Colourless single crystals (about 67 %, based on Co) were recovered by vacuum filtration, drying in air. Elemental analysis — found: C, 42.96 %; H, 4.16 %; N, 6.53 %; calulated for $C_{46}H_{54}Co_3N_6O_{26}S_2$: C, 43.03 %; H, 4.24 %; N 6.55 %.

Experimental details

The C-bound H atoms were geometrically placed (d(C—H) = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C). The O-bound H atoms were located in difference Fourier maps and refined as riding in their as-found relative positions with U_{iso}(H) = 1.2 U_{eq}(O). The high R value is caused by the low quality of the crystal.

Discussion

The rational design and synthesis of metal-directed supramolecular framework is of great current interest due to their potential application in the catalysis, gas absorption, nonlinear optics, ion-exchange, and so on [1-4]. 5-Sulfoisophthalic acid (SIP), containing two kinds of coordinating functional groups and multiple coordination sites, is a good ligand for the construction of metal-organic frameworks [5-12].

The title compound possesses a crystal structure constructed from Co ions and SIP anions and 2,2′-bipy ligands. The asymmetric unit contains two Co(II) atoms. Each Co center has distorted octahedral coordination. The coordination of Co1 is defined by two nitrogen atoms of the 2,2′-bipy ligand, one carboxylate oxygen donor and one bridging aqua ligand at the equatorial positions. The axial positions are occupied by one terminal water molecule and one bridging water molecule. The Co2 center is located on the twofold rotation axis and coordinated by two nitrogen atoms from 2,2′-bipy ligand and four terminal water molecules. Two nitrogen atoms and two terminal water molecules form the equatorial plane and the remaining coordinated water molecules occupy the axial positions. The Co—O bond lengths are in the range of 2.058(4) - 2.195(5) Å and Co—N bond lengths vary from 2.094(5) to 2.156(6) Å. The angles formed by the equatorial atoms range from 77.0(2)° to 95.3(2)°, indicative of slight distortion of the $Co[O_4N_2]$ octahedron. The SIP ligand is monodentate, with O7 coordinated to the Co1 center, and the other carboxylate group and sulfonate group remaining uncoordinated. The complex anions $[Co(2,2'\text{-bipy})(H_2O)_3(SIP)]^-$ are bridged by two water molecules to form a dimeric unit, which is similar to that found in the related crystal structure of [9]. The $[Co(2,2'\text{-bipy})(H_2O)_4]^{2+}$ cations serve for the charge balance. The complex cations and anions align in alternating mode, which is made possible by the well-matched ionic size, and interact with each other *via* hydrogen bonds between the sulfonate groups and the coordinated water molecules, resulting in the formation of infinite

* Correspondence author (e-mail: zhxalian@yahoo.com.cn)

chains. Adjacent chains are linked by the hydrogen bonds formed between the carboxylate groups and coordinated water molecules to a three-dimensional network.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.28 × 0.30 × 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.61 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14396, 5391
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4778
$N(param)_{refined}$:	375
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(8A)	8*f*	0.4899	0.3035	0.4110	0.043
H(8B)	8*f*	0.5599	0.2733	0.4267	0.043
H(9A)	8*f*	0.5573	–0.0558	0.4527	0.030
H(9B)	8*f*	0.5851	0.0405	0.4854	0.030
H(10A)	8*f*	1.0241	0.3085	0.6753	0.037
H(10B)	8*f*	0.9617	0.3924	0.6732	0.037
H(11A)	8*f*	0.8994	0.2151	0.7224	0.049
H(11B)	8*f*	0.9071	0.2085	0.7677	0.049
H(12A)	8*f*	0.6108	–0.0849	0.3919	0.074
H(12B)	8*f*	0.5844	–0.2301	0.3948	0.074
H(13A)	8*f*	0.4664	0.4480	0.6449	0.099
H(13B)	8*f*	0.3932	0.4671	0.6365	0.099
H(1)	8*f*	0.4579	–0.0508	0.3963	0.044
H(2)	8*f*	0.3774	–0.0943	0.3385	0.052
H(3)	8*f*	0.2698	0.0171	0.3349	0.064
H(4)	8*f*	0.2491	0.1888	0.3856	0.052
H(7)	8*f*	0.2342	0.3403	0.4394	0.045
H(8)	8*f*	0.2321	0.5129	0.4930	0.056
H(9)	8*f*	0.3299	0.5470	0.5413	0.050
H(10)	8*f*	0.4275	0.4087	0.5335	0.044
H(12)	8*f*	0.5614	0.4387	0.5867	0.030
H(14)	8*f*	0.7348	0.4770	0.6685	0.034
H(16)	8*f*	0.7335	0.2168	0.5657	0.030
H(19)	8*f*	0.8413	0.4732	0.7365	0.054
H(20)	8*f*	0.7726	0.6788	0.7375	0.080
H(21)	8*f*	0.8248	0.9127	0.7425	0.104
H(22)	8*f*	0.9439	0.9270	0.7501	0.094

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}
Co(1)	8*f*	0.47655(4)	0.1644(1)	0.47579(3)	0.0201(4)	0.0262(5)	0.0213(4)	0.0028(3)	–0.0022(3)	–0.0036(3)
Co(2)	4*e*	0	0.3872(1)	¾	0.0240(6)	0.0227(6)	0.0203(6)	0	0.0013(4)	0
S(1)	8*f*	0.82999(8)	0.2878(2)	0.63638(6)	0.0218(8)	0.042(1)	0.0318(9)	0.0055(7)	–0.0058(6)	–0.0080(7)
O(1)	8*f*	0.5397(2)	0.2605(5)	0.5248(1)	0.019(2)	0.032(3)	0.028(2)	0.005(2)	–0.003(2)	–0.009(2)
O(2)	8*f*	0.6403(2)	0.1711(6)	0.5085(2)	0.022(2)	0.045(3)	0.040(3)	0.000(2)	0.002(2)	–0.022(2)
O(3)	8*f*	0.6411(3)	0.6269(6)	0.6926(2)	0.038(3)	0.053(3)	0.033(3)	0.012(2)	–0.004(2)	–0.021(2)
O(4)	8*f*	0.5467(3)	0.6285(6)	0.6456(2)	0.033(3)	0.050(3)	0.034(3)	0.017(2)	–0.001(2)	–0.009(2)
O(5)	8*f*	0.8539(3)	0.202(1)	0.6027(2)	0.026(3)	0.125(7)	0.062(4)	0.026(3)	–0.008(3)	–0.050(4)
O(6)	8*f*	0.8683(3)	0.4235(7)	0.6455(2)	0.025(3)	0.048(3)	0.061(4)	–0.008(2)	–0.015(2)	0.007(3)
O(7)	8*f*	0.8270(3)	0.2017(8)	0.6753(2)	0.043(3)	0.070(4)	0.062(4)	–0.010(3)	–0.022(3)	0.027(3)
O(8)	8*f*	0.5200(2)	0.2917(6)	0.4314(2)	0.024(2)	0.049(3)	0.035(3)	0.000(2)	–0.001(2)	0.011(2)
O(9)	8*f*	0.5528(2)	–0.0126(5)	0.4751(1)	0.023(2)	0.026(2)	0.026(2)	–0.001(2)	0.002(2)	–0.006(2)
O(10)	8*f*	1.0020(2)	0.3789(6)	0.6836(1)	0.029(2)	0.041(3)	0.021(2)	0.006(2)	–0.002(2)	–0.002(2)
O(11)	8*f*	0.9222(3)	0.2315(6)	0.7454(2)	0.043(3)	0.055(3)	0.023(2)	–0.023(3)	–0.001(2)	0.006(2)
O(12)	8*f*	0.5945(4)	–0.1496(7)	0.4066(2)	0.097(5)	0.042(4)	0.050(4)	–0.006(3)	0.023(4)	–0.006(3)
O(13)	8*f*	0.4282(4)	0.4185(9)	0.6344(3)	0.081(5)	0.053(4)	0.115(7)	0.002(4)	0.015(5)	–0.013(4)
N(1)	8*f*	0.4026(3)	0.0933(6)	0.4250(2)	0.027(3)	0.032(3)	0.022(3)	–0.002(2)	–0.001(2)	0.000(2)
N(2)	8*f*	0.3904(3)	0.2980(6)	0.4828(2)	0.024(3)	0.028(3)	0.028(3)	0.003(2)	0.001(2)	0.002(2)
N(3)	8*f*	0.9311(3)	0.5750(7)	0.7440(2)	0.035(3)	0.030(3)	0.033(3)	0.006(3)	–0.002(2)	0.002(3)
C(1)	8*f*	0.4154(4)	–0.0022(9)	0.3943(2)	0.043(4)	0.038(4)	0.029(4)	–0.003(3)	0.001(3)	–0.004(3)
C(2)	8*f*	0.3671(5)	–0.0298(9)	0.3598(2)	0.064(5)	0.041(5)	0.023(3)	–0.009(4)	0.001(3)	–0.001(3)
C(3)	8*f*	0.3037(5)	0.039(1)	0.3572(3)	0.062(6)	0.053(6)	0.039(4)	–0.018(4)	–0.018(4)	0.000(4)
C(4)	8*f*	0.2912(4)	0.139(1)	0.3876(3)	0.034(4)	0.050(5)	0.041(4)	–0.006(3)	–0.018(3)	0.002(4)
C(5)	8*f*	0.3421(4)	0.1657(8)	0.4222(2)	0.028(3)	0.031(4)	0.034(4)	–0.006(3)	–0.004(3)	0.009(3)
C(6)	8*f*	0.3336(3)	0.2751(8)	0.4551(2)	0.021(3)	0.033(4)	0.032(3)	0.002(3)	–0.001(3)	0.006(3)
C(7)	8*f*	0.2734(4)	0.3557(9)	0.4587(3)	0.020(3)	0.044(4)	0.049(4)	0.002(3)	0.001(3)	0.012(4)
C(8)	8*f*	0.2720(4)	0.4581(9)	0.4906(3)	0.040(4)	0.038(4)	0.064(5)	0.012(3)	0.019(4)	0.006(4)
C(9)	8*f*	0.3299(4)	0.4790(9)	0.5192(3)	0.048(5)	0.032(4)	0.046(4)	0.009(3)	0.013(4)	0.001(3)
C(10)	8*f*	0.3882(4)	0.3959(9)	0.5142(2)	0.032(4)	0.045(4)	0.032(4)	0.004(3)	0.002(3)	–0.012(3)
C(11)	8*f*	0.6412(3)	0.3189(7)	0.5701(2)	0.024(3)	0.024(3)	0.021(3)	0.004(2)	–0.003(2)	0.001(2)
C(12)	8*f*	0.6077(3)	0.4150(7)	0.5947(2)	0.018(3)	0.027(3)	0.029(3)	0.001(2)	–0.001(2)	–0.001(3)
C(13)	8*f*	0.6426(3)	0.4772(7)	0.6314(2)	0.025(3)	0.025(3)	0.022(3)	0.003(2)	0.001(2)	–0.002(2)
C(14)	8*f*	0.7113(3)	0.4381(8)	0.6437(2)	0.027(3)	0.034(4)	0.022(3)	0.007(3)	–0.003(2)	–0.008(3)
C(15)	8*f*	0.7446(3)	0.3410(8)	0.6189(2)	0.017(3)	0.032(4)	0.028(3)	0.005(2)	–0.002(2)	0.000(3)
C(16)	8*f*	0.7106(3)	0.2814(7)	0.5823(2)	0.023(3)	0.026(3)	0.025(3)	0.001(2)	0.002(2)	–0.004(3)
C(17)	8*f*	0.6046(3)	0.2446(7)	0.5308(2)	0.024(3)	0.022(3)	0.025(3)	–0.001(2)	–0.001(2)	–0.004(3)
C(18)	8*f*	0.6066(3)	0.5839(8)	0.6592(2)	0.026(3)	0.034(4)	0.018(3)	0.009(3)	–0.001(2)	–0.011(3)
C(19)	8*f*	0.8620(4)	0.566(1)	0.7397(3)	0.039(4)	0.053(5)	0.042(4)	0.005(4)	0.006(3)	–0.011(4)
C(20)	8*f*	0.8206(5)	0.688(1)	0.7397(4)	0.047(5)	0.065(7)	0.083(7)	0.029(5)	–0.010(5)	–0.014(6)
C(21)	8*f*	0.8516(7)	0.827(1)	0.7431(5)	0.072(8)	0.063(7)	0.12(1)	0.044(6)	–0.016(7)	–0.011(7)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	8*f*	0.9221(6)	0.835(1)	0.7474(4)	0.081(8)	0.028(5)	0.12(1)	0.014(5)	–0.020(7)	–0.014(5)
C(23)	8*f*	0.9613(4)	0.7077(9)	0.7476(3)	0.049(5)	0.031(4)	0.044(4)	0.002(3)	–0.004(4)	–0.008(3)

Acknowledgment. The work was financially supported by the Natural Science Foundation of Henan Institute of Science and Technology (grant nos. 7031 and 06038).

References

1. Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. G.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M.: Modular Chemistry: Sceondary Building Units as a Basis for the Design of Highly Porous and Roubst Metal-Organic Carboxylate Frameworks. Acc. Chem. Res. **34** (2001) 319-330.
2. Aakeröy, C. B.; Desper, J.; Valdés-Martínez, J.: Controlling molecular and supramolecular structure of hydrogen-bonded coordination compounds. CrystEngComm. **6**(2004) 413-418.
3. Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S.: A versatile route to porous solids: organic-inorganic hybrid materials assembled through hydrogen bonds. Angew. Chem., Int. Ed. **38** (1999) 1815-1819.
4. Aakeröy, C. B.; Beatty, A. M.; Helfrich, B. A.: Two-fold interpenetration of 3-D nets assembled *via* three-coodinated silver(I) ions and amide-amide hydrogen bonds. J. Chem. Soc., Dalton Trans. (1998) 1943-1945.
5. Kulynych, A. D.; Shimizu, G. K. H.: A pseudo-honeycomb coordination net formed with 5-sulfoisophthalic acid. CrystEngComm. **4** (2002) 102-105.
6. Sun, D. F.; Cao, R.; Sun, Y. Q.; Li, X.; Bi, W. H.; Hong, M. C.; Zhao, Y. J.: Two New Zeolite-like Supramolecular Copper Complexes. Eur. J. Inorg. Chem. (2003) 94-98.
7. Tao, J.; Yin, X.; Wei, Z. B.; Huang, R. B.; Zheng, L. S.: Hydrothermal syntheses, crystal structures and photoluminescent properties of three metal-cluster based coordination polymers containing mixed organic ligands. Eur. J. Inorg. Chem. (2004) 125-133.
8. Li, X.; Cao, R.; Sun, D. F.; Bi, W. H.; Yuan, D. Q.: A Novel 3D Self-penetrating Topological Network Assembled by Mixed Bridging Ligands. Eur. J. Inorg. Chem. (2004) 2228-2231.
9. Liu, Q. Y.; Wang, Y. L.; Xu, L.: Synthesis, Crystal Structures and Photoluminescent Properties of Three Novel Cadmium(II) Compounds Constructed from 5-sulfoisophthalic acid (H_3SIP). Eur. J. Inorg. Chem. (2006) 4843-4851.
10. Liu, Q. Y.; Xu, Li.: $(H_2O)_{12}$-containing infinite chain encapsulated in supramolecular open framework built of cadmium(II), 1,3-di(4-pyridyl)-propane and 5-sulfoisophtahalic acid monosodium salt. CrystEngComm. **7** (2005) 87-89.
11. Liu, Q. Y.; Xu, Li.: Synthesis, crystal structures and photophysical properties of two supramolecular complexes of cadmium(II). Inorg. Chem. Commun. **8** (2005) 401-405.
12. Liu, Q. Y.; Yuan, D. Q.; Xu, L.: Diversity of Coordination Architecture of Copper(II)-5-sulfoisophthalic Acid: Synthesis, Crystal Structures, and Characterization. Cryst. Growth Des. **7** (2007) 1882-1843.
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.