Crystal structure of diaqua-bis[(5-nitroisophthalato)-(4,4'-dipyridylsulfide)cobalt(II)], $\text{Co}_2(\text{H}_2\text{O})_2(\text{C}_8\text{H}_3\text{NO}_6)_2(\text{C}_{10}\text{H}_8\text{N}_2\text{S})_2$

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Abstract

$\text{C}_{72}\text{H}_{52}\text{Co}_4\text{N}_{12}\text{O}_{28}\text{S}_4$, monoclinic, $P2_1/c$ (no. 13), $a = 14.120(2)$ Å, $b = 8.4612(9)$ Å, $c = 20.550(2)$ Å, $\beta = 129.470(5)^\circ$, $V = 1895.3$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.077$, $T = 291$ K.

Source of material

A mixture of 5-nitroisophthalic acid ($\text{O}_2\text{N-H}_2\text{ip}$, 0.1 mmol, 20.5 mg), 4,4'-bipyridyl sulfide (bps, 0.1 mmol, 18.9 mg), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (24.7 mg, 0.1 mmol), KOH (0.1 mmol, 5.5 mg) and H_2O 18 ml was placed in a Teflon-lined stainless steel vessel, heated to 180 °C for 3 days, and then cooled to room temperature over 48 h. Red block-shaped crystals of the title compound were obtained.

Discussion

The design of metal-organic coordination polymers is of current interest in the fields of supramolecular chemistry and crystal engineering. Major reasons for this interest stem from the intriguing variety of topologies and structural diversity, such as helices and diamondoid nets, and because of their potential applications as functional materials, such as hetero-geneous catalysis, molecular recognition, magnetism, gas storage, ion exchange, nonlinear optics, and electrical conductivity [1,2]. It is well known that organic ligands play crucial roles in the design and construction of desirable frameworks. In this context, benzenedicarboxylic acid and their derivatives (such as 1,3-benzenedicarboxylic acid, 1,4-

benzenedicarboxylic acid, 5-nitroisophthalic acid, 5-hydroxyisophthalic acid etc.) are widely used as building blocks to link metal ions to produce interesting metal-organic framework structures and properties [3,4]. On the other hand, 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. 4,4'-Dipyridyl sulfide (dps) possesses a non-linear backbone due to the bend around the sulfur atom, and may yield various coordination polymers [5].

The fundamental building unit of the title crystal structure contains two cobalt ions, two $\text{O}_2\text{N-ip}$ ligands, two bps ligands and two coordinated water molecules (figure, top). The Co1 ion is 6-coordinated with a distorted octahedral environment. The six atoms coordinated to each Co(II) ion come from two carboxylate oxygen atoms from two $\text{O}_2\text{N-ip}$ ligands, two water molecules and two nitrogen atoms from two bps ligands. Co2 adopts a distorted tetrahedral $[\text{N}_2\text{O}_2]$ coordination, and is coordinated by two carboxylic oxygen atoms from two $\text{O}_2\text{N-ip}$ ligands and two bps nitrogen atoms. The Co—O and Co—N bond lengths are in the range of 1.978(2)–2.173(2) Å and 2.059(2)–2.178(2) Å, respectively.

Every bps ligand adopts a bis-monodentate bridging mode and links neighboring Co(II) ions, resulting in a 1D chain. The 1D chains are further connected by $\text{O}_2\text{N-ip}$ ligands to give a puckered 2D sheet (figure, bottom). It is noteworthy that $\text{O}_2\text{N-ip}$ serves as not only coordinative ligands, but also weak-interaction donor and acceptor. It is interesting to observe that the adjacent 2D layers are connected by $\text{O} \cdots \text{O}$ intermolecular contacts ($d(\text{O4} \cdots \text{O5}) = 3.019$ Å) between the uncoordinated carboxylate oxygens and the $-\text{NO}_2$ groups of $\text{O}_2\text{N-ip}$ ligands, leading to a 3D supramolecular network.

Table 1. Data collection and handling.

Crystal:	red block, size $0.07 \times 0.23 \times 0.39$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	10.64 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\text{max}}$:	51°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	13968, 3533
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2876
$N(\text{param})_{\text{refined}}$:	272
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1W)	4g	0.4841	1.0250	0.3084	0.066
H(2W)	4g	0.3733	0.9474	0.2609	0.066
H(3)	4g	1.1615	0.5834	0.6731	0.036
H(5)	4g	1.0178	0.8625	0.4709	0.034
H(7A)	4g	0.7962	0.6191	0.4939	0.037
H(9)	4g	0.1264	-0.0195	0.2276	0.051
H(10)	4g	0.2721	0.1737	0.2988	0.051

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(12)	4g	0.3201	0.0529	0.5065	0.053
H(13)	4g	0.1756	-0.1398	0.4298	0.052
H(15)	4g	0.2793	0.5084	0.3503	0.045
H(16)	4g	0.3025	0.6684	0.2710	0.042
H(17)	4g	0.6104	0.4650	0.3597	0.047
H(18)	4g	0.5970	0.2982	0.4420	0.048

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co(1)	2f	½	0.75690(5)	¼	0.0243(2)	0.0321(2)	0.0227(2)	0	0.0086(2)	0
Co(2)	2e	0	-0.26464(4)	¼	0.0292(2)	0.0259(2)	0.0266(2)	0	0.0174(2)	0
S(1)	4g	0.43419(6)	0.26976(8)	0.47725(4)	0.0513(4)	0.0521(4)	0.0307(3)	-0.0255(3)	0.0208(3)	-0.0085(3)
O(1)	4g	1.0504(1)	0.3804(2)	0.69275(9)	0.0389(9)	0.0464(9)	0.0369(8)	0.0036(7)	0.0207(8)	0.0180(7)
O(2)	4g	0.8566(2)	0.4496(2)	0.6184(1)	0.050(1)	0.059(1)	0.080(1)	0.0070(9)	0.047(1)	0.028(1)
O(3)	4g	1.3144(1)	0.7522(2)	0.6892(1)	0.0266(8)	0.053(1)	0.0343(9)	0.0039(7)	0.0122(7)	0.0081(7)
O(4)	4g	1.2465(2)	0.8467(2)	0.5688(1)	0.044(1)	0.074(1)	0.048(1)	-0.0020(9)	0.0348(9)	0.0090(9)
O(5)	4g	0.7903(1)	0.9044(2)	0.34383(9)	0.0358(8)	0.0410(9)	0.0286(8)	-0.0006(7)	0.0149(7)	0.0101(7)
O(6)	4g	0.6760(1)	0.7546(2)	0.35992(9)	0.0270(8)	0.052(1)	0.0300(8)	-0.0071(7)	0.0063(7)	0.0121(7)
O(7)	4g	0.4497(2)	0.9417(2)	0.2964(1)	0.052(1)	0.044(1)	0.0404(9)	0.0059(8)	0.0162(8)	-0.0089(8)
N(1)	4g	1.2306(2)	0.7805(2)	0.6145(1)	0.0296(9)	0.036(1)	0.034(1)	0.0037(7)	0.0206(9)	0.0026(8)
N(2)	4g	0.1370(2)	-0.0994(2)	0.3213(1)	0.038(1)	0.0298(9)	0.0288(9)	-0.0066(8)	0.0209(8)	-0.0040(7)
N(3)	4g	0.4599(2)	0.5851(2)	0.3085(1)	0.0272(9)	0.0334(9)	0.0292(9)	-0.0031(7)	0.0156(8)	-0.0047(7)
C(1)	4g	0.9576(2)	0.4632(2)	0.6364(1)	0.040(1)	0.032(1)	0.031(1)	-0.0026(9)	0.022(1)	0.0019(9)
C(2)	4g	0.9755(2)	0.5810(2)	0.5902(1)	0.033(1)	0.027(1)	0.026(1)	-0.0009(8)	0.0177(9)	0.0017(8)
C(3)	4g	1.0928(2)	0.6253(2)	0.6225(1)	0.028(1)	0.032(1)	0.023(1)	0.0039(9)	0.0129(9)	0.0046(8)
C(4)	4g	1.1056(2)	0.7329(2)	0.5779(1)	0.027(1)	0.029(1)	0.029(1)	-0.0003(8)	0.0170(9)	-0.0016(8)
C(5)	4g	1.0063(2)	0.7938(2)	0.5006(1)	0.035(1)	0.026(1)	0.024(1)	-0.0018(8)	0.0178(9)	0.0012(8)
C(6)	4g	0.8889(2)	0.7496(2)	0.4688(1)	0.029(1)	0.026(1)	0.023(1)	-0.0007(8)	0.0127(9)	0.0008(8)
C(7)	4g	0.8748(2)	0.6458(2)	0.5145(1)	0.027(1)	0.031(1)	0.027(1)	-0.0026(8)	0.0139(9)	0.0007(8)
C(8)	4g	0.7769(2)	0.8099(3)	0.3837(1)	0.031(1)	0.031(1)	0.023(1)	-0.0011(9)	0.0120(9)	-0.0002(9)
C(9)	4g	0.1668(2)	-0.0054(3)	0.2847(1)	0.053(1)	0.049(1)	0.028(1)	-0.016(1)	0.027(1)	-0.007(1)
C(10)	4g	0.2541(2)	0.1113(3)	0.3270(1)	0.053(1)	0.046(1)	0.036(1)	-0.020(1)	0.032(1)	-0.009(1)
C(11)	4g	0.3147(2)	0.1348(2)	0.4116(1)	0.035(1)	0.033(1)	0.031(1)	-0.0060(9)	0.021(1)	-0.0054(9)
C(12)	4g	0.2827(2)	0.0392(3)	0.4499(1)	0.057(2)	0.044(1)	0.025(1)	-0.018(1)	0.023(1)	-0.007(1)
C(13)	4g	0.1953(2)	-0.0755(3)	0.4032(1)	0.056(1)	0.042(1)	0.032(1)	-0.016(1)	0.028(1)	-0.003(1)
C(14)	4g	0.4369(2)	0.3858(2)	0.4059(1)	0.036(1)	0.032(1)	0.033(1)	-0.0146(9)	0.020(1)	-0.0105(9)
C(15)	4g	0.3478(2)	0.4979(3)	0.3536(1)	0.028(1)	0.046(1)	0.036(1)	-0.009(1)	0.019(1)	-0.009(1)
C(16)	4g	0.3628(2)	0.5938(3)	0.3063(1)	0.025(1)	0.040(1)	0.030(1)	-0.0009(9)	0.0129(9)	-0.0030(9)
C(17)	4g	0.5434(2)	0.4746(3)	0.3583(1)	0.036(1)	0.036(1)	0.050(1)	0.003(1)	0.029(1)	0.000(1)
C(18)	4g	0.5362(2)	0.3732(3)	0.4080(2)	0.037(1)	0.032(1)	0.047(1)	0.004(1)	0.025(1)	0.005(1)

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