Crystal structure of *catena*-diaquabis(1,3-bis(4-pyridyl)propane)cobalt(II) diperchlorate — 1,3-bis(4-pyridyl)propane — water (1:3:1), $[Co(C_{13}H_{14}N_2)_2(H_2O)_2][ClO_4]_2 \cdot 3C_{13}H_{14}N_2 \cdot H_2O$

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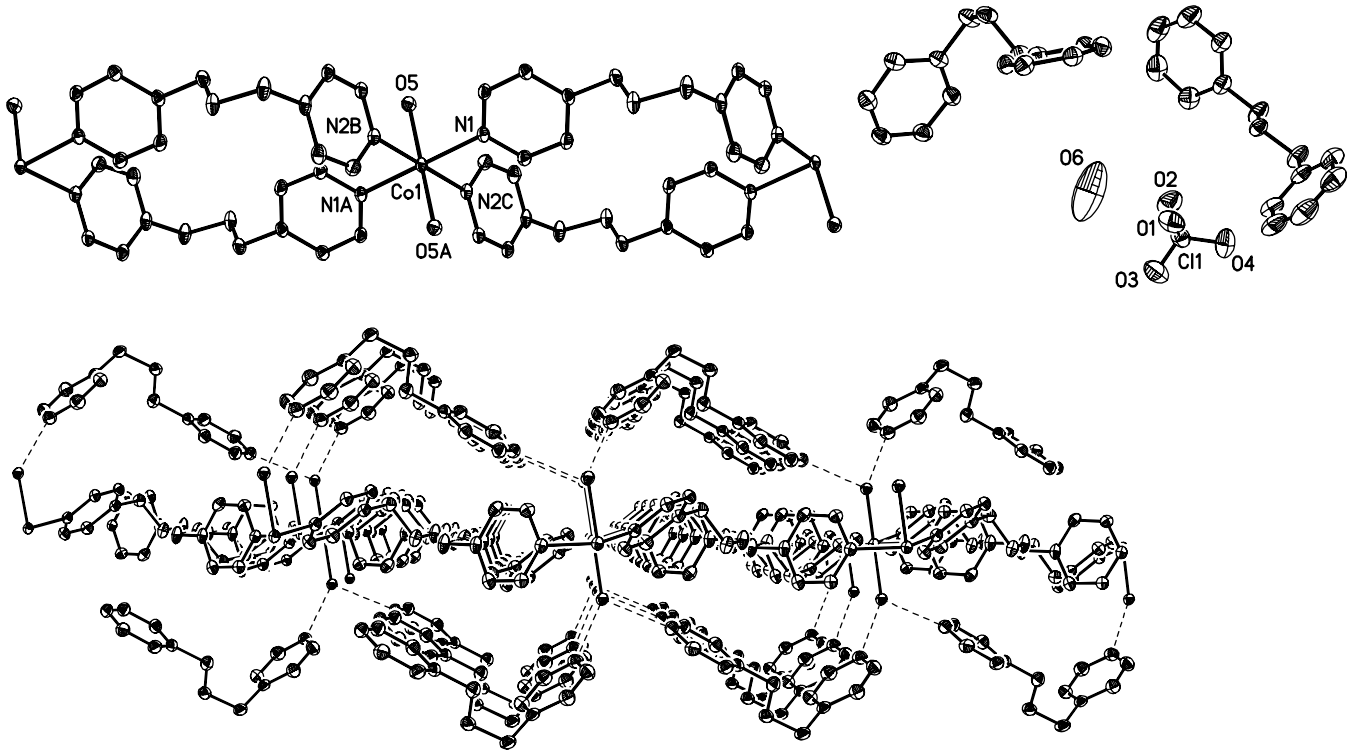

Abstract

$C_{65}H_{76}Cl_2CoN_{10}O_{11}$, monoclinic, *C*12/*c*1 (no. 15), a = 12.787(1) Å, b = 18.713(1) Å, c = 28.391(2) Å, β = 102.550(1)°, V = 6631.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.045, $wR_{ref}(F^2)$ = 0.126, T = 291 K.

Source of material

The title compound was prepared under hydrothermal conditions. A mixture of 1,3-bis(4-pyridyl)propane (bpp, 4 mmol), NaOH (1 mmol), $Co(ClO_4)_2$ (2 mmol), and water (12 ml) was sealed in a 25 mL Teflon-lined reactor and heated in an autoclave at 160 °C for 72 h. Then the autoclave was slowly cooled to room temperature. The title complex, as red block-shaped crystals, was collected by filtration, washed with water, and dried in air.

Discussion

The design and construction of new functional solids based on metal-organic frameworks has been extensively studied [1,2]. This is not only due to their structural diversities but also for their potential or practical application in the area of catalysis, gas storage and nonlinear optics [3,4]. In constructing MOFs, flexible ligands are usually selected because they may act as bridging to extend the architecture to 1D chains, 2D layers and 3D networks [5,6]. 1,3-Bis(4-pyridyl)propane, as a very flexible versatile bifunctional ligand, has been frequently used as a spacer for the construction of the polymeric compounds [7,8]. The longer nitrogen-to-nitrogen span in bpp can lead to larger cavities in coordination networks, and different conformations of bpp can result in different extended structures. Up to now, many *M*(II)-bpp coordination polymers have been synthesized and reported [9,10].

In the title crystal structure, the asymmetric unit consists of one cobalt center bridged by one bpp ligand, one coordinated water molecule, one non-bonded perchlorate ion, one and a half free bpp molecules and one water molecule of crystallization (figure, top). The cobalt ion adopts a distorted octahedron, in which four nitrogen atoms from four bridging bpp ligands occupy the equatorial plane, and two coordinated water molecules occupy the axial positions. The Co1—N1 and Co1—N2 bond distances are 2.157(2) Å and 2.231(2) Å, respectively. The axial Co—O distances have a value of 2.107(2) Å. The Co—O and Co—N dis-

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tances are normal and comparable with literature data [11,12]. The coordinating bpp ligands bridge the cobalt ions into one-dimensional infinite chains. The other bpp molecules do not coordinate with the metal atom, but play an important role in the crystallization process of the title compound. O–H···N hydrogen bonding links the one-dimensional chains into two-dimensional layers via one uncoordinated bpp molecule and coordinated water O5 (figure, bottom). The non-bonded perchlorate ion, the remaining free bpp molecule and the crystallization water molecule occupy the space between the 2D layers. Compared with $[Co(bpp)_2(H_2O)_2][ClO_4]_2 \cdot bpp \cdot H_2O$ obtained from room temperature solution reaction [13], there are different numbers of free bpp molecules in the crystal structures. However, their one-dimensional chains are similar, and they are also related to those found for $[Co(bpp)_2(NO_3)_2] \cdot 2C_6H_6$ and $[Co(bpp)_2(H_2O)_2](NO_3)_2 \cdot bpp \cdot H_2O$ [14,15].

Table 1. Data collection and handling.

Crystal:	red block, size 0.20 × 0.36 × 0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.05 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	25032, 6174
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5035
$N(param)_{refined}$:	417
Programs:	SHELXS-97 [16], SHELXL-97 [17], SHELXTL [18]

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

Atom	Site	x	y	z	U_{iso}
H(1W)	8*f*	1.1386	0.9939	0.0809	0.065
H(2W)	8*f*	1.0438	0.9912	0.0953	0.065
H(3W)	8*f*	0.9384	0.2200	0.2389	0.722
H(1)	8*f*	0.8432	0.8774	–0.0287	0.058
H(2)	8*f*	0.6897	0.8280	–0.0149	0.060
H(4)	8*f*	0.6736	0.9862	0.0771	0.053
H(5A)	8*f*	0.8291	1.0309	0.0618	0.051
H(6A)	8*f*	0.5437	0.8885	0.0699	0.061
H(6B)	8*f*	0.5709	0.8175	0.0459	0.061
H(7A)	8*f*	0.4848	0.8664	–0.0307	0.062
H(7B)	8*f*	0.4476	0.9309	–0.0031	0.062
H(8A)	8*f*	0.3476	0.8506	0.0354	0.069
H(8B)	8*f*	0.3062	0.8488	–0.0209	0.069
H(10)	8*f*	0.3783	0.7477	–0.0664	0.064
H(11)	8*f*	0.4222	0.6297	–0.0654	0.059
H(12)	8*f*	0.4572	0.6215	0.0738	0.052
H(13)	8*f*	0.4091	0.7390	0.0763	0.057
H(14)	8*f*	0.9920	0.8612	0.1476	0.091
H(15)	8*f*	0.8821	0.8345	0.1983	0.085
H(17)	8*f*	0.8493	1.0426	0.2187	0.089
H(18)	8*f*	0.9582	1.0633	0.1662	0.093
H(19A)	8*f*	0.7982	0.9473	0.2769	0.092
H(19B)	8*f*	0.7742	0.8710	0.2542	0.092
H(20A)	8*f*	0.6146	0.9417	0.2480	0.086
H(20B)	8*f*	0.6584	0.9945	0.2140	0.086
H(21A)	8*f*	0.6055	0.8505	0.1913	0.087
H(21B)	8*f*	0.6532	0.9016	0.1576	0.087
H(23)	8*f*	0.4162	0.8380	0.1736	0.079
H(24)	8*f*	0.2494	0.8749	0.1359	0.082
H(25)	8*f*	0.3625	1.0490	0.0928	0.077
H(26)	8*f*	0.5329	1.0184	0.1311	0.074
H(27)	8*f*	0.3594	0.2638	0.0800	0.153
H(28)	8*f*	0.4673	0.2013	0.1383	0.114
H(30)	8*f*	0.2176	0.1551	0.1948	0.131
H(31)	8*f*	0.1125	0.2198	0.1298	0.162
H(32A)	8*f*	0.4732	0.0975	0.1978	0.118
H(32B)	8*f*	0.3855	0.0981	0.2287	0.118
H(33)	8*f*	0.4562	0.2051	0.2656	0.084

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}
Cl(1)	8*f*	0.511(6)	0.73604(8)	0.18289(6)	0.16292(4)	0.0947(7)	0.1051(7)	0.0864(6)	–0.0041(5)	0.0155(5)	0.0359(5)
O(1)	8*f*	0.511	0.6713(8)	0.2485(4)	0.1582(3)	0.212(7)	0.106(4)	0.099(4)	0.055(4)	0.064(4)	0.047(3)
O(2)	8*f*	0.511	0.7940(8)	0.1796(5)	0.2123(2)	0.218(7)	0.135(5)	0.101(4)	–0.012(4)	–0.041(4)	0.005(3)
O(3)	8*f*	0.511	0.8045(8)	0.1871(5)	0.1321(3)	0.155(6)	0.207(5)	0.129(6)	–0.018(5)	0.072(5)	0.013(7)
O(4)	8*f*	0.511	0.6632(5)	0.1258(3)	0.1543(4)	0.126(4)	0.098(4)	0.233(9)	–0.032(3)	–0.001(5)	0.014(4)
Cl(1′)	8*f*	0.489	0.73604(8)	0.18289(6)	0.16292(4)	0.0947(7)	0.1051(7)	0.0864(6)	–0.0041(5)	0.0155(5)	0.0359(5)
O(1′)	8*f*	0.489	0.7268(8)	0.1452(4)	0.2031(3)	0.212(7)	0.106(4)	0.099(4)	0.055(4)	0.064(4)	0.047(3)
O(2′)	8*f*	0.489	0.6996(9)	0.1379(4)	0.1202(2)	0.218(7)	0.135(5)	0.101(4)	–0.012(4)	–0.041(4)	0.005(3)
O(3′)	8*f*	0.489	0.8502(5)	0.1931(6)	0.1636(4)	0.155(6)	0.207(5)	0.129(6)	–0.018(5)	0.072(5)	0.013(7)
O(4′)	8*f*	0.489	0.6845(7)	0.2497(3)	0.1569(4)	0.126(4)	0.098(4)	0.233(9)	–0.032(3)	–0.001(5)	0.014(4)
Co(1)	4*a*		0	0	0	0.0259(2)	0.0356(2)	0.0419(2)	–0.0070(2)	0.0075(2)	–0.0004(2)
O(5)	8*f*		1.0740(1)	1.00486(8)	0.07387(5)	0.0325(8)	0.0526(9)	0.0447(9)	–0.0031(7)	0.0059(6)	0.0004(7)
O(6)	4*e*		0	0.2378(7)	1/4	0.28(1)	0.29(1)	0.21(3)	0	–0.25(2)	0
N(1)	8*f*		0.8528(1)	0.9594(1)	0.01496(7)	0.0299(9)	0.041(1)	0.047(1)	–0.0079(8)	0.0081(8)	0.0003(8)
N(2)	8*f*		0.4456(1)	0.61261(9)	0.00420(7)	0.0325(9)	0.037(1)	0.049(1)	–0.0065(7)	0.0072(8)	–0.0002(8)
N(3)	8*f*		0.9852(2)	0.9648(2)	0.15075(9)	0.053(1)	0.101(2)	0.057(1)	–0.006(1)	0.015(1)	0.004(1)
N(4)	8*f*		0.2879(2)	0.9654(1)	0.11010(9)	0.043(1)	0.082(2)	0.060(1)	0.002(1)	0.004(1)	–0.010(1)
N(5)	8*f*		0.2277(5)	0.2460(3)	0.0989(2)	0.173(5)	0.121(4)	0.103(3)	0.021(4)	–0.053(4)	–0.012(3)
C(1)	8*f*		0.8090(2)	0.8997(1)	–0.00693(9)	0.039(1)	0.052(1)	0.056(2)	–0.012(1)	0.016(1)	–0.011(1)
C(2)	8*f*		0.7162(2)	0.8698(1)	0.00105(9)	0.042(1)	0.049(1)	0.061(2)	–0.018(1)	0.013(1)	–0.011(1)
C(3)	8*f*		0.6621(2)	0.9016(1)	0.03275(8)	0.031(1)	0.046(1)	0.045(1)	–0.0103(9)	0.0058(9)	0.005(1)
C(4)	8*f*		0.7067(2)	0.9628(1)	0.05537(9)	0.036(1)	0.048(1)	0.052(1)	–0.007(1)	0.015(1)	–0.003(1)
C(5)	8*f*		0.8006(2)	0.9895(1)	0.04581(9)	0.035(1)	0.041(1)	0.053(1)	–0.0103(9)	0.010(1)	–0.005(1)
C(6)	8*f*		0.5600(2)	0.8685(2)	0.04082(9)	0.039(1)	0.061(2)	0.055(2)	–0.020(1)	0.014(1)	–0.000(1)
C(7)	8*f*		0.4653(2)	0.8804(1)	–0.0009(1)	0.035(1)	0.035(1)	0.084(2)	–0.0059(9)	0.008(1)	0.007(1)

Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(8)	8*f*		0.3665(2)	0.8375(1)	0.0052(1)	0.029(1)	0.038(1)	0.104(2)	–0.004(1)	0.013(1)	–0.001(1)
C(9)	8*f*		0.3894(2)	0.7582(1)	0.0052(1)	0.022(1)	0.038(1)	0.076(2)	–0.0076(9)	0.010(1)	–0.001(1)
C(10)	8*f*		0.3937(2)	0.7231(1)	–0.0372(1)	0.050(1)	0.043(1)	0.061(2)	–0.003(1)	0.001(1)	0.009(1)
C(11)	8*f*		0.4209(2)	0.6520(1)	–0.03625(9)	0.052(1)	0.045(1)	0.049(1)	–0.005(1)	0.006(1)	–0.001(1)
C(12)	8*f*		0.4407(2)	0.6470(1)	0.04499(9)	0.039(1)	0.041(1)	0.051(1)	–0.011(1)	0.011(1)	–0.001(1)
C(13)	8*f*		0.4125(2)	0.7182(1)	0.0469(1)	0.037(1)	0.042(1)	0.066(2)	–0.011(1)	0.018(1)	–0.009(1)
C(14)	8*f*		0.9619(3)	0.8986(2)	0.1616(1)	0.071(2)	0.088(2)	0.074(2)	0.001(2)	0.027(2)	–0.007(2)
C(15)	8*f*		0.8958(2)	0.8820(2)	0.1923(1)	0.066(2)	0.076(2)	0.074(2)	–0.006(2)	0.020(2)	0.004(2)
C(16)	8*f*		0.8499(2)	0.9357(2)	0.21412(9)	0.038(1)	0.090(2)	0.044(1)	0.003(1)	0.000(1)	0.009(1)
C(17)	8*f*		0.8762(3)	1.0042(2)	0.2041(1)	0.075(2)	0.084(2)	0.068(2)	0.009(2)	0.023(2)	0.002(2)
C(18)	8*f*		0.9425(3)	1.0162(2)	0.1726(1)	0.076(2)	0.082(2)	0.077(2)	–0.006(2)	0.020(2)	0.012(2)
C(19)	8*f*		0.7737(2)	0.9216(2)	0.2469(1)	0.048(2)	0.130(3)	0.049(2)	0.002(2)	0.006(1)	0.014(2)
C(20)	8*f*		0.6580(2)	0.9450(2)	0.2240(1)	0.049(2)	0.113(3)	0.054(2)	0.002(2)	0.014(1)	–0.003(2)
C(21)	8*f*		0.6081(2)	0.8997(2)	0.1810(1)	0.053(2)	0.087(2)	0.074(2)	0.007(2)	0.006(2)	–0.006(2)
C(22)	8*f*		0.4959(2)	0.9237(2)	0.1569(1)	0.045(1)	0.078(2)	0.050(1)	0.005(1)	0.008(1)	–0.010(1)
C(23)	8*f*		0.4078(2)	0.8816(2)	0.1575(1)	0.059(2)	0.079(2)	0.059(2)	–0.002(2)	0.009(1)	0.006(2)
C(24)	8*f*		0.3074(2)	0.9042(2)	0.1344(1)	0.049(2)	0.094(2)	0.061(2)	–0.014(2)	0.008(1)	–0.003(2)
C(25)	8*f*		0.3731(2)	1.0059(2)	0.1095(1)	0.056(2)	0.067(2)	0.066(2)	0.003(1)	0.007(1)	–0.004(1)
C(26)	8*f*		0.4764(2)	0.9876(2)	0.1323(1)	0.046(2)	0.071(2)	0.070(2)	–0.007(1)	0.013(1)	–0.011(2)
C(27)	8*f*		0.3292(6)	0.2407(3)	0.1029(2)	0.202(6)	0.094(3)	0.062(2)	–0.006(4)	–0.021(3)	–0.006(2)
C(28)	8*f*		0.3945(4)	0.2037(2)	0.1380(1)	0.129(3)	0.076(2)	0.069(2)	0.007(2)	0.001(2)	–0.013(2)
C(29)	8*f*		0.3554(3)	0.1693(2)	0.1737(1)	0.099(3)	0.066(2)	0.056(2)	0.004(2)	–0.016(2)	–0.012(2)
C(30)	8*f*		0.2490(4)	0.1757(3)	0.1715(2)	0.104(3)	0.122(4)	0.088(3)	–0.001(3)	–0.007(2)	–0.020(2)
C(31)	8*f*		0.1858(5)	0.2156(3)	0.1320(2)	0.108(4)	0.145(5)	0.128(5)	0.019(3)	–0.027(4)	–0.042(4)
C(32)	8*f*		0.4285(3)	0.1284(2)	0.2126(1)	0.124(3)	0.067(2)	0.080(2)	0.001(2)	–0.029(2)	–0.003(2)
C(33)	4*e*		1/2	0.1747(2)	1/4	0.085(3)	0.065(3)	0.053(2)	0	–0.001(2)	0

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