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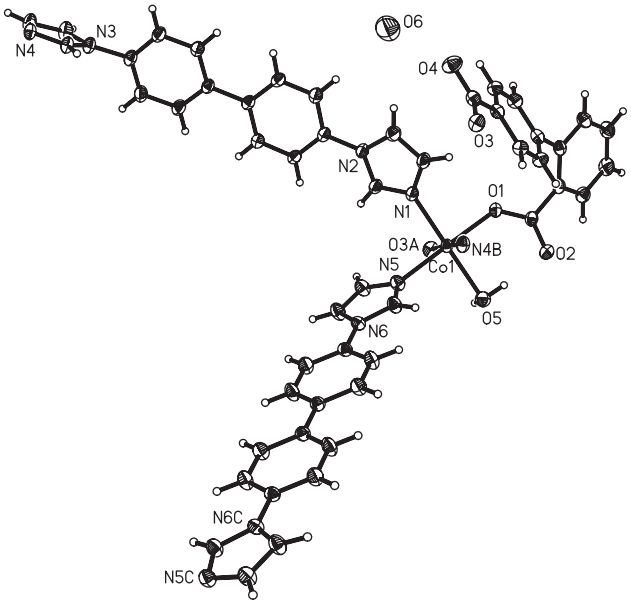
Crystal structure of poly[diaquabis(μ$_2$-biphenyl-2,4′-dicarboxylato-κ^2*O*:*O*′)tris(μ$_2$-1,1′-biphenyl-4,4′-diylbis(1*H*-imidazole)-κ^2*N*:*N*′)dicobalt(II)] monohydrat, $C_{82}H_{64}N_{12}O_{11}Co_2$



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Abstract

$C_{82}H_{64}N_{12}O_{11}Co_2$, orthorhombic, *Pbcn* (no. 60), $a = 22.286(7)$ Å, $b = 22.725(7)$ Å, $c = 14.056(5)$ Å, $V = 7119(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0582$, $wR_{ref}(F^2) = 0.1634$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Red, prism, size 0.19×0.20×0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.39 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, ω scans
$2\theta_{max}$:	55.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	72939, 8195
$N(param)_{refined}$:	489
Programs:	SHELX [12]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5A)	8*d*	0.078(2)	0.211(1)	1.038(1)	0.069
H(5B)	8*d*	0.091(2)	0.2653(7)	0.999(2)	0.069
H(4)	8*d*	0.3304	0.4635	1.0588	0.054
H(5)	8*d*	0.2916	0.5038	1.1969	0.063
H(6)	8*d*	0.2018	0.4703	1.2572	0.066
H(7)	8*d*	0.1498	0.3961	1.1796	0.056
H(9)	8*d*	0.3740	0.3707	0.9827	0.048
H(10)	8*d*	0.4122	0.3450	0.8356	0.048
H(12)	8*d*	0.2497	0.3674	0.7187	0.045
H(13)	8*d*	0.2115	0.3941	0.8650	0.047
H(15)	8*d*	0.2772	0.0984	0.9744	0.050
H(16)	8*d*	0.2987	0.2572	0.8755	0.059
H(17)	8*d*	0.3928	0.2047	0.8475	0.064
H(19)	8*d*	0.4628	0.1340	0.8601	0.061
H(20)	8*d*	0.5304	0.0577	0.8497	0.059
H(22)	8*d*	0.4053	−0.0548	0.9392	0.051
H(23)	8*d*	0.3372	0.0213	0.9525	0.053
H(25)	8*d*	0.5854	−0.0096	0.8178	0.057
H(26)	8*d*	0.6488	−0.0864	0.7820	0.060
H(28)	8*d*	0.5316	−0.1995	0.8948	0.065
H(29)	8*d*	0.4691	−0.1225	0.9336	0.063
H(30)	8*d*	0.6104	−0.1923	0.6532	0.047
H(31)	8*d*	0.7193	−0.3026	0.7799	0.058
H(32)	8*d*	0.6764	−0.2387	0.9039	0.062
H(33)	8*d*	0.1011	0.1518	0.7877	0.054
H(34)	8*d*	0.1722	0.0559	0.9878	0.056
H(35)	8*d*	0.1304	−0.0116	0.8703	0.059
H(37)	8*d*	0.0855	−0.0423	0.7304	0.058
H(38)	8*d*	0.0376	−0.0712	0.5931	0.061
H(40)	8*d*	0.0043	0.0967	0.5298	0.056
H(41)	8*d*	0.0517	0.1258	0.6657	0.057

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	8*d*	0.17447(2)	0.20508(2)	0.96154(3)	0.0348(2)	0.0285(2)	0.0304(2)	0.0036(2)	−0.0041(2)	0.0005(2)
O(1)	8*d*	0.2039(1)	0.28649(9)	1.0135(2)	0.040(1)	0.032(1)	0.047(1)	0.0036(9)	−0.002(1)	−0.0056(9)
O(2)	8*d*	0.1192(1)	0.3402(1)	1.0175(2)	0.038(1)	0.044(1)	0.072(2)	0.007(1)	−0.007(1)	−0.006(1)
O(3)	8*d*	0.3220(1)	0.3348(1)	0.5967(1)	0.048(1)	0.049(1)	0.030(1)	0.005(1)	−0.001(1)	−0.0049(9)
O(4)	8*d*	0.4139(1)	0.3220(1)	0.6579(2)	0.043(1)	0.080(2)	0.047(1)	0.005(1)	0.001(1)	−0.016(1)
O(5)	8*d*	0.0802(1)	0.2299(1)	0.9851(2)	0.046(1)	0.044(1)	0.047(1)	−0.001(1)	−0.002(1)	0.004(1)
O(6)	4*c*	0.5	0.2422(2)	0.75	0.108(4)	0.099(4)	0.140(5)	0.0	−0.042(4)	0.0
N(1)	8*d*	0.2657(1)	0.1820(1)	0.9362(2)	0.037(1)	0.033(1)	0.040(1)	0.007(1)	−0.001(1)	−0.001(1)
N(2)	8*d*	0.3506(1)	0.1332(1)	0.9109(2)	0.036(1)	0.034(1)	0.041(1)	0.007(1)	0.002(1)	0.001(1)
N(3)	8*d*	0.6309(1)	−0.1990(1)	0.7935(2)	0.045(2)	0.043(1)	0.035(1)	0.011(1)	0.003(1)	−0.008(1)
N(4)	8*d*	0.6683(1)	−0.2567(1)	0.6819(2)	0.046(1)	0.035(1)	0.034(1)	0.008(1)	0.005(1)	−0.005(1)
N(5)	8*d*	0.1432(1)	0.1237(1)	0.9038(2)	0.050(2)	0.037(1)	0.037(1)	−0.001(1)	−0.010(1)	0.001(1)
N(6)	8*d*	0.1042(1)	0.0632(1)	0.7971(2)	0.038(1)	0.037(1)	0.036(1)	−0.004(1)	−0.003(1)	−0.002(1)
C(1)	8*d*	0.1746(1)	0.3327(1)	1.0302(2)	0.040(2)	0.034(2)	0.031(1)	0.004(1)	0.002(1)	0.000(1)
C(2)	8*d*	0.2094(1)	0.3838(1)	1.0724(2)	0.042(2)	0.035(2)	0.032(1)	0.005(1)	−0.002(1)	−0.004(1)
C(3)	8*d*	0.2637(1)	0.4051(1)	1.0343(2)	0.043(2)	0.032(1)	0.033(1)	0.002(1)	−0.003(1)	−0.001(1)
C(4)	8*d*	0.2940(2)	0.4497(1)	1.0826(2)	0.052(2)	0.042(2)	0.041(2)	−0.005(2)	−0.004(2)	−0.006(1)
C(5)	8*d*	0.2708(2)	0.4740(2)	1.1657(3)	0.060(2)	0.047(2)	0.050(2)	−0.000(2)	−0.007(2)	−0.018(2)
C(6)	8*d*	0.2173(2)	0.4540(2)	1.2018(3)	0.064(2)	0.057(2)	0.044(2)	0.007(2)	0.006(2)	−0.021(2)
C(7)	8*d*	0.1862(2)	0.4092(2)	1.1553(2)	0.049(2)	0.048(2)	0.043(2)	0.005(2)	0.007(2)	−0.008(2)
C(8)	8*d*	0.2882(1)	0.3850(1)	0.9405(2)	0.044(2)	0.031(1)	0.033(1)	−0.005(1)	0.000(1)	−0.000(1)
C(9)	8*d*	0.3488(1)	0.3702(1)	0.9299(2)	0.041(2)	0.045(2)	0.033(2)	−0.001(1)	−0.005(1)	−0.005(1)
C(10)	8*d*	0.3719(1)	0.3548(1)	0.8412(2)	0.037(2)	0.044(2)	0.040(2)	−0.001(1)	−0.001(1)	−0.002(1)
C(11)	8*d*	0.3353(1)	0.3538(1)	0.7608(2)	0.041(2)	0.032(1)	0.034(2)	−0.005(1)	0.002(1)	−0.001(1)
C(12)	8*d*	0.2749(1)	0.3683(1)	0.7714(2)	0.039(2)	0.042(2)	0.030(1)	−0.001(1)	−0.003(1)	0.001(1)
C(13)	8*d*	0.2518(1)	0.3840(1)	0.8597(2)	0.037(2)	0.047(2)	0.035(2)	0.002(1)	0.001(1)	−0.000(1)
C(14)	8*d*	0.3589(1)	0.3352(1)	0.6641(2)	0.045(2)	0.035(2)	0.033(2)	−0.004(1)	0.003(1)	−0.002(1)
C(15)	8*d*	0.2941(1)	0.1315(1)	0.9462(2)	0.037(2)	0.036(2)	0.051(2)	0.007(1)	0.004(1)	0.005(1)
C(16)	8*d*	0.3061(2)	0.2183(1)	0.8921(3)	0.045(2)	0.034(2)	0.067(2)	0.009(1)	0.008(2)	0.011(2)
C(17)	8*d*	0.3585(2)	0.1896(2)	0.8761(3)	0.043(2)	0.040(2)	0.076(2)	0.003(1)	0.011(2)	0.012(2)
C(18)	8*d*	0.3925(1)	0.0858(1)	0.9056(2)	0.036(2)	0.039(2)	0.036(2)	0.009(1)	−0.001(1)	−0.003(1)
C(19)	8*d*	0.4508(2)	0.0960(2)	0.8757(3)	0.045(2)	0.038(2)	0.070(2)	0.006(1)	0.012(2)	0.002(2)
C(20)	8*d*	0.4913(2)	0.0498(1)	0.8690(3)	0.036(2)	0.042(2)	0.068(2)	0.005(1)	0.015(2)	−0.000(2)
C(21)	8*d*	0.4755(1)	−0.0076(1)	0.8901(2)	0.035(2)	0.041(2)	0.032(1)	0.008(1)	−0.001(1)	−0.004(1)
C(22)	8*d*	0.4170(1)	−0.0169(1)	0.9225(2)	0.039(2)	0.036(2)	0.053(2)	0.005(1)	0.002(2)	−0.002(1)
C(23)	8*d*	0.3758(1)	0.0288(1)	0.9305(2)	0.033(2)	0.041(2)	0.058(2)	0.006(1)	0.007(2)	0.001(2)
C(24)	8*d*	0.5184(1)	−0.0571(1)	0.8757(2)	0.036(2)	0.040(2)	0.031(1)	0.008(1)	−0.000(1)	−0.006(1)
C(25)	8*d*	0.5737(2)	−0.0479(2)	0.8324(3)	0.044(2)	0.037(2)	0.063(2)	0.004(1)	0.013(2)	−0.001(2)
C(26)	8*d*	0.6119(2)	−0.0939(2)	0.8105(3)	0.044(2)	0.043(2)	0.063(2)	0.008(2)	0.017(2)	−0.001(2)
C(27)	8*d*	0.5951(1)	−0.1508(1)	0.8311(2)	0.042(2)	0.045(2)	0.033(2)	0.010(1)	0.002(1)	−0.007(1)
C(28)	8*d*	0.5422(2)	−0.1613(2)	0.8782(3)	0.056(2)	0.035(2)	0.072(2)	0.005(2)	0.017(2)	−0.002(2)
C(29)	8*d*	0.5046(2)	−0.1149(2)	0.9008(3)	0.048(2)	0.045(2)	0.065(2)	0.005(2)	0.024(2)	−0.004(2)
C(30)	8*d*	0.6322(1)	−0.2122(1)	0.6995(2)	0.045(2)	0.038(2)	0.035(2)	0.010(1)	0.002(1)	−0.003(1)
C(31)	8*d*	0.6918(2)	−0.2725(2)	0.7697(2)	0.057(2)	0.047(2)	0.042(2)	0.021(2)	−0.005(2)	−0.003(2)
C(32)	8*d*	0.6684(2)	−0.2371(2)	0.8390(2)	0.070(2)	0.053(2)	0.031(2)	0.019(2)	−0.010(2)	−0.005(2)
C(33)	8*d*	0.1138(2)	0.1195(1)	0.8230(2)	0.056(2)	0.034(2)	0.044(2)	−0.001(1)	−0.015(2)	0.002(1)
C(34)	8*d*	0.1527(2)	0.0669(1)	0.9322(2)	0.060(2)	0.038(2)	0.042(2)	−0.005(2)	−0.012(2)	0.006(1)
C(35)	8*d*	0.1295(2)	0.0293(2)	0.8677(2)	0.066(2)	0.035(2)	0.047(2)	−0.004(2)	−0.014(2)	0.003(1)
C(36)	8*d*	0.0742(1)	0.0448(1)	0.7122(2)	0.036(2)	0.040(2)	0.032(1)	−0.003(1)	−0.001(1)	−0.006(1)
C(37)	8*d*	0.0694(2)	−0.0141(2)	0.6899(2)	0.056(2)	0.039(2)	0.049(2)	0.004(2)	−0.015(2)	−0.002(1)
C(38)	8*d*	0.0404(2)	−0.0313(2)	0.6071(2)	0.066(2)	0.035(2)	0.052(2)	−0.001(2)	−0.020(2)	−0.009(2)
C(39)	8*d*	0.0153(1)	0.0092(1)	0.5442(2)	0.035(2)	0.042(2)	0.037(2)	−0.001(1)	−0.001(1)	−0.008(1)
C(40)	8*d*	0.0207(2)	0.0682(1)	0.5697(2)	0.055(2)	0.040(2)	0.045(2)	−0.002(2)	−0.010(2)	0.001(1)
C(41)	8*d*	0.0491(2)	0.0860(1)	0.6512(2)	0.065(2)	0.035(2)	0.043(2)	−0.002(2)	−0.007(2)	−0.004(1)

Source of material

A mixture of 4,4′-bis(imidazolyl)biphenyl (bibp, 0.1 mmol, 28.6 mg), 2,4′-biphenyldicarboxylic acid (H_2bpdc, 0.1 mmol, 24.2 mg) and $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 29.6 mg) in H_2O (10 mL) was sealed into a 25 mL stainless steel reactor with a Teflon liner and heated at 443 K for 3 d. The reactor was cooled slowly to room temperature. Red prism crystals of the title complex were obtained.

Experimental details

The coordinates of the aromatic H atoms were idealized and refined using a riding model (AFIX 43 option of the SHELX-2013 program [11]). The O—H distances in the coordinated water are restrained to 0.85(1) Å (DFIX option of the SHELX-2013 program [11]). The H atoms on the free water were not found in the Fourier synthesis and therefore not included in the refinement.

Discussion

In the last two decades, Co(II)-based coordination polymers (Co-CPs) have drawn considerable attention because of their huge diversity and versatility structure and potential applications in the areas of magnetism, catalysis, adsorption/separation, nonlinear optics etc [1–4]. According to a survey of the previous references, bis(imidazole) ligands, as well-known N-donor ligands, have been widely utilized for tunability of structural frameworks [5, 6]. As part of our investigations on the structural diversity, magnetism and photocatalytic properties of metal aromatic polycarboxylic frameworks, some novel Co-CPs with gas adsorption and photocatalysis and magnetic properties are reported [7–10]. Herein, 2,4′-biphenyldicarboxylic acid (H_2bpdc) is selected to form a bridging ligand after deprotonation and reacted with a Co(II) salt. Then the bis(imidazole) ligand, bibp (4,4′-bis(imidazolyl)biphenyl) is indroduced which gives the title compound shown in the figure. The central Co(II) ion is six-coordinated by three nitrogen atoms of three bibp and two *cis* oxygen atoms from two bpdc and one water ligand. The Co—N bond lengths are in the range of 2.131(3)–2.199(2) Å and the Co—O ones are in the range of 2.094(2)–2.201(3) Å, respectively. Both carboxylate groups of bpdc are deprotonated and display monodentate coordination to two Co(II). The adjacent Co(II) ions are bridged by bpdc to form a 1D chain. Such 1D chains are further interlinked by rigid bibp ligands to generate a 3D network. In order to minimize the big void cavities and stabilize the framework, the potential voids formed by a single 3D network show incorporation of another identical one rotated 90° around *c* axis resulting in an interpenetrated frameworks [11]. Analysis of the network topology of the title complex reveals that each Co(II) acts as a 5-connected node to connect five Co(II) atoms via two bpdc and three bibp. Thus, a uninodal 5-connected 3D network with the point symbol of $(4^4 \cdot 6^6)$ is constituted.

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