# Crystal structure of diaqua-bis(2-(4-carboxyphenyl)acetato-κ*O*)-bis(1,3-di(pyridin-4-yl)propane-κ*N*)cobalt(II), $C_{44}H_{46}CoN_4O_{10}$

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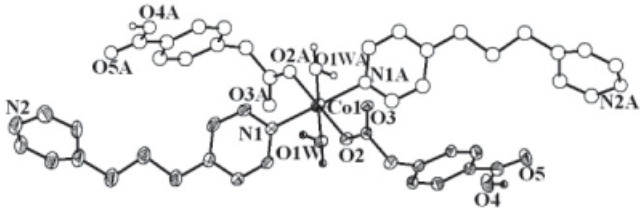


**Abstract**

$C_{44}H_{46}CoN_4O_{10}$, monoclinic, *C*2/*c* (no. 15), $a$ = 43.953(6) Å, $b$ = 8.375(1) Å, $c$ = 11.404(2) Å, $\beta$ = 101.210(1)°, $V$ = 4117.7 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0322, $wR_{ref}(F^2)$ = 0.0836, $T$ = 296 K.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | brown blocks, size 0.21×0.32×0.47 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 4.81 cm$^{-1}$ |
| Diffractometer, scan mode: | CCD area detector, $\varphi$ and $\omega$ |
| $2\theta_{max}$: | 51° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 14816, 3829 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 3123 |
| $N(param)_{refined}$: | 307 |
| Programs: | SHELX [10] |

## Source of material

The mixtures of 4-carboxyphenylacetic acid (0.2 mmol, 37.4 mg), 1,3-di(pyridin-4-yl)propane (*bpp*) (0.1 mmol, 19.8 mg), $Co(OAC)_2{\cdot}4H_2O$ (0.1 mmol, 24.9 mg), NaOH (0.1 mmol), and $H_2O$ (7.0 ml) were placed in a 23 ml Teflon lined stainless steel reactor. The vessel was heated to 393K for 4 days, and then slowly cooled to room temperature. Brown, block-shaped crystals were obtained, crystals were filtered off, washed with mother liquid, and dried under ambient conditions.

## Discussion

Metal-organic frameworks (MOFs) with well-regulated network structures have provoked significant interest as functional materials displaying potential applications in such fields as magnetism, molecular separation, catalysis, luminescence, and molecule storage [1-5]. Aromatic multi-carboxylate ligands are good candidates for the construction of the layers, wherein diverse binding modes of the carboxylates help enhance the robustness of metal-carboxylate networks [6,7]. Dipyridyl-type ligands are desired pillar spacers, which can allow easy control of channel dimensions between the metal-carboxylate layers. The key to synthesize MOFs with permanent porosity is to prevent the disruption of framework integrity even after guest elimination. Though the reports concerning this aspect are emerging, it has still been a tremendous challenge to obtain the dynamic microporous MOFs [8,9]. The asymmetric unit of the title complex contains one 1,3-di(pyridin-4-yl)propane (*bpp*) ligand, one-half Co ion, one 2-(4-carboxyphenyl)acetato ligand and one coordinated water molecule as shown in Fig. 1. The Co metal center is sixfold-coordinated by two N atoms at the axial positions of the coordination sphere belonging to two symmetry-related *bpp* molecules (Co(1)–N(1)/N(1A) = 2.1595(15) Å), two oxygen atoms from two symmetry-related 2-(4-carboxyphenyl)acetato ligands (Co(1)–O(2)/O(2A) = 2.0561(12) Å) and two symmetry-related coordinated water molecules (Co(1)–O(1)/O(1A) = 2.1322(12) Å). The $[CoO_4N_2]$ environment is best described as octahedrally coordination geometry. The flexible $-CH_2COO^-$ groups adopts a single-coordination mode to connect one Co(II) atom. In the complex, there are two kinds of H-bonds. Firstly, the H-bonding interactions of the H atom of the –COOH group and one of the N atoms of *bpp* (O(4)–H(4)···N(2)#3 distances are 1.82 Å) connect the complexes to a 1D sub. Secondly, hydrogen in coordinated water and the carboxylate oxygen in adjacent 2-(4-carboxyphenyl)acetato ligands (O(1)–H(2W)···O(3)#2 1.94 Å; O(1)–H(1W)···O(3)#1 1.93 Å) form hydrogen bonds which further result in a 3D structure.

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

| Atom | Site | Occ. | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|---|
| H(19) | 8*f* | 0.499 | 0.4669 | 0.8923 | 0.6184 | 0.095 |
| H(20) | 8*f* | 0.499 | 0.5164 | 0.8044 | 0.7066 | 0.090 |
| H(21) | 8*f* | 0.499 | 0.5256 | 0.6105 | 0.4072 | 0.078 |
| H(22) | 8*f* | 0.499 | 0.4785 | 0.6845 | 0.3183 | 0.076 |
| H(19') | 8*f* | 0.501 | 0.4552 | 0.6792 | 0.5496 | 0.068 |
| H(20') | 8*f* | 0.501 | 0.5033 | 0.6017 | 0.6457 | 0.073 |
| H(21') | 8*f* | 0.501 | 0.5419 | 0.8239 | 0.4142 | 0.072 |
| H(22') | 8*f* | 0.501 | 0.4939 | 0.9127 | 0.3143 | 0.068 |
| H(2W) | 8*f* | | 0.2317 | 0.7538 | 0.2553 | 0.060 |
| H(1W) | 8*f* | | 0.2465 | 0.6166 | 0.3139 | 0.060 |
| H(4) | 8*f* | | 0.0649 | 0.8641 | 0.1291 | 0.121 |
| H(2A) | 8*f* | | 0.2038 | 1.3014 | 0.5213 | 0.048 |
| H(2B) | 8*f* | | 0.2162 | 1.2618 | 0.4043 | 0.048 |
| H(4A) | 8*f* | | 0.1855 | 1.0641 | 0.2581 | 0.047 |
| H(5) | 8*f* | | 0.1373 | 0.9647 | 0.1748 | 0.051 |
| H(7) | 8*f* | | 0.1032 | 1.1366 | 0.4501 | 0.061 |
| H(8) | 8*f* | | 0.1512 | 1.2390 | 0.5317 | 0.057 |
| H(10) | 8*f* | | 0.3207 | 0.7291 | 0.6066 | 0.056 |
| H(11) | 8*f* | | 0.3678 | 0.7896 | 0.5630 | 0.062 |
| H(13) | 8*f* | | 0.3240 | 0.9983 | 0.2627 | 0.050 |
| H(14) | 8*f* | | 0.2782 | 0.9301 | 0.3135 | 0.047 |
| H(15A) | 8*f* | | 0.3852 | 1.0495 | 0.3705 | 0.074 |
| H(15B) | 8*f* | | 0.3795 | 0.9057 | 0.2816 | 0.074 |
| H(16A) | 8*f* | | 0.4157 | 0.8951 | 0.5149 | 0.074 |
| H(16B) | 8*f* | | 0.4070 | 0.7393 | 0.4392 | 0.074 |
| H(17A) | 8*f* | | 0.4404 | 0.9934 | 0.3622 | 0.086 |
| H(17B) | 8*f* | | 0.4333 | 0.8313 | 0.2944 | 0.086 |

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**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | Occ. | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C(18) | 8*f* | | 0.46874(5) | 0.8136(3) | 0.4385(3) | 0.035(1) | 0.064(2) | 0.085(2) | 0.004(1) | 0.002(1) | 0.000(1) |
| N(2) | 8*f* | | 0.52704(4) | 0.7069(3) | 0.5531(2) | 0.040(1) | 0.079(2) | 0.083(2) | 0.011(1) | 0.001(1) | 0.004(1) |
| C(19) | 8*f* | 0.499 | 0.4796(1) | 0.8414(9) | 0.5735(5) | 0.044(3) | 0.119(6) | 0.073(4) | 0.015(3) | 0.009(2) | –0.018(4) |
| C(20) | 8*f* | 0.499 | 0.5087(1) | 0.7880(9) | 0.6255(5) | 0.055(3) | 0.115(5) | 0.052(3) | –0.001(3) | 0.002(2) | –0.001(3) |
| C(21) | 8*f* | 0.499 | 0.5146(1) | 0.6742(7) | 0.4509(5) | 0.045(3) | 0.075(4) | 0.076(4) | 0.015(3) | 0.013(3) | –0.004(3) |
| C(22) | 8*f* | 0.499 | 0.4858(1) | 0.7227(7) | 0.3951(4) | 0.048(3) | 0.081(4) | 0.057(3) | 0.006(3) | 0.003(2) | –0.007(3) |
| C(19') | 8*f* | 0.501 | 0.4725(1) | 0.7187(6) | 0.5232(5) | 0.044(3) | 0.066(3) | 0.063(3) | –0.005(2) | 0.014(2) | 0.009(3) |
| C(20') | 8*f* | 0.501 | 0.5022(1) | 0.6695(7) | 0.5805(5) | 0.048(3) | 0.077(4) | 0.057(3) | 0.014(3) | 0.008(2) | 0.013(3) |
| C(21') | 8*f* | 0.501 | 0.5242(1) | 0.8002(7) | 0.4442(4) | 0.036(2) | 0.083(4) | 0.063(3) | 0.000(2) | 0.012(2) | 0.002(3) |
| C(22') | 8*f* | 0.501 | 0.4960(1) | 0.8541(7) | 0.3846(4) | 0.041(2) | 0.075(4) | 0.056(3) | 0.006(2) | 0.013(2) | 0.009(2) |
| Co(1) | 4*c* | | $\frac{1}{4}$ | $\frac{3}{4}$ | $\frac{1}{2}$ | 0.0308(2) | 0.0310(2) | 0.0286(2) | 0.0013(1) | 0.0002(1) | –0.0017(1) |
| N(1) | 8*f* | | 0.29452(3) | 0.8210(2) | 0.4640(1) | 0.0347(8) | 0.0324(8) | 0.0375(8) | 0.0030(6) | 0.0007(6) | 0.0004(7) |
| O(1) | 8*f* | | 0.23393(3) | 0.6932(2) | 0.3161(1) | 0.0483(8) | 0.0380(7) | 0.0312(6) | 0.0010(6) | 0.0001(6) | –0.0012(5) |
| O(2) | 8*f* | | 0.23327(3) | 0.9771(1) | 0.4613(1) | 0.0427(7) | 0.0350(7) | 0.0335(7) | 0.0050(6) | 0.0036(5) | –0.0020(5) |
| O(3) | 8*f* | | 0.22977(3) | 1.0743(2) | 0.6400(1) | 0.0555(8) | 0.0459(8) | 0.0328(7) | 0.0072(6) | 0.0027(6) | –0.0051(6) |
| O(4) | 8*f* | | 0.08286(3) | 0.8899(3) | 0.1560(2) | 0.0386(9) | 0.123(2) | 0.080(1) | –0.023(1) | 0.0081(8) | –0.033(1) |
| O(5) | 8*f* | | 0.06157(4) | 0.9958(3) | 0.2981(2) | 0.0407(9) | 0.142(2) | 0.085(1) | –0.015(1) | 0.0210(9) | –0.015(1) |
| C(1) | 8*f* | | 0.22452(4) | 1.0792(2) | 0.5283(2) | 0.0257(9) | 0.0306(9) | 0.037(1) | –0.0046(7) | 0.0023(7) | –0.0022(7) |
| C(2) | 8*f* | | 0.20566(4) | 1.2178(2) | 0.4643(2) | 0.039(1) | 0.033(1) | 0.045(1) | 0.0000(8) | –0.0005(8) | –0.0016(8) |
| C(3) | 8*f* | | 0.17369(4) | 1.1601(2) | 0.4053(2) | 0.034(1) | 0.033(1) | 0.040(1) | 0.0049(8) | 0.0026(8) | 0.0059(8) |
| C(4) | 8*f* | | 0.16899(4) | 1.0786(2) | 0.2972(2) | 0.0311(9) | 0.048(1) | 0.040(1) | 0.0020(8) | 0.0073(8) | 0.0011(8) |
| C(5) | 8*f* | | 0.14013(4) | 1.0189(2) | 0.2473(2) | 0.038(1) | 0.051(1) | 0.036(1) | –0.0001(9) | 0.0040(8) | –0.0026(9) |
| C(6) | 8*f* | | 0.11521(4) | 1.0389(2) | 0.3043(2) | 0.031(1) | 0.051(1) | 0.041(1) | 0.0019(8) | 0.0034(8) | 0.0082(9) |
| C(7) | 8*f* | | 0.11969(5) | 1.1217(3) | 0.4111(2) | 0.041(1) | 0.068(1) | 0.047(1) | 0.006(1) | 0.0141(9) | 0.001(1) |
| C(8) | 8*f* | | 0.14859(5) | 1.1823(3) | 0.4603(2) | 0.047(1) | 0.053(1) | 0.041(1) | 0.006(1) | 0.0067(9) | –0.0059(9) |
| C(9) | 8*f* | | 0.08395(5) | 0.9728(3) | 0.2536(2) | 0.036(1) | 0.070(2) | 0.053(1) | –0.002(1) | 0.006(1) | 0.011(1) |
| C(10) | 8*f* | | 0.32131(4) | 0.7827(2) | 0.5357(2) | 0.041(1) | 0.052(1) | 0.042(1) | 0.0013(9) | –0.0030(9) | 0.0097(9) |
| C(11) | 8*f* | | 0.34986(5) | 0.8188(3) | 0.5099(2) | 0.032(1) | 0.060(1) | 0.057(1) | 0.0050(9) | –0.0069(9) | 0.010(1) |
| C(12) | 8*f* | | 0.35192(4) | 0.8984(2) | 0.4052(2) | 0.035(1) | 0.038(1) | 0.057(1) | 0.0026(8) | 0.0047(9) | –0.0004(9) |
| C(13) | 8*f* | | 0.32408(4) | 0.9415(2) | 0.3328(2) | 0.039(1) | 0.041(1) | 0.043(1) | 0.0036(8) | 0.0062(8) | 0.0052(8) |
| C(14) | 8*f* | | 0.29655(4) | 0.9006(2) | 0.3644(2) | 0.034(1) | 0.039(1) | 0.041(1) | 0.0046(8) | 0.0001(8) | 0.0059(8) |
| C(15) | 8*f* | | 0.38184(5) | 0.9350(3) | 0.3652(2) | 0.035(1) | 0.066(2) | 0.084(2) | 0.004(1) | 0.011(1) | 0.010(1) |
| C(16) | 8*f* | | 0.41083(5) | 0.8529(3) | 0.4342(2) | 0.036(1) | 0.071(2) | 0.076(2) | 0.001(1) | 0.004(1) | 0.002(1) |
| C(17) | 8*f* | | 0.43804(5) | 0.8795(3) | 0.3731(3) | 0.038(1) | 0.077(2) | 0.098(2) | 0.004(1) | 0.007(1) | 0.011(2) |

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