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Crystal structure of the 2D coordination polymer poly[*diaqua-bis*(μ_2 -3-methoxyisonicotinato- $\kappa^2N:O$)cobalt(II)] – dimethylformamide (1/1), $C_{20}H_{30}CoN_4O_{10}$

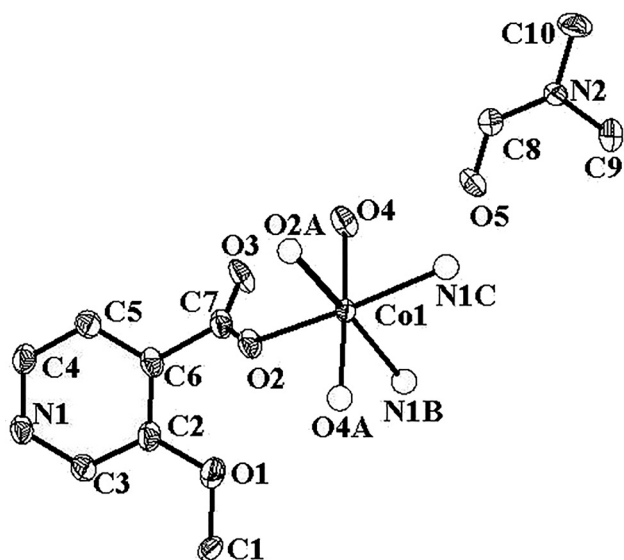


Table 1: Data collection and handling.

Crystal:	Violet block
Size:	0.35 × 0.31 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.78 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{\max} , completeness:	28.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13809, 2692, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2486
$N(\text{param})_{\text{refined}}$:	162
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The mixtures of 3-methoxy-4-pyridinecarboxylic acid (mpca) (0.1 mmol, 15.3 mg), $Co(OAc)_2 \cdot 4H_2O$ (0.1 mmol, 24.9 mg), DMF (2.0 ml) and H_2O (2.0 ml) were placed in a 23 ml Teflon liner stainless steel reactor. The vessel was heated to 393 K for four days, then cooled slowly to the room temperature. Light violet crystals were obtained, and further crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield 47% (based on mpca).

Experimental details

A suitable crystal was selected and mounted on a SuperNova, Single source at offset/far, EosS2 diffractometer. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program using Intrinsic Phasing and

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Abstract

$C_{20}H_{30}CoN_4O_{10}$, monoclinic, $C2/c$ (no. 15), $a = 13.4752(4)$ Å, $b = 12.8563(3)$ Å, $c = 15.0144(5)$ Å, $\beta = 113.429(4)^\circ$, $V = 2386.66(14)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0291$, $wR_{\text{ref}}(F^2) = 0.0719$, $T = 293(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure (Hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 contains

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Co1	0.5000	0.26859 (2)	0.2500	0.01906 (9)
O1	0.14822 (10)	0.15723 (9)	0.19780 (10)	0.0398 (3)
O2	0.38912 (8)	0.15437 (8)	0.25597 (8)	0.0256 (2)
O3	0.41089 (12)	0.15230 (12)	0.41147 (9)	0.0493 (4)
O4	0.57023 (9)	0.26334 (9)	0.40186 (8)	0.0310 (3)
H4A	0.5990	0.3216	0.4245	0.046*
H4B	0.5240	0.2312	0.4169	0.046*
N1	0.12150 (10)	-0.11318 (10)	0.26005 (10)	0.0250 (3)
C1	0.03986 (15)	0.17600 (15)	0.13067 (16)	0.0437 (5)
H1A	0.0206	0.1266	0.0785	0.066*
H1B	0.0344	0.2452	0.1051	0.066*
H1C	-0.0083	0.1688	0.1632	0.066*
C2	0.17226 (12)	0.06045 (12)	0.23658 (12)	0.0258 (3)
C3	0.09733 (12)	-0.01953 (12)	0.21677 (12)	0.0265 (3)
H3	0.0273	-0.0079	0.1716	0.032*
C4	0.22319 (12)	-0.12973 (12)	0.32268 (13)	0.0284 (3)
H4	0.2414	-0.1945	0.3524	0.034*
C5	0.30271 (12)	-0.05408 (12)	0.34513 (12)	0.0281 (3)
H5	0.3725	-0.0685	0.3895	0.034*
C6	0.27861 (12)	0.04285 (12)	0.30173 (11)	0.0243 (3)
C7	0.36672 (12)	0.12498 (12)	0.32547 (12)	0.0250 (3)
O5	0.63074 (11)	0.44757 (11)	0.49054 (10)	0.0474 (3)
N2	0.78216 (12)	0.53833 (12)	0.57444 (11)	0.0386 (4)
C8	0.72914 (16)	0.45240 (15)	0.53709 (13)	0.0383 (4)
H8	0.7687	0.3911	0.5465	0.046*
C9	0.7244 (2)	0.63510 (18)	0.5639 (2)	0.0719 (8)
H9A	0.7209	0.6700	0.5062	0.108*
H9B	0.7614	0.6784	0.6194	0.108*
H9C	0.6525	0.6213	0.5591	0.108*
C10	0.89875 (17)	0.5407 (2)	0.62035 (18)	0.0661 (7)
H10A	0.9262	0.4709	0.6297	0.099*
H10B	0.9210	0.5749	0.6821	0.099*
H10C	0.9266	0.5779	0.5798	0.099*

refined with the ShelXL [4] refinement package. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model except for those bound to water, which were initially located in a difference Fourier map and included in the final refinement and $U_{iso}(H)$ set to 1.5 times of $U_{eq}(O)$.

Comment

In the past few decades, coordination compounds (CPs) have been becoming one of the most rapidly developing fields in chemical and material science not only because of their highly diversified topologies, but also due to their potential applications in many areas, such as magnetism

[5, 6], catalysis [6, 7], luminescence [8, 9], sensing [10, 11], conductivity [12, 13] and so on. At present, many multi-topic organic ligands have been employed to prepare such materials and rapid progress in this flourishing field has been made [14, 15]. However, it is still a great challenge to obtain the desired structure relying on reaction conditions in the self-assembly. Among many organic ligands, isonicotinic acid and its derivatives as bifunctional ligands containing both pyridyl and carboxylate donor groups, thus are useful building blocks in the assembly of CPs. Such as, isonicotinic acid, 3,5-dichloroisonicotinic acid, 2,6-dichloroisonicotinic acid, etc. have been used as educts to construct diverse CPs in our and other previous work [16–19]. The 3-methoxy-4-pyridinecarboxylate (mpca) is an ideal bifunctional connector in the exploration for CPs due to possess potential coordination sites involving the ingenious combination of carboxyl groups with an pyridyl ring. In this regard, we hope to reveal some structural factors of the H_2 mpca for dominating the self-assembly, and this will provide more useful information of the substituent effect. Though as a good bifunctional ligand, mpca remains largely unexplored, and only few CPs have been reported.

The asymmetric unit of compound contains half a cobalt atom, one mpca anion, one ligated water molecule and one free *N,N*-dimethylformamide (DMF) molecule. Each cobalt atom is six-coordinated by two O donors and two N donors of four symmetry-related mpca ligands in the equatorial plane with two coordinated water molecule in the axial positions. The Co–O bond lengths are 2.1220(10) and 2.0935(11) Å, respectively. The Co–N bond lengths are 2.1948(12) Å. The $[CoO_4N_2]$ environment are bridged by two N atoms and two O atoms of four mpca molecules resulting in stepwise (4,4) grids layers. Each layer is corrugated with four mpca molecules and four Co atoms forming repeating quadrate grid with a side length of 9.312/9.312 Å. Notably, the presences of coordinated water molecules lead to the formation of hydrogen-bonding interactions. Besides intralayer O(4)–H(4B)⋯O(3) hydrogen bonds, the parallel layers are connected by hydrogen-bonds between coordination H_2O and O atom of the DMF molecule [O(4)–H(4A)⋯O(5); $d(O4\cdots O5) = 2.6297(17)$ Å; degree $(H-O\cdots O5) = 163.0^\circ$] to develop the 2D layer. The adjacent 2D layers are stacked in a parallel fashion and cohered together by van der Waals forces into the entire 3D supramolecular networks of compound.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Agilent Technologies. CrysAlis^{PRO}; Agilent Technologies: Santa Clara, CA, USA, 2017.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
3. Sheldrick G. M. SHELXTL – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, A71, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
5. Shekurov R., Miluykov V., Kataeva O., Krivolapov D., Sinyashin O., Gerasimova T., Katsyuba S., Kovalenko V., Krupskaya Y., Kataev V., Buchner B., Senkovska I. Reversible water-induced structural and magnetic transformations and selective water adsorption properties of poly(manganese 1,1'-ferrocenediyl-bis(*H*-phosphinate)). *Cryst. Growth Des.* 2016, 16, 5084–5090.
6. Li J. X., Du Z. X., Xiong L. Y., Fu L. L., Bo W. B. Supramolecular isomerism in two nickel(II) coordination polymers constructed with the flexible 2-carboxyphenoxyacetate linker: syntheses, structure analyses and magnetic properties. *J. Solid State Chem.* 2021, 293, 121799.
7. Shen J. Q., Liao P. Q., Zhou D. D., He C. T., Wu J. X., Zhang W. X., Zhang J. P., Chen X. M. Modular and stepwise synthesis of a hybrid metal-organic framework for efficient electrocatalytic oxygen evolution. *J. Am. Chem. Soc.* 2017, 139, 1778–1781.
8. Xue L. P., Li Z. H., Zhang T., Cui J. J., Gao Y., Yao J. X. Construction of two Zn(II)/Cd(II) multifunctional coordination polymers with mixed ligands for catalytic and sensing properties. *New J. Chem.* 2018, 42, 14203–14209.
9. Wang X. Y., Yao X., Huang Q., Li Y. X., An G. H., Li G. M. Triple-wavelength-region luminescence sensing based on a color-tunable emitting lanthanide metal organic framework. *Anal. Chem.* 2018, 90, 6675–6682.
10. Xin L. Y., Liu G. Z., Ma L. F., Zhang X., Wang L. Y. Structural diversity and fluorescence regulation of three Zn_{II} coordination polymers assembled from mixed ligands tectons. *Aust. J. Chem.* 2015, 68, 758–765.
11. Zhang Y. M., Yuan S., Day G., Wang X., Yang X. Y., Zhou H. C. Luminescent sensors based on metal-organic frameworks. *Coord. Chem. Rev.* 2018, 354, 28–45.
12. Xin L. Y., Li Y. P., Ju F. Y., Li X. L., Liu G. Z. Syntheses, structure and luminescent detection for trace Ag⁺ of a coordination polymer with lewis basic sites. *Chin. J. Inorg. Chem.* 2017, 33, 1474–1480.
13. Pan J., Ma Y. J., Han S. D., Hu J. X., Mu Y., Wang G. M. Construction of the lanthanide diphosphonates via a template-synthesis strategy: structures, proton conduction, and magnetic behavior. *Cryst. Growth Des.* 2019, 19, 3045–3051.
14. Chen D. M., Sun C. X., Liu C. S., Du M. Stable layered semiconductive Cu(I)-organic framework for efficient visible-light-driven Cr(VI) reduction and H₂ evolution. *Inorg. Chem.* 2018, 57, 7975–7981.
15. Liu G. Z., Li X. L., Xin L. Y., Wang L. Y. Two topologically new trinodal cobalt(II) metal-organic frameworks characterized as a 1D metallic oxide and a 2D-3D penetrated porous solid. *CrystEngComm* 2012, 14, 5315–5321.
16. Li X. L., Liu G. Z., Xin L. Y., Wang L. Y. Binuclear and tetranuclear Mn(II) clusters in coordination polymers derived from semirigid tetracarboxylate and *N*-donor ligands: syntheses, new topology structures and magnetism. *J. Solid State Chem.* 2017, 246, 252–257.
17. Zhou L., Zhou B. L., Cui Z., Qin B. W., Zhang X. Y., Li W. L., Zhang J. P. Charge control of the formation of two neutral/cationic metal-organic frameworks based on neutral/cationic triangular clusters and isonicotinic acid: structure, gas adsorption and magnetism. *CrystEngComm* 2018, 20, 5402–5408.
18. Xin L. Y., Ji Z. R., Guo R. R. Crystal structure of diaqua-bis(3,5-dichloroisonicotinato- κ^1O)-bis(1,3-di(pyridin-4-yl) propane- κ^1N)cobalt(II), C₃₈H₃₆Cl₄N₆O₆Co. *Z. Kristallogr. NCS* 2019, 234, 495–497.
19. Liu G. Z., Xin L. Y., Li X. L. Crystal structure of coordination polymer *catena*-poly [diaqua-(2,6-dichloropyridine-4-carboxylato- κ^2O,O')-bis(μ_2 -2,6-dichloropyridine-4-carboxylato- $\kappa^2O:O'$) terbium(III), C₁₈H₁₀Cl₆N₃O₈Tb. *Z. Kristallogr. NCS* 2019, 234, 449–450.