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Crystal structure of *catena*-poly[(μ_2 -azido- $\kappa^2N:N$)(μ_2 -4-cyanobenzoato- $\kappa^2O:O'$)-(μ_2 -methanol- $\kappa^2O:O$)copper(II)], $C_9H_8CuN_4O_3$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.28 × 0.22 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.94 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
$\theta_{\max}$, completeness:	30.6°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3767, 2760, 0.009
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2241
$N(\text{param})_{\text{refined}}$:	159
Programs:	Olex2 [1], SHELX [2], CrysAlis ^{PRO} [3]

Source of material

The title complex was prepared by mixing a 1:1:0.5 molar ratio of 4-cyanobenzoic acid (147 mg, 1 mmol), NaN_3 (65 mg, 1 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (185 mg, 0.5 mmol) in a 15 mL of water/MeOH (v:v = 1:2). The reaction solution was filtered and blue block crystals were obtained by slow evaporation of the solvent at ambient environment for two weeks (34% yielding based on 4-cyanobenzoic acid).

Experimental details

H atoms bonded to C atoms from organic ligands were positioned geometrically and refined using a riding model, with C–H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$.

Comment

The constructions of one-dimensional (1D) coordination polymer architectures have received much attention in recent years due to their potential functions as new materials in the field of molecular magnets [4]. The para-substituted benzoic acid ligands have been largely explored in the construction of 1D coordination polymers for their specific coordination patterns [5–8]. Aside from the organic ligands, the ancillary ligands such as N_3^- and alkoxido can also bridge the adjacent metal ions and help with the formation of 1D coordination polymers. For instance, a series of new azido–Cu(II) coordination polymers have been constructed from the para-substituted benzoic acid and the azido ligands, which show interesting magnetic properties [8]. However, to the best of

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Abstract

$C_9H_8CuN_4O_3$, triclinic, $P\bar{1}$ (no. 2), $a = 6.3568(4)$ Å, $b = 8.8323(6)$ Å, $c = 10.8584(7)$ Å, $\alpha = 103.891(1)^\circ$, $\beta = 94.868(1)^\circ$, $\gamma = 105.453(1)^\circ$, $V = 563.16(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0245$, $wR_{\text{ref}}(F^2) = 0.0701$, $T = 296(2)$ K.

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A part of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Cu1	0.000000	1.000000	1.000000	0.02763(9)
Cu2	0.500000	1.000000	1.000000	0.02698(9)
O1	0.3303(2)	0.79590(16)	0.87270(13)	0.0363(3)
O2	−0.0234(2)	0.79116(16)	0.87816(13)	0.0372(3)
O3	0.2810(2)	1.13561(17)	0.88830(13)	0.0392(3)
H3	0.264365	1.095471	0.810449	0.059*
N1	0.7402(2)	1.01663(19)	0.89270(14)	0.0311(3)
N2	0.7012(3)	0.9447(2)	0.77861(15)	0.0389(4)
N3	0.6655(4)	0.8782(3)	0.67195(18)	0.0646(6)
N4	−0.2238(4)	−0.0024(2)	0.38051(18)	0.0538(5)
C1	0.1258(3)	0.7324(2)	0.83971(16)	0.0284(3)
C2	0.0505(3)	0.5686(2)	0.74126(16)	0.0294(4)
C3	−0.1679(3)	0.4726(3)	0.7219(2)	0.0438(5)
H3A	−0.267317	0.509875	0.770006	0.053*
C4	−0.2387(4)	0.3223(3)	0.6319(2)	0.0483(6)
H4	−0.384243	0.257263	0.620428	0.058*
C5	−0.0905(3)	0.2695(2)	0.55884(18)	0.0365(4)
C6	0.1276(3)	0.3653(2)	0.57588(19)	0.0391(4)
H6	0.225658	0.329723	0.525654	0.047*
C7	0.1974(3)	0.5139(2)	0.66801(18)	0.0357(4)
H7	0.343952	0.577650	0.681034	0.043*
C8	−0.1653(4)	0.1162(2)	0.46021(19)	0.0418(5)
C9	0.3451(6)	1.3064(3)	0.9155(3)	0.0721(9)
H9A	0.474228	1.342503	0.877934	0.108*
H9B	0.377800	1.353577	1.006881	0.108*
H9C	0.227142	1.340111	0.880311	0.108*

knowledge, there are no reports for the coordination polymers constructed from the 4-cyanobenzoate and the azido ligand simultaneously, which might be due to the formation of the 4-carboxyphenyl-1H-tetrazole ligand in the reaction process. In this study, we have successfully prepared a chain polymer [9].

There are two crystallographically unique Cu(II) atoms, one cbc[−] ligand, one bridged N₃[−] group and one MeOH in the asymmetric unit. Both Cu1 and Cu2 ions are located on inversion centers and exhibit the same coordination environment which is shaped by two O atoms from two different cbc[−] ligands, two N atoms from two N₃[−] and two O atoms from two MeOH ligands, resulting in the distorted octahedral geometry. The Cu1 and Cu2 atoms are coupled *via* the carboxyl and N₃[−] groups in the [001] direction with the Cu1–Cu2 separation of 3.178(3) Å, which results in the 1D chain structure, similar to the fundamental work of Escuer *et al.* [10]. Further analysis of the structure reveals that there may be weak π – π

interaction between the adjacent chains with the plane (C2–C3–C4–C5–C6–C7) to plane (C2A–C3A–C4A–C5A–C6A–C7A, symmetrical code A: $-x, 1-y, 1-z$) distance of 3.839 Å. The structure is similar to the Cu(II)-based coordination polymers with para-substituted benzoate ligands [7, 8].

References

1. 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.* **42** (2009) 339–341.
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Agilent Technologies. CrysAlis^{PRO}, Version 1.171.35.15. Agilent Technologies UK Ltd, Oxford, UK (2011).
4. Zheng, Y.-Z.; Tong, M.-L.; Zhang, W.-X.; Chen, X.-M.: Assembling magnetic nanowires into networks: a layered coil carboxylate coordination polymer exhibiting single-chain-magnet behavior. *Angew. Chem. Int. Ed.* **45** (2006) 6310–6314.
5. Yuan, R.-X.; Xiong, R.-G.; Chen, Z.-F.; You, X.-Z.; Peng, S.-M.; Lee, G.-H.: Preparation, characterization, and X-ray crystal structure of a one-dimensional calcium-based coordination polymer with strong blue fluorescent emission. *Inorg. Chem. Commun.* **4** (2001) 430–433.
6. Sun, J.-Y.; Wang, L.; Zhang, D.-J.; Li, D.; Cao, Y.; Zhang, L.-Y.; Zeng, S.-L.; Pang, G.-S.; Fan, Y.; Xu, J.-N.; Song, T.-Y.: Construction of metal–organic coordination polymers derived from 4-substituted tetrazole–benzoate ligands: synthesis, structure, luminescence, and magnetic behaviors. *CrystEngComm* **15** (2013) 3402–3411.
7. Stamatatos, T. C.; Vlahopoulou, G.; Raptopoulou, C. P.; Psycharis, V.; Escuer, A.; Christou, G.; Perlepes, S. P.: Single-strand molecular wheels and coordination polymers in copper(II) benzoate chemistry by the employment of α -benzoin oxime and azides: synthesis, structures, and magnetic characterization. *Eur. J. Inorg. Chem.* **2012** (2012) 3121–3131.
8. Cen, P.; Yuan, W.; Luo, S.; Liu, X.; Xie, G.; Chen, S.: Solvent coligands fine-tuned the structures and magnetic properties of triple-bridged 1D azido-copper(II) coordination polymers. *New J. Chem.* **43** (2019) 601–608.
9. Sun, J.-Y.; Wang, L.; Zhang, D.-J.; Li, D.; Cao, Y.; Zhang, L.-Y.; Zeng, S.-L.; Pang, G.-S.; Fan, Y.; Xu, J.-N.; Song, T.-Y.: Construction of metal–organic coordination polymers derived from 4-substituted tetrazole–benzoate ligands: synthesis, structure, luminescence, and magnetic behaviors. *CrystEngComm* **15** (2013) 3402–3411.
10. Escuer, A.; Vicente, R.; Mautner, F. A.; Goher, M. A. S.: Structure and magnetic behavior of a new 1-D compound with simultaneous end-on azido and carboxylate bridges. Unexpected strong ferromagnetic coupling for a Cu–N–Cu bond angle of 111.9° as a consequence of ligand HOMOs countercomplementarity. *Inorg. Chem.* **36** (1997) 1233–1236.