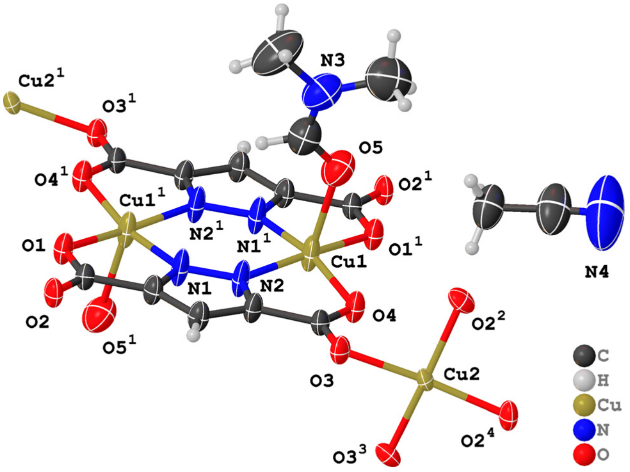
DE GRUYTER Z. Kristallogr. - N. Cryst. Struct. 2023; 238(6): 1069–1070

Yan-Qing Wang*, Wen-Qing Yan, Li-Xue Nie, Ping-Ping Luan and Chao-Qun Li

Crystal structure of polybis(μ_4-3,5-dicarboxylatopyrazol-1-yl)-bis(*N*,*N*-dimethylformamide)tri-copper(II)–acetonitrile (1/2), $C_{20}H_{22}Cu_3N_8O_{10}$



https://doi.org/10.1515/ncrs-2023-0308
Received July 2, 2023; accepted August 20, 2023;

Abstract

$C_{20}H_{22}Cu_3N_8O_{10}$, monoclinic, $C2/c$ (no. 15), a = 12.0766(11) Å, b = 16.2778(14) Å, c = 14.7605(13) Å, β = 97.8580(10)°, V = 2874.4(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0420, $wR_{ref}(F^2)$ = 0.0988, T = 298.15 K.

CCDC no.: 2267389

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.18 × 0.17 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.26 mm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD 6000, φ and ω
θ_{max}, completeness:	25.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7417, 2630, 0.053
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1939
$N(param)_{refined}$:	189
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

1 Source of materials

The 3,5-pyrazoledicarboxylic acid (H_3PDC) was purchased from Anhui Zesheng Technology Co., Ltd. Other reagents were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$, 0.0170 g, 0.1 mmol) and H_3PDC (0.0174 g, 0.1 mmol) were dissolved in 8 mL N,N–dimethylformamide (DMF) and 4 mL acetonitrile (CH_3CN). The mixture was then transfered to a 20 mL stainless steel vessel, heated to 120 °C for 3 days and cooled to room temperature at a rate of 15 °C/h. Clear light blue block crystals of the title complex were obtained, yielding 39 % (based on the ligand).

2 Experimental details

The initial structure of the title complex was solved by the SHELXT program. The refinement process was performed by the SHELXL program. The H-atoms were placed in their idealized positions with isotropic thermal parameters.

3 Comment

As a robust multidentate ligand containing both N- and O-coordination sites, 3,5-pyrazoledicarboxylic acid (H_3PDC) has been applied to build metal complexes. However, the reported Cu(II)-complexes are either monometallic structures

---

***Corresponding author: Yan-Qing Wang**, College of Chemistry and Chemical Engineering, Weifang University, Weifang, Shandong 261061, P.R. China, E-mail: wangyqwfu@outlook.com. https://orcid.org/0009-0003-9986-772X
Wen-Qing Yan, Li-Xue Nie, Ping-Ping Luan and Chao-Qun Li, College of Chemistry and Chemical Engineering, Weifang University, Weifang, Shandong 261061, P.R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6408 (3)	0.9050 (2)	0.3210 (3)	0.0284 (9)
C2	0.7073 (4)	0.8279 (2)	0.3236 (3)	0.0318 (10)
C3	0.7532 (4)	0.7755 (2)	0.2635 (3)	0.0330 (10)
H3	0.752597	0.781782	0.200846	0.040*
C4	0.7994 (4)	0.7124 (2)	0.3185 (3)	0.0313 (10)
C5	0.8639 (4)	0.6356 (2)	0.3114 (3)	0.0301 (10)
C6	0.5815 (5)	0.5752 (4)	0.4138 (4)	0.0641 (15)
H6	0.565399	0.631057	0.411143	0.077*
C7	0.5206 (7)	0.4368 (4)	0.3809 (5)	0.097 (2)
H7A	0.549252	0.420900	0.325935	0.146*
H7B	0.451781	0.408298	0.384645	0.146*
H7C	0.573987	0.423167	0.432970	0.146*
C8	0.3870 (5)	0.5546 (5)	0.3430 (5)	0.105 (3)
H8A	0.333900	0.533051	0.379588	0.158*
H8B	0.368172	0.536208	0.280970	0.158*
H8C	0.385488	0.613522	0.344660	0.158*
C9	0.8544 (5)	0.3952 (3)	0.4851 (4)	0.0733 (18)
H9A	0.903427	0.433399	0.460993	0.110*
H9B	0.849428	0.408498	0.547746	0.110*
H9C	0.781487	0.398217	0.450039	0.110*
C10	0.8969 (6)	0.3150 (4)	0.4799 (5)	0.089 (2)
Cu1	0.82569 (5)	0.64141 (3)	0.49417 (3)	0.0404 (2)
Cu2	1.000000	0.52545 (4)	0.250000	0.02145 (18)
N1	0.7266 (3)	0.7964 (2)	0.4080 (2)	0.0425 (10)
N2	0.7827 (3)	0.7264 (2)	0.4055 (2)	0.0403 (10)
N3	0.5003 (4)	0.5253 (3)	0.3794 (3)	0.0711 (14)
N4	0.9345 (8)	0.2527 (5)	0.4762 (6)	0.173 (4)
O1	0.6150 (2)	0.92923 (16)	0.39738 (17)	0.0344 (7)
O2	0.6123 (2)	0.94018 (16)	0.24630 (17)	0.0314 (7)
O3	0.8874 (2)	0.61283 (15)	0.23483 (17)	0.0304 (7)
O4	0.8944 (2)	0.59660 (16)	0.38576 (17)	0.0343 (7)
O5	0.6750 (3)	0.5560 (2)	0.4487 (3)	0.0635 (10)

with low dimensionality or three-dimensional structures obtained by mixing metal ions or ligands [5–8]. Hence, to extend the family of the monometallic Cu(II)–H_3PDC-based structures with high-dimensional, the title 3D Cu(II)-complex was synthesized under hydrothermal condition.

The asymmetric unit contains one and a half copper(II) ions, one deprotonated H_3PDC ligand, one coordinated DMF molecule and one free CH_3CN molecule. The Cu1(II) and Cu2(II) display two different coordination modes. Cu1(II) is penta-coordinated, bonded with three O-atoms (O4, O5, $O1^{3/2-x,3/2-y,1-z}$) and two N-atoms (N2, $N1^{3/2-x,3/2-y,1-z}$). Unlike Cu1(II), Cu2(II) is tetra-coordinated, bonded with four O-atoms (O3, $O2^{3/2-x,-1/2+y,1/2-z}$, $O2^{1/2+x,-1/2+y,z}$, $O3^{2-x,y,1/2-z}$). The distances of Cu–O and Cu–N are in the range of 1.946(3) – 2.315(4) Å and 1.926(3) – 1.938(3) Å, respectively. The bond lengths are comparable to the reported H_3PDC-based crystal structures [9–11]. It is worth noting that the hydrogen atom belonging to the nitrogen atom (N1 or N2) of the ligand is also deprotonated. Two deprotonated H_3PDC ligands, two Cu1 and two DMF molecules formed a $[Cu_2(H_3PDC)_2(DMF)_2]$ unit. Those units are further linked by Cu2 and finally resulted in a 3D supermolecular network.

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

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was supported by the Shandong Province Natural Science Foundation (No. ZR2021QB053), and research startup funds of Weifang University (No. 196100040020).

References

1. BRUKER. SAINT and SADABS; Bruker AXS Inc: Madison, Wisconsin, USA, 2000.
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. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
5. King P., Clérac R., Anson C. E., Powell A. K. The building block approach to extended solids: 3,5-pyrazoledicarboxylate coordination compounds of increasing dimensionality. *Dalton Trans*. 2004, 852–861; https://doi.org/10.1039/b315067d.
6. Zhou X.-H., Peng Y.-H., Du X.-D., Wang C.-F., Zuo J.-L., You X.-Z. New 3d-4f heterometallic coordination polymers based on pyrazole-bridged $Cu^{II}Ln^{III}$ dinuclear units and sulfate anions: syntheses, structures, and magnetic properties. *Cryst. Growth Des*. 2008, *9*, 1028–1035.
7. Yang T. H., Silva A. R., Shi F. N. Six new 3d-4f heterometallic coordination polymers constructed from pyrazole-bridged $Cu^{II}Ln^{III}$ dinuclear units. *Dalton Trans*. 2013, *42*, 13997–14005.
8. Branzea D. G., Guerri A., Fabelo O., Ruiz-Pérez C., Chamoreau L.-M., Sangregorio C., Caneschi A., Andruh M. Heterobinuclear complexes as tectons in designing coordination polymers. *Cryst. Growth Des*. 2008, *8*, 941–949.
9. Dou Q.-Q., He Y.-K., Zhang L.-T., Han Z.–B. *catena*–Poly [4,4′-bipyridinium [bis(μ_3-pyrazole-3,5-dicarboxylato-$\kappa^5O^5,N^1:N^2,O^3:O^3$) dicopper(II)]]. *Acta Crystallogr.* 2007, *E63*, m2908–m2909.
10. Wang L., Guo B., Li H.-X., Li Q., Li H.-Y., Lang J.-P. Polynuclear copper(ii) pyrazolate complexes: temperature-dependent protonolysis reactions, crystal structures and high catalytic activity toward the condensation of nitriles with 2-aminoalcohol. *Dalton Trans*. 2013, *42*, 15570–15580.
11. Klongdee F., Sasada Y., Nakano M., Chainok K., Youngme S., Synthesis B. J. X-ray structures, and magnetic properties of seven polynuclear Cu(II) complexes containing pyrazole-3,5-dicarboxylate with various ancillary ligands. *New J. Chem.* 2023, *47*, 9669–9680.