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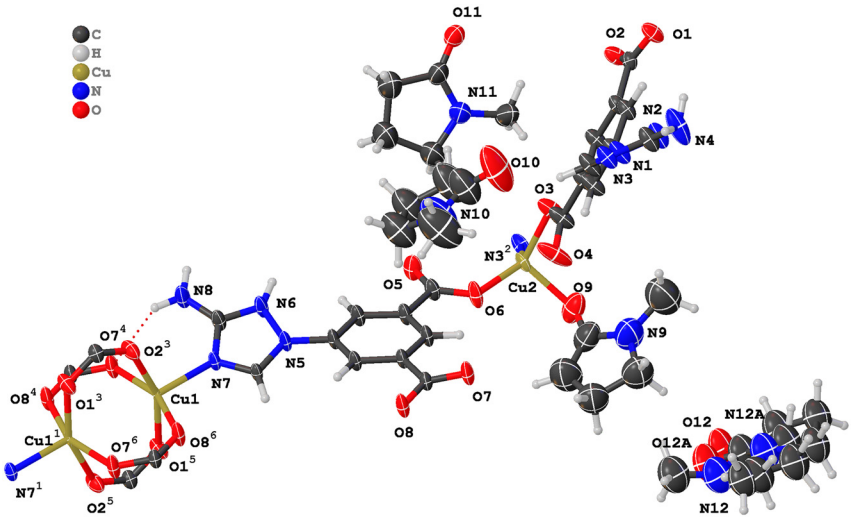
Crystal structure of poly[(μ4-(3-amino-1*H*-1,2,4-triazol-1-yl)benzene-1,3-dicarboxylato-κ^4*N*:*O*:*O*':O')(1-methylpyrroldin-2-one-κ^{1}O) dicopper(II)] – 1-methylpyrroldin-2-one (1/3), $C_{40}H_{48}Cu_2N_{12}O_{12}$



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Abstract

$C_{40}H_{48}Cu_2N_{12}O_{12}$, monoclinic, $P2_1/n$ (no. 14), a = 10.9519(1) Å, b = 17.4351(2) Å, c = 24.4288(3) Å, β = 102.143(1)°, V = 4560.25(9) Å^3, Z = 4, $R_{gt}(F)$ = 0.0647, w$R_{ref}(F^2)$ = 0.1904, T = 120 K.

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The molecular 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 1: Data collection and handling.

Crystal:	Blue block
Size:	0.26 × 0.22 × 0.04 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	1.78 mm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD 6000, φ and ω
θ_{max}, completeness:	68.2°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28,368, 8311, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 7622
$N(param)_{refined}$:	656
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

1 Source of materials

The 5-(3-amino-1H-1,2,4-triazol-1-yl)-1,3-benzenedicarboxylic acid (H_2L–NH_2) and 1-methyl-2-pyrrolidinone (NMP) were commercial purchased from Shanghai Accela ChemBio Co., Ltd. Other reagents were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. In a 20 mL capped vial, $CuCl_2{\cdot}2H_2O$ (0.0170 g, 0.1 mmol) and H_2L–NH_2 (0.0248 g,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	−0.38778 (4)	0.54794 (2)	0.52401 (2)	0.01653 (16)
Cu2	0.51734 (5)	0.93450 (3)	0.66025 (2)	0.03025 (18)
O1	1.0514 (3)	0.89476 (17)	0.95136 (13)	0.0448 (7)
O2	0.8909 (3)	0.96950 (17)	0.91477 (12)	0.0447 (7)
O3	0.6404 (3)	0.91395 (17)	0.72876 (14)	0.0515 (8)
O4	0.6793 (4)	0.8115 (2)	0.68238 (17)	0.0823 (15)
O5	0.2298 (3)	0.88405 (17)	0.65550 (15)	0.0507 (8)
O6	0.4054 (3)	0.85697 (17)	0.62653 (15)	0.0503 (8)
O7	0.4718 (2)	0.60520 (16)	0.55220 (14)	0.0424 (7)
O8	0.3080 (2)	0.53242 (17)	0.51722 (14)	0.0427 (7)
O9	0.6190 (5)	0.9572 (3)	0.6030 (2)	0.0833 (13)
N1	1.0094 (3)	0.66584 (19)	0.82380 (16)	0.0439 (9)
N2	1.1337 (3)	0.6573 (2)	0.84648 (18)	0.0494 (9)
N3	1.0380 (3)	0.54281 (18)	0.82897 (17)	0.0428 (9)
N4	1.2563 (4)	0.5457 (3)	0.8683 (3)	0.085 (2)
H4A	1.282740	0.558833	0.903032	0.102*
H4B	1.244444	0.496450	0.866833	0.102*
N5	−0.0510 (3)	0.65666 (18)	0.58279 (14)	0.0331 (7)
N6	−0.1131 (3)	0.6865 (2)	0.62208 (16)	0.0448 (9)
H6	−0.084863	0.718156	0.649899	0.054*
N7	−0.2373 (3)	0.60899 (17)	0.56077 (13)	0.0287 (6)
N8	−0.3181 (3)	0.6658 (2)	0.63452 (18)	0.0525 (11)
H8A	−0.306332	0.695206	0.664474	0.063*
H8B	−0.390783	0.643419	0.622497	0.063*
N9	0.7911 (7)	0.8990 (5)	0.5774 (4)	0.117 (2)
C1	0.9587 (3)	0.9122 (2)	0.91419 (16)	0.0307 (7)
C2	0.9262 (4)	0.8597 (2)	0.86486 (17)	0.0348 (8)
C3	0.9873 (4)	0.7898 (2)	0.86512 (18)	0.0366 (8)
H3	1.053081	0.776430	0.895599	0.044*
C4	0.9516 (4)	0.7402 (2)	0.82081 (19)	0.0427 (9)
C5	0.8607 (4)	0.7597 (2)	0.7743 (2)	0.0503 (11)
H5	0.839746	0.725761	0.743367	0.060*
C6	0.8009 (4)	0.8302 (2)	0.7740 (2)	0.0474 (10)
C7	0.8322 (4)	0.8791 (2)	0.81968 (18)	0.0410 (9)
H7	0.788835	0.926272	0.819926	0.049*
C8	0.7001 (5)	0.8521 (3)	0.7240 (2)	0.0524 (11)
C9	0.9543 (4)	0.5983 (2)	0.8141 (2)	0.0471 (10)
H9	0.868033	0.590508	0.798741	0.056*
C10	1.1463 (4)	0.5817 (2)	0.8486 (2)	0.0491 (11)
C11	0.2951 (4)	0.8422 (2)	0.63298 (19)	0.0384 (8)
C12	0.2446 (3)	0.7658 (2)	0.60889 (18)	0.0352 (8)
C13	0.1211 (3)	0.7458 (2)	0.60812 (18)	0.0350 (8)
H13	0.068519	0.779220	0.623470	0.042*
C14	0.0760 (3)	0.6763 (2)	0.58461 (17)	0.0323 (7)
C15	0.1505 (3)	0.6253 (2)	0.56297 (16)	0.0312 (7)
H15	0.117634	0.577962	0.547098	0.037*
C16	0.2751 (3)	0.6451 (2)	0.56500 (16)	0.0302 (7)
C17	0.3210 (3)	0.7149 (2)	0.58741 (17)	0.0343 (8)
H17	0.405450	0.728206	0.588177	0.041*
C18	0.3580 (3)	0.5898 (2)	0.54291 (16)	0.0290 (7)
C19	−0.1258 (3)	0.60990 (19)	0.54784 (15)	0.0268 (7)
H19	−0.102893	0.581665	0.518297	0.032*
C20	−0.2254 (3)	0.6553 (2)	0.60724 (18)	0.0383 (9)
C26	0.6635 (8)	0.9116 (5)	0.5717 (4)	0.0968 (18)
C27	0.6058 (10)	0.8655 (7)	0.5284 (5)	0.131 (2)

Table 2: (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
H27	0.517648	0.862358	0.516125	0.157*
C28	0.6900 (9)	0.8235 (6)	0.5039 (4)	0.117 (2)
H28A	0.677484	0.835102	0.463464	0.140*
H28B	0.678740	0.767776	0.508664	0.140*
C29	0.8187 (10)	0.8486 (6)	0.5345 (4)	0.123 (2)
H29A	0.869711	0.804248	0.551086	0.148*
H29B	0.863198	0.876334	0.509148	0.148*
C30	0.8927 (13)	0.9333 (8)	0.6220 (6)	0.162 (4)
H30A	0.915119	0.897202	0.653266	0.242*
H30B	0.862693	0.981265	0.635516	0.242*
H30C	0.966232	0.943849	0.606305	0.242*
O10	0.6705 (6)	0.6302 (5)	0.8041 (4)	0.172 (3)
N10	0.4953 (9)	0.5959 (5)	0.7478 (4)	0.143 (3)
C31	0.4844 (10)	0.7131 (7)	0.7778 (6)	0.144 (3)
H31A	0.486366	0.732020	0.816186	0.173*
H31B	0.519217	0.753553	0.757102	0.173*
C32	0.3591 (9)	0.6971 (5)	0.7505 (4)	0.115 (2)
H32A	0.329511	0.735222	0.720585	0.138*
H32B	0.303465	0.698872	0.777542	0.138*
C33	0.3593 (10)	0.6206 (6)	0.7266 (5)	0.131 (2)
H33A	0.337045	0.621983	0.685212	0.157*
H33B	0.300913	0.585998	0.740607	0.157*
C34	0.5337 (13)	0.5210 (7)	0.7399 (7)	0.182 (4)
H34A	0.532775	0.490524	0.773535	0.273*
H34B	0.618482	0.521830	0.732819	0.273*
H34C	0.476626	0.497986	0.707762	0.273*
C35	0.5631 (9)	0.6407 (6)	0.7804 (5)	0.127 (2)
O11	0.4603 (3)	0.9464 (2)	0.93764 (15)	0.0558 (8)
N11	0.4282 (5)	0.9451 (3)	0.8430 (2)	0.0695 (13)
C21	0.4017 (6)	0.9269 (4)	0.8923 (3)	0.0763 (15)
C22	0.2847 (8)	0.8768 (7)	0.8816 (3)	0.114 (2)
H22A	0.303704	0.825388	0.898416	0.137*
H22B	0.218435	0.900623	0.897931	0.137*
C23	0.2440 (8)	0.8708 (6)	0.8200 (3)	0.112 (2)
H23A	0.159426	0.892898	0.807544	0.134*
H23B	0.241629	0.816392	0.808222	0.134*
C24	0.3406 (7)	0.9163 (6)	0.7939 (3)	0.101 (2)
H24A	0.382878	0.882361	0.771219	0.121*
H24B	0.299880	0.958996	0.770132	0.121*
C25	0.5346 (7)	0.9894 (5)	0.8372 (3)	0.089 (2)
H25A	0.587143	0.999015	0.874275	0.134*
H25B	0.506782	1.038355	0.819129	0.134*
H25C	0.582724	0.961127	0.814221	0.134*
C36	1.0676 (8)	0.8452 (6)	0.4389 (4)	0.1118 (19)
O12[a]	0.9849 (11)	0.8936 (9)	0.4405 (7)	0.104 (4)
N12[a]	1.0272 (16)	0.7641 (11)	0.4178 (8)	0.119 (3)
C37[a]	1.1274 (18)	0.7079 (17)	0.4189 (17)	0.116 (3)
H37A[a]	1.123146	0.682769	0.382194	0.140*
H37B[a]	1.130819	0.668724	0.448548	0.140*
C38[a]	1.246 (2)	0.7735 (14)	0.4346 (11)	0.114 (3)
H38A[a]	1.311930	0.754044	0.465642	0.137*
H38B[a]	1.283715	0.781534	0.401551	0.137*
C39[a]	1.1936 (19)	0.8518 (15)	0.4521 (11)	0.115 (3)
H39A[a]	1.222792	0.860785	0.492762	0.138*
H39B[a]	1.221482	0.894953	0.431458	0.138*
C40[a]	0.9180 (18)	0.7372 (15)	0.4197 (11)	0.131 (4)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H40A[a]	0.896638	0.751671	0.455305	0.196*
H40B[a]	0.918848	0.681205	0.416565	0.196*
H40C[a]	0.855764	0.758503	0.388626	0.196*
O12A[b]	0.9590 (11)	0.8463 (9)	0.4247 (6)	0.124 (3)
N12A[b]	1.1570 (12)	0.7963 (10)	0.4452 (7)	0.113 (2)
C37A[b]	1.2898 (15)	0.8210 (11)	0.4517 (9)	0.113 (3)
H37C[b]	1.316385	0.825577	0.415544	0.136*
H37D[b]	1.348820	0.788149	0.477873	0.136*
C38A[b]	1.160 (2)	0.7284 (13)	0.4222 (13)	0.122 (3)
H38C[b]	1.080387	0.702094	0.420887	0.183*
H38D[b]	1.228052	0.698052	0.444537	0.183*
H38E[b]	1.174001	0.734339	0.384125	0.183*
C39A[b]	1.2659 (14)	0.9050 (10)	0.4790 (8)	0.112 (3)
H39C[b]	1.290680	0.903465	0.520375	0.134*
H39D[b]	1.314194	0.945805	0.464925	0.134*
C40A[b]	1.1409 (15)	0.9179 (11)	0.4622 (9)	0.123 (3)
H40D[b]	1.126962	0.958116	0.432988	0.147*
H40E[b]	1.108122	0.937197	0.494439	0.147*

[a]Occupancy: 0.444 (6), [b]Occupancy: 0.556 (6).

0.1 mmol) were dissolved by NMP and ethyl alcohol (8 mL, *V*/*V* = 6:2). The vial was then sealed, transfered to an oven and heated to 110 °C for 72 h and cooled to room temperature at a rate of 15 °C/h. Blue block-like crystals of the title complex were obtained, yielding 41 % (based on the H_2L–NH_2 ligand).

2 Experimental details

The initial crystal structure was solved by SHELXT program and refined by SHELXL program. Cu-, C-, N- and O-atoms were refined with anisotropic displacement parameters and H-atoms were placed in idealized positions with isotropic thermal parameters. One of the guest NMP molecules was disordered and split treatment were performed with DFIX and SIMU command.

3 Comment

As a ligand bearing two kinds of potential coordinating atoms (carbonyl oxygen atom and triazole nitrogen atom), 5-(1H-1,2,4-triazol-1-yl)-1,3-benzenedicarboxylic acid (H_2L) has been applied to construct complexes with a series of metal salts [5–8]. However, up to now, the metal complexes based on the amino functionalized H_2L, i.e., 5-(3-amino-1H-1,2,4-triazol-1-yl)-1,3-benzenedicarboxylic acid (H_2L–NH_2) has never been reported. Hence, to enrich the family of the metal complexes based on H_2L–NH_2, the title 3D Cu(II)-complex was synthesized under hydrothermal condition.

The asymmetric unit contains two copper(II) ions, two deprotonated H_2L–NH_2 ligands, three free NMP molecules and one coordinated NMP molecule. The Cu1(II) cation is penta-coordinated, bonded with four O-atoms ($O1^{-3/2+x,3/2-y,-1/2+z}$, $O2^{1/2-x,-1/2+y,+3/2-z}$, $O7^{-1+x,y,z}$, $O8^{-x,1-y,1-z}$) derived from four different H_2L–NH_2 ligands and one N-atom (N7) from another H_2L–NH_2 ligand. The Cu2(II) caion is tetra-coordinated, bonded with three O-atoms (O3, O6, O9) derived from two different H_2L–NH_2 ligands and the coordinated NMP molecule, and one N-atom ($N3^{3/2-x,1/2+y,3/2-z}$) derived from another H_2L–NH_2 ligand. The Cu–O and Cu–N bond lengths are within the normal range of 1.893(3)–2.069(3) Å and 2.008(3)–2.017(3) Å, respectively. The bond lengths are comparable to the reported crystal structures containing analogous H_2L–NH_2 ligand with similar coordination environments [9–10]. The dihedral angle between the triazole heterocyclic ring and centre benzene ring of the two crystallographic independent H_2L–NH_2 ligands are 26.77° and 39.97°, respectively. The two H_2L–NH_2 ligands displayed unified coordination modes, i.e., each ligand coordinated with four copper(II) ions. The two carboxyl groups in each H_2L–NH_2 ligand revealed different coordination mode. Significantly, two Cu1(II) cations, four carboxyl groups formed classical dinuclear [$Cu_2(COOR)_4$] paddle-wheel type secondary building units (SBUs; see the figure). In the end, the copper(II) ions and H_2L–NH_2 ligands connected with each other and with the help of intramolecular N–H···O hydrogen bonding interactions ($N4–H4B\cdots O5^{3/2-x,-1/2+y,3/2-z}$, $N8–H8A\cdots O4^{-1+x,y,z}$, $N8–H8B\cdots O7^{-1+x,y,z}$), resulted in the 3D supermolecule framework of the title Cu(II)-complex.

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

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. Yuan F., Ma H.-X., Yuan C.-M., Zhou C.-S., Hu H.-M., Kumar A., Muddassir M. Syntheses of a series of lanthanide metal-organic frameworks for efficient UV-light-driven dye degradation: experiment and simulation. *CrystEngComm* **2021**, *23*, 2404–2413.
6. Zhu Z.-X., Wang C.-J., Luo D., Liu C., Liu D.-N., Xiao Y.-M., Chen S., Wang Y.-Y. Six new lanthanide metal-organic frameworks as luminescent sensors for the detection of 1–N, TDGA, UA, and HA in urine. *J. Coord. Chem.* **2019**, *72*, 3526–3543.
7. Sun J., Xi Y., Gao L., Hu M., Liu W., Ma E., Huang R., Qin W., Wu G. Two isostructural Ln–MOFs containing triazole groups as luminescent probes for efficient sensing of NACs and Fe^{3+}. *Inorg. Chim. Acta* **2023**, *547*, 121376.
8. Yuan F., Li Y., Yuan C.-M., Liu Y.-L., Zhou C.-S., Chen F.-Y., Cao B.-Y., Li Z.-J., Li K.-B., Yu H.-S. Effect of pH on the construction of zinc coordination polymers based on carboxylate functionalized triazole derivative ligand. *J. Mol. Struct.* **2019**, *1198*, 126905.
9. Wu M. Z., Ma Z. L., Shi J. Y., Tian L. A Zn(II) metal-organic framework based on bimetallic paddle wheels as a luminescence indicator for carcinogenic organic pollutants: phthalate esters. *RSC Adv.* **2019**, *9*, 37101–37108.
10. Ma Z. L., Liu P. X., Liu Z. Y., Wang J. J., Li L. B., Tian L. A thermally and chemically stable copper(II) metal-organic framework with high performance for gas adsorption and separation. *Inorg. Chem.* **2021**, *60*, 6550–6558.