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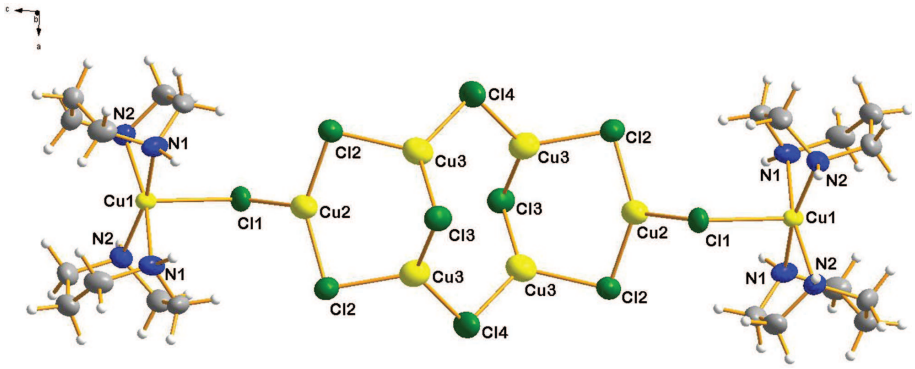
# Crystal structure of (1,4-diazepane)$_4$Cu$^{II}_2$(μ-Cl)$_{10}$Cu$^{I}_6$, $C_{20}H_{48}Cl_{10}Cu_8N_8$

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## Abstract

$C_{20}H_{48}Cl_{10}Cu_8N_8$, orthorhombic, *Cmce* (no. 64), $a = 16.477(10)$ Å, $b = 10.008(6)$ Å, $c = 24.201(15)$ Å, $V = 3991(4)$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.0364$, $wR_{ref}(F^2) = 0.0798$, $T = 296(2)$ K.

**CCDC no.:** 1533505

The molecular crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

## Source of material

The title compound is easily available by a literature known synthesis [5]. The mixtures of CuCl (1 mmol, 0.1 g), 1,4-diazepane (0.5 mmol, 0.05 g), ethanol (1 mL) and water (0.2 mL) were placed in a thick Pyrex tube (*ca* 20 cm in length). The Pyrex tube was frozen with liquid $N_2$, evacuated under vacuum and sealed with a torch. The tube was heated at 70 °C for 3 days. After being cooled slowly to room temperature, purple block crystals of the title compound were obtained.

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**Table 1:** Crystal collection and handling.

| | |
|---|---|
| Crystal: | Block, purple |
| Size: | 0.20 × 0.18 × 0.16 mm |
| Wavelength: | Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) |
| $\mu$: | 4.87 mm$^{-1}$ |
| Diffractometer, scan mode: | APEX2, $\Phi$ and $\omega$-scans |
| $\theta_{max}$, completeness: | 27.5°, 97% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 8599, 2291, 0.0355 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 1691 |
| $N(param)_{refined}$: | 111 |
| Programs: | Bruker programs [1], SHELX [2], OLEX2 [3], DIAMOND [4] |

## Experimental details

Hydrogen atoms were positioned using the standard options of the SHELX system.

## Discussion

Heterocyclic N atoms can bind metal centers and halogen anions may coordinate in a bridging mode, forming different MOFs with novel stereostructures and useful properties [6]. Two new 3-D MOFs $[Cu_4I_4(hpip)_2]$ and $[Cu_4I_4(bpp)_2]$ were prepared from two new organic bridging-type ligands homopiperazine (hpip) and 1,3-bis(4-piperidyl)propane (bpp) which are extended into different topologies based on the cubane $Cu_4I_4$ clusters as the connecting nodes [7]. Based on homopiperazine, a series of new lipophilic platinum(II) complexes of $[Pt(hpip)L_2]$ and $[Pt(hpip)L]$ were synthesized and characterized. Single crystal X-ray diffraction showed that the hpip molecule was in a boat conformation and formed five- and six-member chelating rings with platinum [8].

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

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 1.0000 | 0.07143(6) | 0.34162(2) | 0.02823(15) |
| Cu2 | 1.0000 | 0.07820(8) | 0.17281(3) | 0.0519(2) |
| Cu3 | 0.90466(3) | 0.11646(5) | 0.05148(2) | 0.05576(18) |
| Cl1 | 1.0000 | −0.06713(14) | 0.24680(5) | 0.0416(3) |
| Cl2 | 0.87703(6) | 0.13308(11) | 0.14429(4) | 0.0449(2) |
| Cl3 | 1.0000 | 0.25828(15) | 0.02218(6) | 0.0500(4) |
| Cl4 | 0.82003(9) | 0.0000 | 0.0000 | 0.0576(4) |
| N1 | 0.90729(17) | 0.1978(3) | 0.32823(13) | 0.0391(8) |
| H1 | 0.9246 | 0.2686 | 0.3028 | 0.047 |
| N2 | 0.90424(16) | −0.0313(3) | 0.37094(11) | 0.0335(7) |
| H2 | 0.9190 | −0.1254 | 0.3760 | 0.040 |
| C1 | 0.8818(2) | 0.2583(4) | 0.38174(17) | 0.0456(10) |
| H1A | 0.8462 | 0.3335 | 0.3745 | 0.055 |
| H1B | 0.9293 | 0.2918 | 0.4009 | 0.055 |
| C2 | 0.8425(2) | 0.1188(4) | 0.30237(16) | 0.0476(11) |
| H2A | 0.8529 | 0.1101 | 0.2631 | 0.057 |
| H2B | 0.7908 | 0.1636 | 0.3072 | 0.057 |
| C3 | 0.8394(2) | −0.0197(4) | 0.32905(16) | 0.0457(10) |
| H3A | 0.7869 | −0.0331 | 0.3463 | 0.055 |
| H3B | 0.8465 | −0.0879 | 0.3010 | 0.055 |
| C4 | 0.8791(2) | 0.0274(4) | 0.42477(15) | 0.0405(9) |
| H4A | 0.9266 | 0.0378 | 0.4481 | 0.049 |
| H4B | 0.8422 | −0.0336 | 0.4431 | 0.049 |
| C5 | 0.8385(2) | 0.1601(4) | 0.41824(16) | 0.0423(9) |
| H5A | 0.8323 | 0.1998 | 0.4546 | 0.051 |
| H5B | 0.7846 | 0.1455 | 0.4034 | 0.051 |

It is notable that delocalized mixed-valence $Cu_2$ center play an important part in metallo protein systems because they involve long-distances electron, and the Cu—Cu bond of the $Cu_2$ core represents the first –metal-metal bond in biology. Hydroxylation of bpy and phen ligands in two delocalized mixed-valence Cu(I)/Cu(II) represents a new route to the stable mixed-valence dicopper complexes [9–14].

For the title compound, X-ray single crystal structure determination reveals that copper atoms have two different coordination environments in its crystal structure, presenting a mixed-valence Cu(I/II) complex. Cu1(II) is coordinated in distorted tetrahedral geometry, which is defined by four N atoms from two homopiperazine ligand. $Cu_2$(I) and $Cu_3$(I) are linked with three Cl atoms separately. At the same time, each Cl atom acts as linker to bridge two Cu atoms, presenting six-member cycle configuration [15]. The Cu—Cl bond lengths in the complex range from 2.204(1) Å to 2.681(1) Å. The Cu—N bond lengths are 2.010(1) Å and 2.013(1) Å for Cu1—N1 and Cu1—N2, respectively. The structure of the compound extends into two-dimensional framework through hydrogen bonds.

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