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Crystal structure of dichlorido- $1\kappa\text{Cl}, 2\kappa\text{Cl}$ - $(\mu_2$ -3,5-dimethyl-1*H*-pyrazolato- $1\kappa\text{N}^2:2\kappa\text{N}^1$)(3,5-dimethyl-1*H*-pyrazole- $2\kappa\text{N}^2$){ μ -2-[(2-hydroxyethyl)amino- $1\kappa^2\text{N}, \text{O}$]ethanolato-1:2 $\kappa^2\text{O}:\text{O}$ }dicopper(II)

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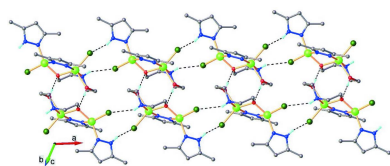
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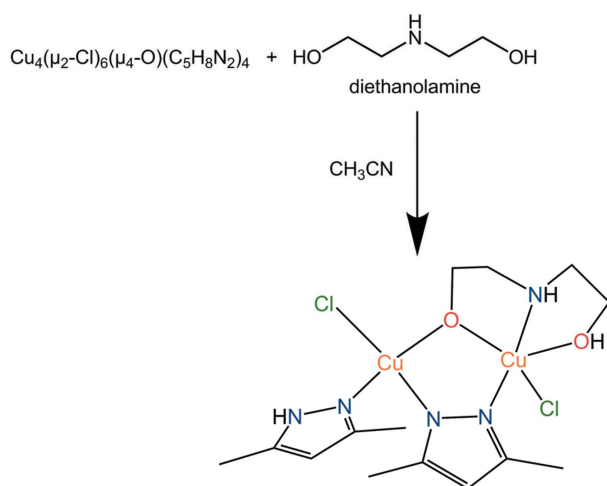
The title compound, $[\text{Cu}_2(\text{C}_5\text{H}_7\text{N}_2)(\text{C}_4\text{H}_{10}\text{NO}_2)\text{Cl}_2(\text{C}_5\text{H}_8\text{N}_2)]$, is a pyrazolate aminoalcohol complex which contains two dimethylpyrazole molecules in monodentate and bidentate-bridged coordination modes and a monodeprotonated diethanolamine molecule. Both copper atoms are involved in the formation of non-planar five-membered chelate rings. One Cu atom is in a distorted tetrahedral environment formed by the pyridine nitrogen atom of the protonated dimethylpyrazole molecule, the N atom of the deprotonated bridged dimethylpyrazole, the Cl atom and the bridged O atom of the monodeprotonated diethanolamine. The second Cu atom has an intermediate environment between trigonal bipyramidal and square pyramidal, formed by the N atom of the deprotonated bridged dimethylpyrazole, the Cl atom and the N atom of the aminoalcohol, and two O atoms of the deprotonated and protonated OH groups. In the crystal, $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds link the molecules into antisymmetric chains running along the *a*-axis direction. Adjacent chains are connected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds involving the hydroxyl group as donor.

1. Chemical context

Metal complexes of paramagnetic metal ions formed by polynucleative or polydentate ligands are of great interest as they often exhibit non-trivial magnetic behaviour (Gumienna-Kontecka *et al.*, 2007; Suleimanov *et al.*, 2015; Gural'skiy *et al.*, 2012). Among polydentate and polynucleative ligands, those containing both nitrogen and oxygen donor atoms are probably the most versatile and efficient chelators for the vast majority of metal ions (Pavlishchuk *et al.*, 2010, 2011; Strotmeyer *et al.*, 2003). Amino alcohol ligands and their derivatives are one of the most widely used representatives of *N,O*-chelators and attract attention as strong polydentate ligands that can form coordination compounds with transition metals (Hughes *et al.*, 1972). Amino alcohols contain both amino and hydroxyl groups within the same molecule, and therefore they are good chelating and bridging ligands. Polynuclear complexes of 3*d* metals with amino alcohols or their deprotonated forms can show non-trivial properties as catalysts, materials with different magnetic properties or biologically active compounds (Reiter *et al.*, 2006). Amino alcohol ligands are used to prepare copper(II) amino alcoholates that can self-assemble to form both mono- and multinuclear complexes. In



bionuclear copper complexes, the metal atoms can be connected by bridged oxygen atoms (alkoxy) from two different diethanolamine molecules (Tudor *et al.*, 2003; Marin *et al.*, 2005), or combined by a single oxygen atom from an amino alcohol and a bridged ligand molecule (Ashurov *et al.*, 2015). There are several typical binding modes of tridentate amino alcohol ligands to copper(II) ions and other metals such as lanthanides, yttrium, and alkaline-earth metals (Breeze & Wang, 1994; Chen *et al.*, 1995; Wang *et al.*, 1995). It is a well-known fact that copper coordination compounds can be modified with amino alcohols. For example, copper complexes with theophylline show promising potential antitumor action and can be modified with diethanolamine by similar coordination of amino alcohols to the copper atom (Madarász *et al.*, 2000). Studies of both tridentate- and bidentate-coordinated amino alcohol ligands to the copper atom have been carried out (Wang, 1995). Complexes of *3d* metals with a tricoordinated diethanolamine are interesting objects for synthesis and further studies (Buvaylo *et al.*, 2009). Considering the above, we understand the importance of accumulating a theoretical information base on such coordination compounds, and therefore in this article we report the synthesis and crystal structure of a new binuclear mixed-ligand copper(II) complex containing 3,5-dimethylpyrazole and diethanolamine (Fig. 1).



2. Structural commentary

The crystal structure of the title compound (Fig. 2) consists of dinuclear $\text{Cu}_2(\text{Hdmpz})(\text{dmpz-H})(\text{HDEA})\text{Cl}_2$ (Hdmpz = 3,5-dimethyl-1*H*-pyrazole, dmpz-H = deprotonated 3,5-dimethylpyrazole, and HDEA = monodeprotonated diethanolamine) units enclosed in two antisymmetrically oriented rows along the *a* axis. The unit cell consists of two unrelated structural fragments from both rows (Fig. 2). Along the *a* axis within one row, each molecule is bonded to the preceding and subsequent ones by hydrogen bonds of the same length. Along the *b* axis, the formation of molecules into dimers is due to hydrogen bonds of equal length between the bridged oxygen atom and the non-deprotonated hydroxy group of the adjacent molecule. The title dinuclear pyrazolate amino-alcohol compound forms a cyclic structure. Two copper atoms bridged by an

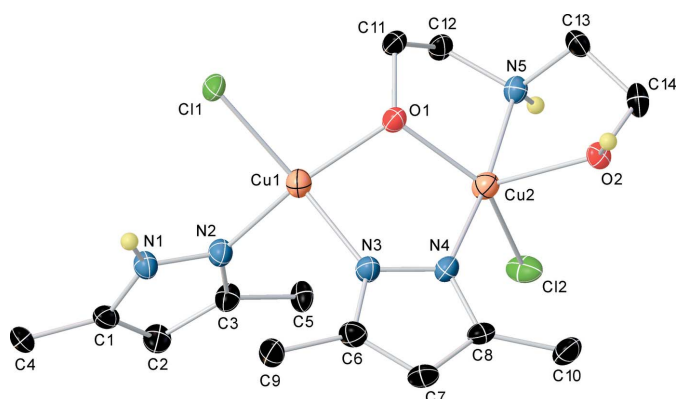


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

oxygen atom of a deprotonated diethanolamine and by a molecule of deprotonated dimethylpyrazole form a five-membered bimetallic ring. The five-membered metalocycle has a non-planar structure. The N atoms of the bridging molecule of dimethylpyrazole are in the plane of the metalocycle while the bridging O atom is out of this plane by 0.802 (1) Å. The angle between the Cu1/O1/Cu2 and Cu1/Cu2/N3/N4 planes is 45.85 (8)°. The geometrical environment of Cu1 with a coordination number of 4 is different from that of Cu2, which exhibits a coordination number of 5. The Cu1 atom is in a distorted tetrahedral environment formed by the pyridine N atom of the non-deprotonated dimethylpyrazole molecule, the N atom of the deprotonated bridging dimethylpyrazole, the Cl atom and the bridging O atom of the monodeprotonated diethanolamine. The environment of the Cu2 metal center is intermediate between trigonal bipyramidal and square pyramidal, formed by the N atom of the deprotonated bridged dimethylpyrazole, the Cl atom and the aminoalcohol N atom, and two O atoms of the deprotonated and non-deprotonated OH groups. The intermetallic distance

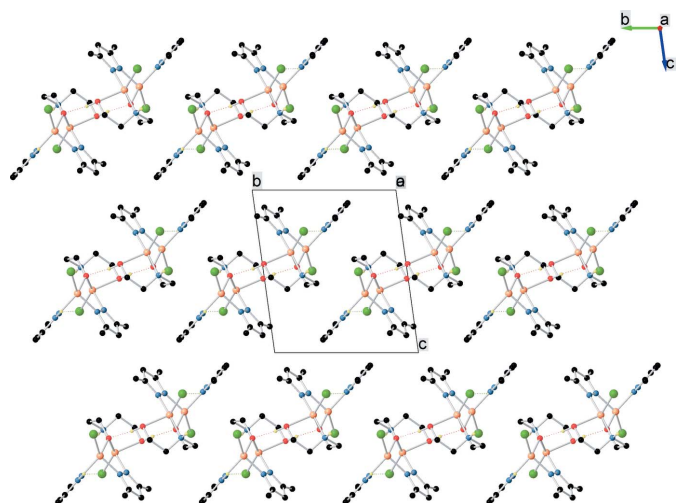


Figure 2
The crystal packing of the title compound viewed along the *a*-axis direction.

Table 1
Selected bond lengths (Å).

| | | | |
|---------|-------------|--------|-------------|
| Cu1—Cl1 | 2.2403 (6) | Cu2—N4 | 1.9268 (17) |
| Cu1—N2 | 1.9635 (16) | Cu2—N5 | 1.9916 (17) |
| Cu1—N3 | 1.9770 (17) | Cu2—O1 | 2.0001 (13) |
| Cu1—O1 | 1.9388 (13) | Cu2—O2 | 2.2441 (14) |
| Cu2—Cl2 | 2.2937 (6) | | |

between Cu1 and Cu2 is 3.2439 (4) Å. The diethanolamine fragment is coordinated by all donor atoms to copper in a tridentate mode (with atom O1 bridging the two metal centers Cu1 and Cu2) and forms two similar non-planar five-membered metalocycles. It is worth mentioning that the Cu1—O1 distance of 1.9388 (13) Å (Table 1) differs significantly from the Cu2—O2 distance of 2.2441 (14) Å.

3. Supramolecular features

In the crystal, hydrogen bonds (Table 2) are observed between the N and Cl atoms (N1—H1···Cl2 and N5—H5···Cl1) leading to the formation of antisymmetric chains running along the *a*-axis direction (Fig. 3). Adjacent chains are connected by hydrogen bonds between the hydroxyl group as donor and the O1 atom of the adjacent molecule as acceptor. There are different fragments that are potential H-atom donors or acceptors and further analysis of the structure indicates the presence of multiple non-covalent intermolecular interactions.

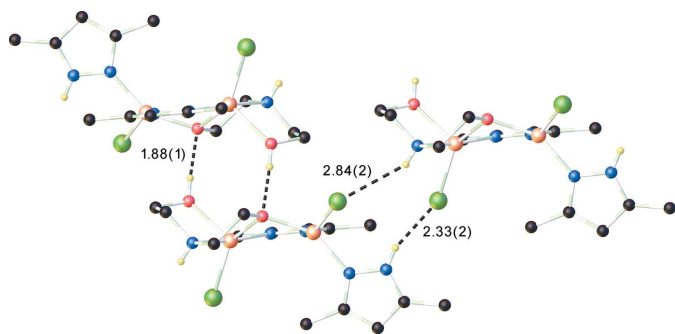


Figure 3
The hydrogen bonds (dotted lines) in the crystal structure of the title compound.

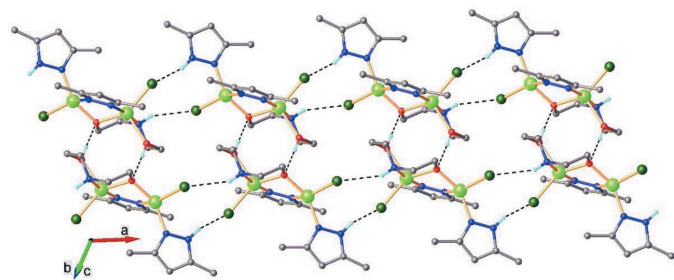


Figure 4
Partial view of the one-dimensional architecture in the crystal structure of the title compound. Non-relevant H atoms are omitted for clarity.

Table 2
Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1···Cl2 ⁱ | 0.87 (2) | 2.33 (2) | 3.1201 (18) | 152 (2) |
| N5—H5···Cl1 ⁱⁱ | 0.80 (2) | 2.84 (2) | 3.5593 (18) | 150 (2) |
| O2—H2A···O1 ⁱⁱⁱ | 0.85 (1) | 1.88 (1) | 2.7264 (19) | 174 (2) |

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $-x, -y, -z + 1$.

The crystal structure (Fig. 4) consists of discrete parallel-packed one-dimensional supramolecular formations, which are assembled by connecting two infinite chains (formed by N—H···Cl hydrogen bonds) *via* O—H···O hydrogen-bonding interactions.

The Hirshfeld surface analysis and the associated two-dimensional fingerprint plots were generated using *Crystal Explorer 17.5* software (Turner *et al.*, 2018), with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed colour scale of -0.6711 (red) to 1.7846 (blue) a.u. The pale-red spots in Fig. 5 represent short contacts and negative d_{norm} values on the surface corresponding to the interactions described above. The overall two-dimensional fingerprint plot is illustrated in Fig. 6*a*. The Hirshfeld surfaces mapped over d_{norm} are shown for the H···H, H···C/C···H, H···Cl/Cl···H, H···O/O···H, and H···N/N···H contacts, and the two-dimensional fingerprint plots are given in Fig. 6*b*. At 64.1%, the largest contribution to the overall crystal packing comes from H···H interactions, which are located in the middle region of the fingerprint plot. H···C/C···H contacts contribute 8.2%, and H···N/N···H contacts contribute 2.4% to the Hirshfeld surface, both resulting in a pair of characteristic wings. The H···O/O···H contacts make a 2.7% contribution, forming the inner sharp tips of the Hirshfeld surface, while H···Cl/Cl···H contacts contribute 19.1% and form the outer sharp tips in the fingerprint plot.

4. Database survey

A search of the Cambridge Structural database (CSD version 5.41; November 2019; Groom *et al.*, 2016) for the CuNH(CCO)₂ moiety (diethanolamine is coordinated to the

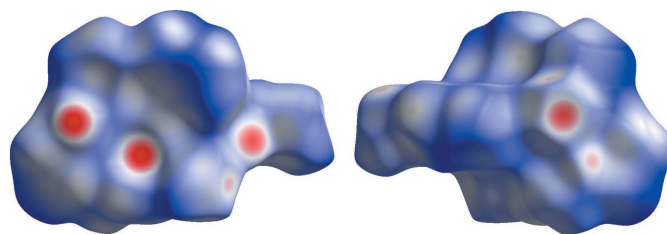


Figure 5
Two projections of Hirshfeld surfaces mapped over d_{norm} showing the intermolecular interactions within the molecule. Red areas represent contacts shorter than the sum of the van der Waals radii, while blue areas represent regions where contacts are longer than the sum of van der Waals radii, and white areas are zones close to the sum of van der Waals radii.

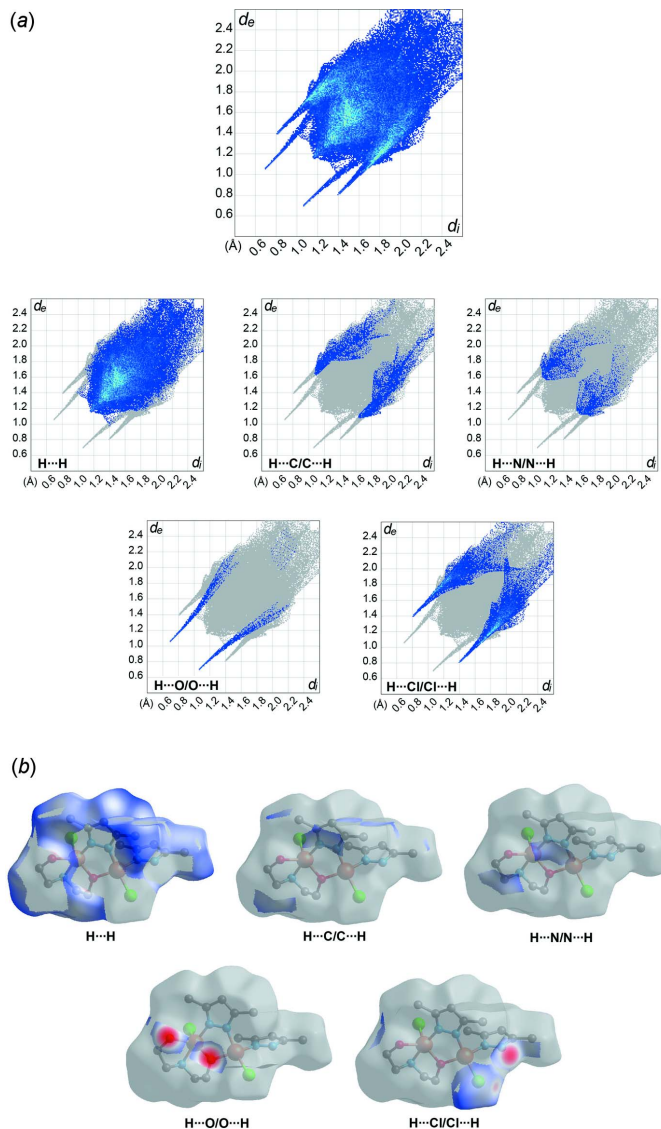


Figure 6
 (a) The overall two-dimensional fingerprint plot and those delineated into specified interactions. (b) Hirshfeld surface representations with the function d_{norm} plotted onto the surface for the different interactions.

copper atom) gave 168 hits. Most similar to the title compound are the dinuclear complexes with coordinated diethanolamine molecules, and copper atoms connected by a bridging oxygen atom and some other ligands, see: refcodes ELESAP (Tudor *et al.*, 2003), FARKAL (Marin *et al.*, 2005) and WITBAC (Madarász *et al.*, 2000).

5. Synthesis and crystallization

A 1.76 mmol diethanolamine solution was added dropwise to a 1.15 mmol acetonitrile solution of complex $\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})(\text{C}_5\text{H}_8\text{N}_2)_4$ under stirring. The mixture was stirred for a further 2 h with oxygen access and without heating. Amino alcohol was added to the brown solution and the colour of the mixture changed to green. Dark-green crystals of the title compound suitable for a single crystal X-ray analysis were

Table 3
 Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | $[\text{Cu}_2(\text{C}_5\text{H}_7\text{N}_2)(\text{C}_4\text{H}_{10}\text{NO}_2)\text{Cl}_2\text{-}(\text{C}_5\text{H}_8\text{N}_2)]$ |
| M_r | 493.37 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 180 |
| a, b, c (Å) | 9.0732 (5), 10.7460 (6), 11.5578 (6) |
| α, β, γ (°) | 92.373 (4), 102.383 (5), 112.703 (5) |
| V (Å ³) | 1005.70 (10) |
| Z | 2 |
| Radiation type | Mo $K\alpha$ |
| μ (mm ⁻¹) | 2.40 |
| Crystal size (mm) | 0.4 × 0.3 × 0.3 |
| Data collection | |
| Diffractometer | Rigaku Oxford Diffraction Xcalibur, Eos |
| Absorption correction | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2019) |
| $T_{\text{min}}, T_{\text{max}}$ | 0.553, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8833, 4681, 4108 |
| R_{int} | 0.018 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.693 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$ | 0.027, 0.061, 1.05 |
| No. of reflections | 4681 |
| No. of parameters | 239 |
| No. of restraints | 3 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.36, -0.43 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

obtained in 55% yield by slow gas diffusion in an acetonitrile/hexane isolated system. Elemental analysis of $\text{C}_{14}\text{H}_{25}\text{Cl}_2\text{Cu}_2\text{N}_5\text{O}_2$: found C 33.96, H 5.267 and N 14.13% (calculated C 34.08, H 5.1, N 14.19%). The starting compound $\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})(\text{C}_5\text{H}_8\text{N}_2)_4$ is a polymorphic modification of the already known tetranuclear copper pyrazole-containing cluster $\text{Cu}_4\text{OCl}_6(\text{C}_5\text{H}_8\text{N}_2)_4$ and was obtained from the $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ -Hdmpz system.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C-methyl})$. The O2–H2A distance was restrained to 0.85 ± 0.01 Å. The N and O atoms were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$.

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supporting information

Acta Cryst. (2020). E76, 1503-1507 [https://doi.org/10.1107/S2056989020011184]

Crystal structure of dichlorido-1 κ Cl,2 κ Cl-(μ -2-3,5-dimethyl-1H-pyrazolato-1 κ N²:2 κ N¹)(3,5-dimethyl-1H-pyrazole-2 κ N²){ μ -2-[(2-hydroxyethyl)-amino-1 κ ²N,O]ethanolato-1:2 κ ²O:O}dicopper(II)

Oleksandr S. Vynohradov, Vadim A. Pavlenko, Inna S. Safyanova, Kateryna Znovjyak, Sergiu Shova and Safarmamad M. Safarmamadov

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Dichlorido-1 κ Cl,2 κ Cl-(μ -2-3,5-dimethyl-1H-pyrazolato-1 κ N²:2 κ N¹)(3,5-dimethyl-1H-pyrazole-2 κ N²){ μ -2-[(2-hydroxyethyl)amino-1 κ ²N,O]ethanolato-1:2 κ ²O:O}dicopper(II)

Crystal data

[Cu₂(C₅H₇N₂)(C₄H₁₀NO₂)Cl₂(C₅H₈N₂)]

$M_r = 493.37$

Triclinic, $P\bar{1}$

$a = 9.0732$ (5) Å

$b = 10.7460$ (6) Å

$c = 11.5578$ (6) Å

$\alpha = 92.373$ (4)°

$\beta = 102.383$ (5)°

$\gamma = 112.703$ (5)°

$V = 1005.70$ (10) Å³

$Z = 2$

$F(000) = 504$

$D_x = 1.629$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4259 reflections

$\theta = 1.8$ – 29.2 °

$\mu = 2.40$ mm⁻¹

$T = 180$ K

Prism, clear intense green

$0.4 \times 0.3 \times 0.3$ mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Eos diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)

$T_{\min} = 0.553$, $T_{\max} = 1.000$

8833 measured reflections

4681 independent reflections

4108 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 29.5$ °, $\theta_{\min} = 1.8$ °

$h = -11 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.061$

$S = 1.05$

4681 reflections

239 parameters
 3 restraints
 Primary atom site location: dual
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.5005P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|------------|--------------|----------------------------------|
| C1 | 0.8325 (3) | 0.5970 (2) | 0.87558 (18) | 0.0213 (4) |
| C2 | 0.7173 (3) | 0.6360 (2) | 0.9068 (2) | 0.0303 (5) |
| H2 | 0.737259 | 0.705862 | 0.966030 | 0.036* |
| C3 | 0.5648 (3) | 0.5504 (2) | 0.8325 (2) | 0.0249 (5) |
| C4 | 1.0153 (3) | 0.6516 (2) | 0.9206 (2) | 0.0299 (5) |
| H4A | 1.053223 | 0.583541 | 0.900423 | 0.045* |
| H4B | 1.045118 | 0.675213 | 1.005925 | 0.045* |
| H4C | 1.065349 | 0.731079 | 0.884536 | 0.045* |
| C5 | 0.3987 (3) | 0.5503 (3) | 0.8250 (3) | 0.0427 (7) |
| H5A | 0.360893 | 0.577420 | 0.750146 | 0.064* |
| H5B | 0.405616 | 0.612959 | 0.889610 | 0.064* |
| H5C | 0.322664 | 0.460389 | 0.830295 | 0.064* |
| C6 | 0.3858 (3) | 0.1471 (2) | 0.84323 (18) | 0.0222 (5) |
| C7 | 0.2607 (3) | 0.0678 (2) | 0.89308 (19) | 0.0237 (5) |
| H7 | 0.271158 | 0.021651 | 0.958574 | 0.028* |
| C8 | 0.1163 (3) | 0.0714 (2) | 0.82511 (17) | 0.0189 (4) |
| C9 | 0.5663 (3) | 0.1797 (3) | 0.8802 (2) | 0.0411 (7) |
| H9A | 0.604540 | 0.168147 | 0.810855 | 0.062* |
| H9B | 0.585441 | 0.119540 | 0.934917 | 0.062* |
| H9C | 0.624799 | 0.272188 | 0.918419 | 0.062* |
| C10 | -0.0560 (3) | 0.0091 (2) | 0.8396 (2) | 0.0265 (5) |
| H10A | -0.073035 | 0.071365 | 0.891799 | 0.040* |
| H10B | -0.072923 | -0.073948 | 0.873356 | 0.040* |
| H10C | -0.132710 | -0.010057 | 0.762932 | 0.040* |
| C11 | 0.1643 (3) | 0.2883 (2) | 0.41712 (17) | 0.0192 (4) |
| H11A | 0.113125 | 0.213856 | 0.351586 | 0.023* |
| H11B | 0.265007 | 0.353315 | 0.401922 | 0.023* |
| C12 | 0.0478 (3) | 0.3565 (2) | 0.42571 (19) | 0.0209 (4) |
| H12A | 0.107248 | 0.443231 | 0.477042 | 0.025* |
| H12B | 0.002000 | 0.373194 | 0.347020 | 0.025* |
| C13 | -0.2144 (2) | 0.1487 (2) | 0.39115 (18) | 0.0210 (4) |
| H13A | -0.163870 | 0.108472 | 0.343581 | 0.025* |
| H13B | -0.289446 | 0.177492 | 0.337517 | 0.025* |

| | | | | |
|------|---------------|--------------|--------------|--------------|
| C14 | -0.3067 (3) | 0.0466 (2) | 0.4624 (2) | 0.0234 (5) |
| H14A | -0.363395 | 0.085052 | 0.505581 | 0.028* |
| H14B | -0.388495 | -0.033863 | 0.409321 | 0.028* |
| C11 | 0.57083 (6) | 0.33924 (5) | 0.50253 (4) | 0.02235 (12) |
| C12 | -0.05593 (7) | 0.31818 (6) | 0.74647 (5) | 0.02968 (14) |
| Cu1 | 0.41923 (3) | 0.31469 (2) | 0.63633 (2) | 0.01473 (7) |
| Cu2 | 0.02665 (3) | 0.20789 (2) | 0.61602 (2) | 0.01395 (7) |
| N1 | 0.7493 (2) | 0.49360 (18) | 0.78604 (15) | 0.0175 (4) |
| H1 | 0.788 (3) | 0.446 (2) | 0.749 (2) | 0.021* |
| N2 | 0.5853 (2) | 0.46264 (17) | 0.75898 (15) | 0.0182 (4) |
| N3 | 0.3203 (2) | 0.19520 (17) | 0.74924 (14) | 0.0172 (4) |
| N4 | 0.1545 (2) | 0.14748 (17) | 0.73807 (14) | 0.0166 (3) |
| N5 | -0.0860 (2) | 0.26688 (17) | 0.47523 (15) | 0.0156 (3) |
| H5 | -0.133 (3) | 0.308 (2) | 0.499 (2) | 0.019* |
| O1 | 0.20146 (16) | 0.23756 (13) | 0.52738 (11) | 0.0144 (3) |
| O2 | -0.19285 (18) | 0.01036 (14) | 0.54515 (13) | 0.0228 (3) |
| H2A | -0.200 (2) | -0.0673 (12) | 0.5176 (19) | 0.034* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| C1 | 0.0227 (11) | 0.0187 (11) | 0.0162 (10) | 0.0030 (8) | 0.0029 (8) | 0.0002 (8) |
| C2 | 0.0311 (13) | 0.0258 (12) | 0.0283 (12) | 0.0063 (10) | 0.0088 (10) | -0.0104 (10) |
| C3 | 0.0250 (12) | 0.0215 (11) | 0.0293 (12) | 0.0088 (9) | 0.0111 (9) | -0.0017 (9) |
| C4 | 0.0221 (12) | 0.0329 (13) | 0.0233 (12) | 0.0027 (10) | -0.0004 (9) | -0.0024 (10) |
| C5 | 0.0312 (15) | 0.0431 (16) | 0.0576 (18) | 0.0179 (12) | 0.0162 (13) | -0.0080 (14) |
| C6 | 0.0232 (11) | 0.0251 (12) | 0.0208 (11) | 0.0128 (9) | 0.0044 (8) | 0.0053 (9) |
| C7 | 0.0303 (12) | 0.0264 (12) | 0.0174 (10) | 0.0135 (10) | 0.0071 (9) | 0.0093 (9) |
| C8 | 0.0247 (11) | 0.0188 (10) | 0.0149 (10) | 0.0090 (9) | 0.0076 (8) | 0.0027 (8) |
| C9 | 0.0271 (14) | 0.0578 (19) | 0.0427 (15) | 0.0214 (13) | 0.0059 (11) | 0.0249 (13) |
| C10 | 0.0276 (12) | 0.0299 (12) | 0.0251 (11) | 0.0108 (10) | 0.0132 (9) | 0.0106 (9) |
| C11 | 0.0163 (10) | 0.0270 (11) | 0.0155 (10) | 0.0085 (9) | 0.0058 (8) | 0.0080 (8) |
| C12 | 0.0192 (11) | 0.0214 (11) | 0.0231 (11) | 0.0078 (8) | 0.0067 (8) | 0.0115 (9) |
| C13 | 0.0162 (10) | 0.0233 (11) | 0.0206 (10) | 0.0076 (8) | 0.0003 (8) | -0.0015 (9) |
| C14 | 0.0148 (10) | 0.0187 (11) | 0.0344 (12) | 0.0053 (8) | 0.0054 (9) | -0.0027 (9) |
| Cl1 | 0.0171 (3) | 0.0277 (3) | 0.0228 (3) | 0.0076 (2) | 0.00912 (19) | 0.0017 (2) |
| Cl2 | 0.0361 (3) | 0.0433 (3) | 0.0217 (3) | 0.0284 (3) | 0.0089 (2) | -0.0001 (2) |
| Cu1 | 0.01202 (13) | 0.01529 (13) | 0.01474 (12) | 0.00332 (9) | 0.00345 (9) | 0.00108 (9) |
| Cu2 | 0.01386 (13) | 0.01565 (13) | 0.01402 (12) | 0.00676 (10) | 0.00508 (9) | 0.00341 (9) |
| N1 | 0.0144 (9) | 0.0178 (9) | 0.0193 (9) | 0.0061 (7) | 0.0034 (7) | -0.0003 (7) |
| N2 | 0.0153 (9) | 0.0193 (9) | 0.0192 (9) | 0.0059 (7) | 0.0052 (7) | 0.0006 (7) |
| N3 | 0.0149 (9) | 0.0198 (9) | 0.0177 (8) | 0.0073 (7) | 0.0047 (7) | 0.0048 (7) |
| N4 | 0.0160 (9) | 0.0173 (9) | 0.0175 (8) | 0.0063 (7) | 0.0069 (7) | 0.0041 (7) |
| N5 | 0.0144 (9) | 0.0148 (9) | 0.0192 (9) | 0.0068 (7) | 0.0060 (7) | 0.0014 (7) |
| O1 | 0.0129 (7) | 0.0162 (7) | 0.0143 (7) | 0.0053 (5) | 0.0046 (5) | 0.0047 (5) |
| O2 | 0.0245 (8) | 0.0128 (7) | 0.0268 (8) | 0.0043 (6) | 0.0040 (6) | 0.0010 (6) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|---------------|-------------|
| C1—C2 | 1.372 (3) | C11—H11B | 0.9700 |
| C1—C4 | 1.490 (3) | C11—C12 | 1.517 (3) |
| C1—N1 | 1.341 (3) | C11—O1 | 1.432 (2) |
| C2—H2 | 0.9300 | C12—H12A | 0.9700 |
| C2—C3 | 1.393 (3) | C12—H12B | 0.9700 |
| C3—C5 | 1.490 (3) | C12—N5 | 1.473 (3) |
| C3—N2 | 1.335 (3) | C13—H13A | 0.9700 |
| C4—H4A | 0.9600 | C13—H13B | 0.9700 |
| C4—H4B | 0.9600 | C13—C14 | 1.499 (3) |
| C4—H4C | 0.9600 | C13—N5 | 1.478 (2) |
| C5—H5A | 0.9600 | C14—H14A | 0.9700 |
| C5—H5B | 0.9600 | C14—H14B | 0.9700 |
| C5—H5C | 0.9600 | C14—O2 | 1.432 (3) |
| C6—C7 | 1.386 (3) | Cu1—C11 | 2.2403 (6) |
| C6—C9 | 1.494 (3) | Cu1—N2 | 1.9635 (16) |
| C6—N3 | 1.344 (3) | Cu1—N3 | 1.9770 (17) |
| C7—H7 | 0.9300 | Cu1—O1 | 1.9388 (13) |
| C7—C8 | 1.391 (3) | Cu2—C12 | 2.2937 (6) |
| C8—C10 | 1.494 (3) | Cu2—N4 | 1.9268 (17) |
| C8—N4 | 1.341 (3) | Cu2—N5 | 1.9916 (17) |
| C9—H9A | 0.9600 | Cu2—O1 | 2.0001 (13) |
| C9—H9B | 0.9600 | Cu2—O2 | 2.2441 (14) |
| C9—H9C | 0.9600 | N1—H1 | 0.87 (2) |
| C10—H10A | 0.9600 | N1—N2 | 1.353 (2) |
| C10—H10B | 0.9600 | N3—N4 | 1.363 (2) |
| C10—H10C | 0.9600 | N5—H5 | 0.80 (2) |
| C11—H11A | 0.9700 | O2—H2A | 0.853 (9) |
| C2—C1—C4 | 131.7 (2) | N5—C12—H12B | 109.9 |
| N1—C1—C2 | 106.26 (19) | H13A—C13—H13B | 108.4 |
| N1—C1—C4 | 122.0 (2) | C14—C13—H13A | 110.0 |
| C1—C2—H2 | 126.7 | C14—C13—H13B | 110.0 |
| C1—C2—C3 | 106.60 (19) | N5—C13—H13A | 110.0 |
| C3—C2—H2 | 126.7 | N5—C13—H13B | 110.0 |
| C2—C3—C5 | 129.4 (2) | N5—C13—C14 | 108.28 (16) |
| N2—C3—C2 | 109.4 (2) | C13—C14—H14A | 109.8 |
| N2—C3—C5 | 121.1 (2) | C13—C14—H14B | 109.8 |
| C1—C4—H4A | 109.5 | H14A—C14—H14B | 108.3 |
| C1—C4—H4B | 109.5 | O2—C14—C13 | 109.25 (16) |
| C1—C4—H4C | 109.5 | O2—C14—H14A | 109.8 |
| H4A—C4—H4B | 109.5 | O2—C14—H14B | 109.8 |
| H4A—C4—H4C | 109.5 | N2—Cu1—C11 | 96.92 (5) |
| H4B—C4—H4C | 109.5 | N2—Cu1—N3 | 96.00 (7) |
| C3—C5—H5A | 109.5 | N3—Cu1—C11 | 144.30 (5) |
| C3—C5—H5B | 109.5 | O1—Cu1—C11 | 98.89 (4) |
| C3—C5—H5C | 109.5 | O1—Cu1—N2 | 148.51 (7) |

| | | | |
|---------------|--------------|----------------|--------------|
| H5A—C5—H5B | 109.5 | O1—Cu1—N3 | 86.76 (6) |
| H5A—C5—H5C | 109.5 | N4—Cu2—Cl2 | 95.29 (5) |
| H5B—C5—H5C | 109.5 | N4—Cu2—N5 | 171.92 (7) |
| C7—C6—C9 | 129.3 (2) | N4—Cu2—O1 | 87.45 (6) |
| N3—C6—C7 | 108.86 (19) | N4—Cu2—O2 | 99.70 (6) |
| N3—C6—C9 | 121.9 (2) | N5—Cu2—Cl2 | 92.21 (5) |
| C6—C7—H7 | 127.0 | N5—Cu2—O1 | 84.77 (6) |
| C6—C7—C8 | 105.95 (19) | N5—Cu2—O2 | 81.29 (6) |
| C8—C7—H7 | 127.0 | O1—Cu2—Cl2 | 142.41 (4) |
| C7—C8—C10 | 130.0 (2) | O1—Cu2—O2 | 112.12 (5) |
| N4—C8—C7 | 108.08 (19) | O2—Cu2—Cl2 | 104.35 (4) |
| N4—C8—C10 | 121.88 (19) | C1—N1—H1 | 127.8 (15) |
| C6—C9—H9A | 109.5 | C1—N1—N2 | 111.74 (17) |
| C6—C9—H9B | 109.5 | N2—N1—H1 | 120.4 (15) |
| C6—C9—H9C | 109.5 | C3—N2—Cu1 | 129.29 (15) |
| H9A—C9—H9B | 109.5 | C3—N2—N1 | 105.97 (16) |
| H9A—C9—H9C | 109.5 | N1—N2—Cu1 | 124.74 (13) |
| H9B—C9—H9C | 109.5 | C6—N3—Cu1 | 132.39 (15) |
| C8—C10—H10A | 109.5 | C6—N3—N4 | 107.94 (17) |
| C8—C10—H10B | 109.5 | N4—N3—Cu1 | 119.66 (13) |
| C8—C10—H10C | 109.5 | C8—N4—Cu2 | 132.78 (14) |
| H10A—C10—H10B | 109.5 | C8—N4—N3 | 109.16 (16) |
| H10A—C10—H10C | 109.5 | N3—N4—Cu2 | 117.88 (13) |
| H10B—C10—H10C | 109.5 | C12—N5—C13 | 115.41 (16) |
| H11A—C11—H11B | 108.3 | C12—N5—Cu2 | 105.06 (12) |
| C12—C11—H11A | 109.9 | C12—N5—H5 | 111.3 (17) |
| C12—C11—H11B | 109.9 | C13—N5—Cu2 | 111.35 (13) |
| O1—C11—H11A | 109.9 | C13—N5—H5 | 106.2 (16) |
| O1—C11—H11B | 109.9 | Cu2—N5—H5 | 107.3 (16) |
| O1—C11—C12 | 108.86 (16) | C11—O1—Cu1 | 122.25 (12) |
| C11—C12—H12A | 109.9 | C11—O1—Cu2 | 111.54 (11) |
| C11—C12—H12B | 109.9 | Cu1—O1—Cu2 | 110.88 (6) |
| H12A—C12—H12B | 108.3 | C14—O2—Cu2 | 104.53 (12) |
| N5—C12—C11 | 108.97 (17) | C14—O2—H2A | 108.4 (13) |
| N5—C12—H12A | 109.9 | Cu2—O2—H2A | 131.5 (13) |
| | | | |
| C1—C2—C3—C5 | -177.8 (3) | C9—C6—C7—C8 | 179.7 (2) |
| C1—C2—C3—N2 | 0.1 (3) | C9—C6—N3—Cu1 | -0.9 (3) |
| C1—N1—N2—C3 | 0.9 (2) | C9—C6—N3—N4 | 179.7 (2) |
| C1—N1—N2—Cu1 | -178.30 (15) | C10—C8—N4—Cu2 | 2.8 (3) |
| C2—C1—N1—N2 | -0.8 (3) | C10—C8—N4—N3 | 177.58 (18) |
| C2—C3—N2—Cu1 | 178.58 (16) | C11—C12—N5—C13 | -76.2 (2) |
| C2—C3—N2—N1 | -0.5 (3) | C11—C12—N5—Cu2 | 46.87 (17) |
| C4—C1—C2—C3 | 178.4 (2) | C12—C11—O1—Cu1 | -111.63 (16) |
| C4—C1—N1—N2 | -179.0 (2) | C12—C11—O1—Cu2 | 22.96 (19) |
| C5—C3—N2—Cu1 | -3.4 (3) | C13—C14—O2—Cu2 | 41.26 (17) |
| C5—C3—N2—N1 | 177.5 (2) | C14—C13—N5—C12 | 161.80 (17) |
| C6—C7—C8—C10 | -177.5 (2) | C14—C13—N5—Cu2 | 42.16 (19) |

| | | | |
|--------------|--------------|---------------|--------------|
| C6—C7—C8—N4 | 1.0 (2) | Cu1—N3—N4—C8 | -178.77 (13) |
| C6—N3—N4—C8 | 0.7 (2) | Cu1—N3—N4—Cu2 | -3.11 (18) |
| C6—N3—N4—Cu2 | 176.41 (13) | N1—C1—C2—C3 | 0.5 (3) |
| C7—C6—N3—Cu1 | 179.33 (14) | N3—C6—C7—C8 | -0.6 (2) |
| C7—C6—N3—N4 | -0.1 (2) | N5—C13—C14—O2 | -56.9 (2) |
| C7—C8—N4—Cu2 | -175.87 (14) | O1—C11—C12—N5 | -46.9 (2) |
| C7—C8—N4—N3 | -1.1 (2) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...Cl2 ⁱ | 0.87 (2) | 2.33 (2) | 3.1201 (18) | 152 (2) |
| N5—H5...Cl1 ⁱⁱ | 0.80 (2) | 2.84 (2) | 3.5593 (18) | 150 (2) |
| O2—H2A...O1 ⁱⁱⁱ | 0.85 (1) | 1.88 (1) | 2.7264 (19) | 174 (2) |

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $-x, -y, -z+1$.