X-Ray and EPR study on copper(II) complexes with an enamine ligand

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Abstract: The enamine (HEAID) obtained from aniline and 2-acetyl-1,3-indandione (2AID) behaves as a bidentate ligand in coordination with copper(II) ion. Two types of crystals, apparently different in shape, were isolated and studied by single-crystal X-ray diffraction. The X-ray data for the brown rhombic crystals of compound **1** shows a mononuclear complex of Cu(II) coordinated with two EAID$^-$ anions, Cu(EAID)$_2$. The X-ray data for the green crystals of compound **2** shows a dinuclear Cu(II) complex with two OH$^-$ groups acting as bridging ligands, [Cu$_2$(μ-OH)$_2$(EAID)$_2$]. In both cases the ligand coordinates after deprotonation of the amine group.

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1   Introduction

We have already reported that the reaction of 2-acetyl-1,3-indandione with aniline leads to formation of a condensation product where the exocyclic O atom is involved, as shown in Scheme I. The enamine tautomeric form was found to be energetically more favorable according to *ab initio* quantum chemical calculations [1]. This result was confirmed by detailed ^{13}C-NMR studies and single-crystal X-ray diffraction [1]. The enamine tautomeric form (or strictly speaking, enaminone form) of the compound (HEAID) is stabilized by strong intramolecular hydrogen bonding of N-H...O type. Stabilization of the enaminone form, in Schiff base enaminone equilibrium (Scheme 1), of other organic compounds is well described in the literature [2, 3]. Besides, the application of enamines in enantioselective C-C bond forming reactions is also reported [4, 5].

On the other hand, the good complexation properties of a number of Schiff bases are already well documented [6–10]. The coordination chemistry of enaminones is also attracting interest in the last decades [11, 12]. The complexation ability of this newly synthesized organic compound (HEAID), which is found to exist in an enamine form (both in the solid state and in solution), and its reaction products with copper (II) were studied. Here we report the single-crystal X-ray data for two types of Cu(II) complexes of the enamine of 2-acetyl-1,3-indandione (HEAID).
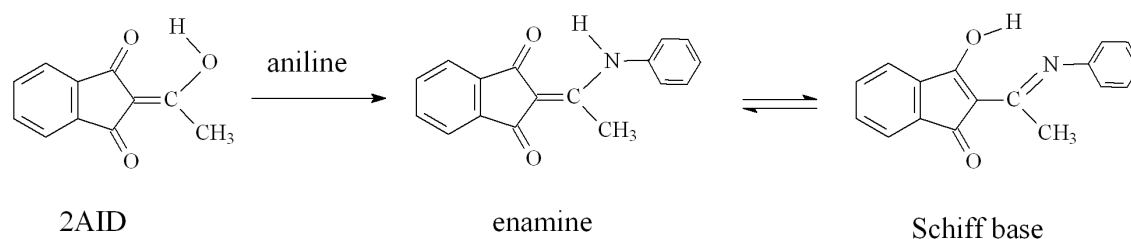
Scheme 1 Reaction path of HEAID formation and its possible tautomeric forms.

2   Experimental

All reagents and solvents used were of AR grade. The IR spectra were recorded on a Perkin-Elmer FTIR-1600 spectrophotometer (KBr pellets). The EPR spectra were recorded on an X-band EPR spectrometer Bruker B-ER 420.

The ligand (HEAID) was obtained according to previously described procedure [1]. The copper complexes of HEAID were synthesized by mixing methanol solutions of $Cu(CH_3COO)_2.H_2O$ (1mmol) and HEAID (2mmol) in presence of NaOH (2mmol) dissolved in methanol. The mixture was refluxed for half an hour and the formed powder was filtrated after cooling. The elemental analysis data of the isolated powder is consistent with a mononuclear copper bis-chelate $Cu(EAID)_2$; $[C_{34}H_{24}CuN_2O_4]$, (MW=588.12) calc. (exp.) %C 69.40 (68.70); %H 4.11 (4.25); %N 4.76(4.61). IR (KBr tablets): 1667 (s), 1612 (s), 1565 (vs) cm^{-1}.

The subsequent recrystalization of the isolated powder in methanol leads to formation

of two types of crystals apparently different in shape: brown rhombic crystals of compound **1** and green prismatic crystals of compound **2**. Both types of crystals were separated manually and studied by means of single-crystal X-ray diffraction.

It was possible to obtain single crystals of each type separately, following the procedures described further on. Single crystals of compound **1** were obtained after slow evaporation of dichloromethane/methanol (1:1) solution. Compound **2** has been synthesized when excess of the copper salt was used. Methanol solutions of $Cu(CH_3COO)_2.H_2O$, NaOH and HEAID in molar ratio 3:2:1 were mixed and the reaction mixture was heated for half an hour until the volume is reduced from 70mL to 30mL. The so-formed light blue precipitate of $Cu(OH)_2$, resulting from the excess of copper salt and NaOH used, was filtrated and the light green solution was kept in refrigerator for 10 days. Green prismatic crystals of compound **2** were isolated in a very small amount and studied by IR spectroscopy. IR (KBr tablets): 3476(m), 3312 (sh) 1680 (s), 1612(s), 1566(vs) cm^{-1}.

A suitable brown rhombic crystal of **1** was studied on an Enraf-Nonius CAD-4 X-ray diffractometer (MoKα, λ=0.71073 Å, graphite monochromator) at ambient temperature. The compound crystallizes in the monoclinic space group P2$_1$/c with Z=2. The data set was corrected for Lorentz and polarisation effects and absorption correction was made using Ψ-scan method. The structure was solved by direct methods with SIR97 software and the refinement was carried out using the SHELXL-97 software package [13]. Crystallographic details on data collection and structure refinement are deposited on the Cambridge Crystallographic Data Center - CCDC 197838.

A green crystal of compound **2** was studied on a Siemens Smart CCD X-ray diffractometer (CuKα, λ=1.54180 Å, Gobel Mirrors) at low temperature (100(2) K). It should be noted that the crystals of **2** lose their quality in air. The unit cell was assigned as monoclinic space group P2/n with Z=4. Structure refinement was based on 1941 unique reflections using the SHELXL-97 software package [13]. The hydrogen atoms of the bridging OH groups were found from the electron density map and no structural restrictions were applied. CCDC 198103 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Detailed information for data collection and structure refinement for both complexes is presented in Table 1.

3 Results and discussion

Complex formation between Cu(II) and HEAID takes place in presence of NaOH, (the latter is necessary for deprotonation of the amine group of the ligand molecule) and results in formation of mononuclear Cu(II) complex (see the Experimental Section) in polycrystalline form. Metal –to-Ligand ratio of 1:2 was found, which suggests that a copper bis-chelate is formed. The complex was studied by IR and EPR spectroscopy. In

Compound	$C_{34}H_{24}CuN_2O_4$ $Cu(EAID)_2$	$C_{34}H_{30}Cu_2N_2O_8$ $Cu_2(\mu\text{-}OH)_2(EAID)_2 \cdot 2H_2O$
Formula weight	588.12	717.64
Temperature	293(2) K	100(2) K
Wavelength	0.71069 Å	1.54180 Å
Crystal system space group	Monoclinic, $P2_1/c$	Monoclinic, $P2/n$
Unit cell dimensions	a=12.043(2)Å b=8.949(2)Å c=12.923(3)Å $\alpha = 90.000°(5)$ $\beta = 100.89°(3)$ $\gamma = 90.000°(5)$	a=11.288(1)Å b=11.243(1)Å c=13.070(1)Å $\alpha = 90.000°(5)$ $\beta = 113.573°(5)$ $\gamma = 90.000°(5)$
Volume	1367.7(11)Å^3	1520.3(2) Å^3
Z	2	4
Calculated density	1.428 g/cm^3	1.568 g/cm^3
Absorption coefficient	0.842 mm^{-1}	2.209 mm^{-1}
F(000)	606	732
Crystal size	0.7×0.2×0.2 mm	0.7×0.2×0.2 mm
θ range for data collection	2.78° to 24.97°	3.93 to 56.01
Limiting indices	0≤h≤14 0≤k≤10 -15≤l≤15	-12≤h≤11 -11≤k≤11 -14≤l≤13
Reflections collected/ unique	2530 / 2409 [R(int)=0.0507]	5428 / 1941 [R(int)=0.0546]
Completeness to theta	24.97 99.9%	50.00 100.0%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2409 / 0 / 182	1941 / 0 / 221
GooF on F^2	1.048	1.066
Final R indices, [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1315	R1 = 0.0693, wR2 = 0.1880
R indices (all data)	R1 = 0.0981	R1 = 0.0999

Table 1 Crystal data and structure refinement parameters of componds **1** ($C_{34}H_{24}CuN_2O_4$) and **2** ($C_{34}H_{30}Cu_2N_2O_8$).

the IR spectrum of the complex the stretching band for N-H bond (3168 cm^{-1}) is missing and the corresponding band for one of the carbonyl groups is shifted to lower frequencies (from 1642 to 1612 cm^{-1}). These data indicate that the enamine is coordinated through N atom from the deprotonated amine group and the O atom from the adjacent carbonyl group and therefore behaves as a bidentate ligand. It is worth noting that another carbonyl group from the ligand remains non-coordinated, and could give rise to some intermolecular interactions.

The EPR spectra of a powder sample of the complex were recorded at ambient and low (120K) temperatures. Both spectra show an axial anisotropy with g-values equal to

$g_{\perp}$=2.0730±0.0004 and $g_{||}$=2.2300±0.0004, and the average value for g_i calculated from Eq. 1 is 2.125.

$$g_i = \frac{2 \times g_{\perp} + g_{||}}{3} \tag{1}$$

The EPR spectrum of the CH_2Cl_2 solution of the complex at room temperature (Figure 1) exhibits well-resolved hyperfine structure due to magnetic coupling between the unpaired electron and $^{63,65}Cu$ nuclei (I=3/2). The hyperfine lines differ in intensity due to the so-called tumbling effect [14]. The value of the isotropic hyperfine coupling constant A_i is equal to 63 Gauss (62×10^{-4} cm^{-1}). The value of the isotropic g-factor is 2.1290±0.0005, which is close to this calculated from the solid state EPR spectrum. According to this result it could be supposed that the structure of the complex remains unchanged in solution. Superhyperfine structure due to interaction with ^{14}N nuclei (I=1) is also observable at the high-field end of the spectrum. In the case of frozen solution spectrum (at 120K) the superhyperfine structure for one of the hyperfine copper lines in the perpendicular region is more pronounced as could be seen in Figure 2. The other perpendicular lines, as well as the hyperfine lines in the parallel region, are not visible most likely because they are too broad. The splitting between the superhyperfine lines is equal to 14 Gauss. The number of the superhyperfine lines is 5 which corresponds to two N atoms coordinated to the metal center (the number of the superhyperfine lines is equal to **2nI+1,** where **I** is the nuclear magnetic moment and **n** is the number of the corresponding nuclei). The relative intensity of the superhyperfine lines is 1:2:3:2:1, as it is expected for two equivalent nitrogen nuclei [15]. These results are in agreement with the IR and elemental analyses data for the structure of the complex.
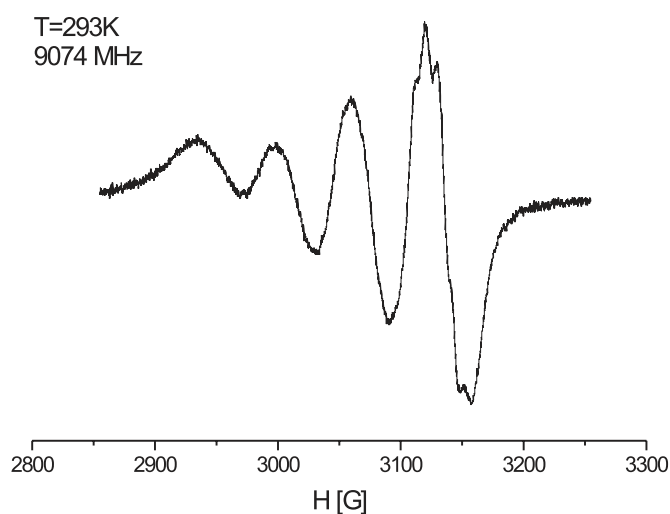

Fig. 1 X-band EPR spectrum of dichloromethane solution of copper bis-chelate, Cu(EAID)$_2$, recorded at room temperature.

T=120 K
9503 MHz

H [G]

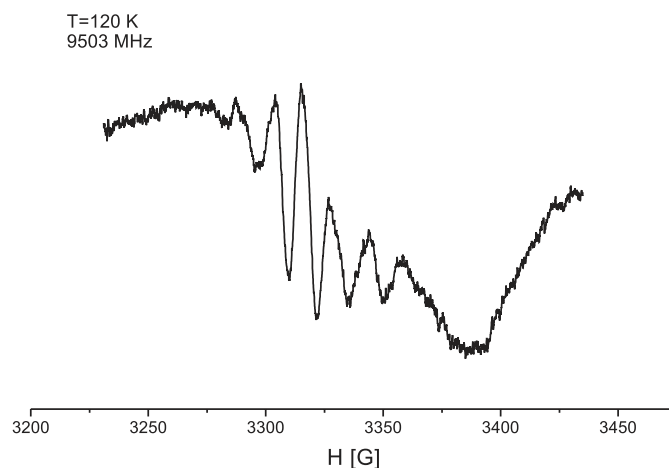**Fig. 2** X-band EPR spectrum of frozen dichloromethane solution of copper bis-chelate, Cu(EAID)$_2$, recorded at 120 K.

The single-crystal X-ray data for the brown rhombic crystals of compound **1** shows a mononuclear complex of Cu(II) coordinated with two EAID$^-$ anions - the expected and already described mononuclear bis-chelate. The donor atoms from the EAID$^-$ anions are positioned in one plane with the copper ion. Taking into consideration the short contacts with adjacent molecules, however, a strongly elongated octahedral geometry of each metal center becomes more accurate description (see Figure 3). The two apical positions of each Cu(II) ion are occupied by the O atoms from carbonyl groups, which are not involved in the bis-chelate structure, of two neighboring complex molecules. The distances from the metal ion to these O atoms are much longer (2.624(2) Å) compared to the Cu-N and Cu-O bond lengths in the equatorial plane, which are 2.022(3) and 1.936(3)Å, respectively. These structural parameters show the main trigonal distortions of the octahedron. On the other hand, the O-Cu-N bond angle in the equatorial plane is equal to $92.41(1)^0$. The metal center lies on the same line with the apical O atoms, which makes an angle of $84.39(1)^0$ with the equatorial plane. These data show the main deviations from the octahedral geometry and are consistent with a Cu(II) complex with a strong Jahn-Teller distortion [16–18]. The resolved crystal structure is shown in Figure 3, while selected bond lengths and angles are listed in Table 2. The benzene rings from the ligands molecules are almost perpendicular to the plane of the donor atoms. The way of packing of the molecules in the crystal is represented in Figure 4. It could be seen that a two-dimensional network is formed along **b** and **c** axes. No intermolecular interactions are present along **a** axis.

The X-ray data of the green crystals of compound **2** shows that the molecular structure consists of two Cu(II) centers and two OH$^-$ groups acting as bridging ligands. Each of the metal centers is coordinated with an EAID$^-$ anion in the same way as in the case of mononuclear species. The molecule has C2 symmetry with the O atoms from the bridging ligands lying on the C2 axis. The resolved X-ray structure of this complex is presented
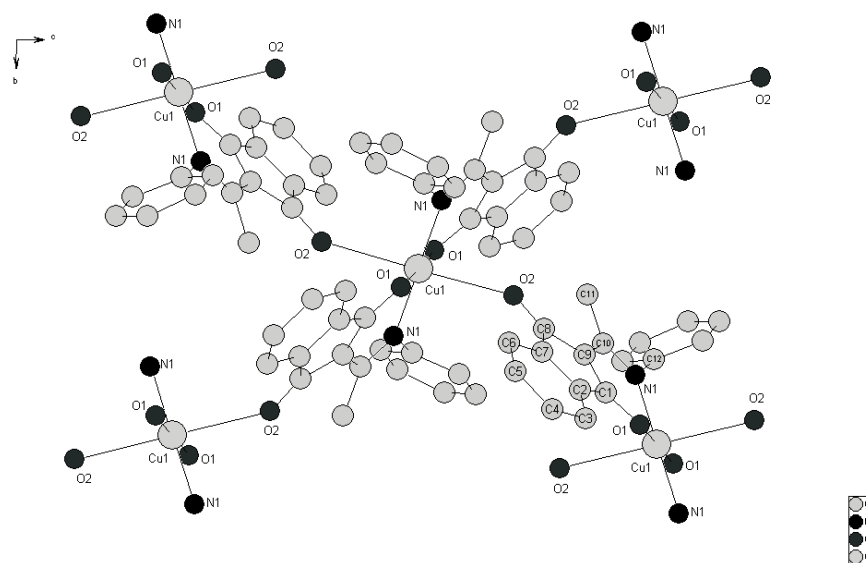
Fig. 3 Crystal structure of the Cu(II) bis-chelate, Cu(EAID)$_2$. The hydorgen atoms are omitted for clarity.
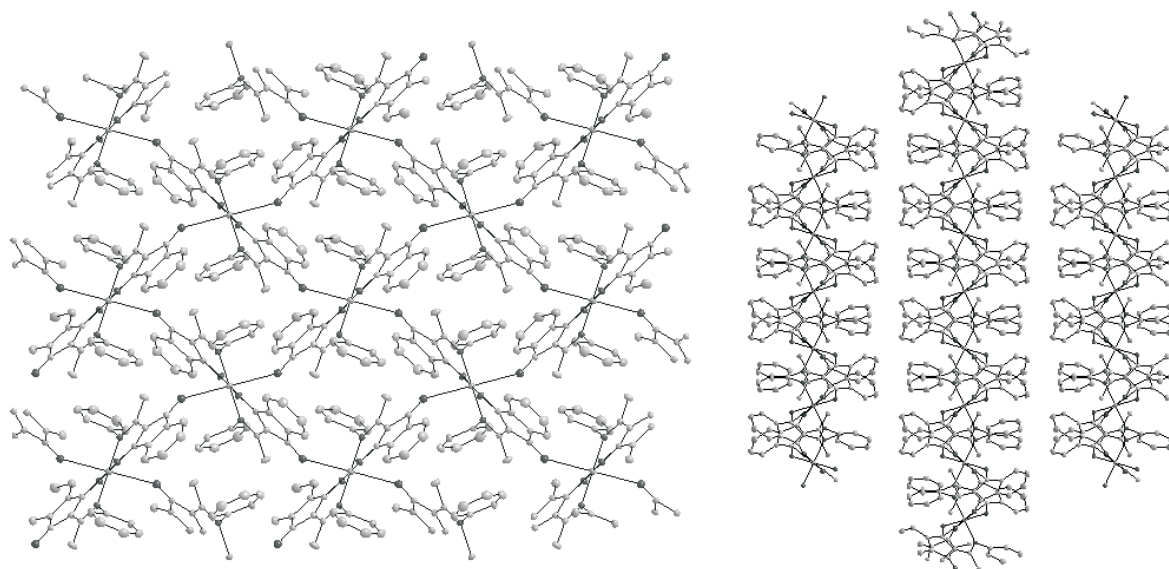

Fig. 4 Crystal packing of Cu(EAID)$_2$ in 1 0 0 plane (on left) and the 0 0 1 plane (on right).

in Figure 5. Some structural parameters are listed in Table 3. The two metal ions and the O atoms from the bridging ligands lie in one plane. The distance between the two Cu(II) ions is 2.980(2) Å.

Crystal packing, perpendicular to **b** axis, is shown in Figure 6. It could be seen that the molecules are layered in mosaic architecture. Additionally, disordered water molecules are incorporated in the space between the individual molecules. The best final R indexes were obtained when the O atom of the disordered water molecule was located at two different positions (labeled as O1G and O1H) with different occupation factors (0.6 and
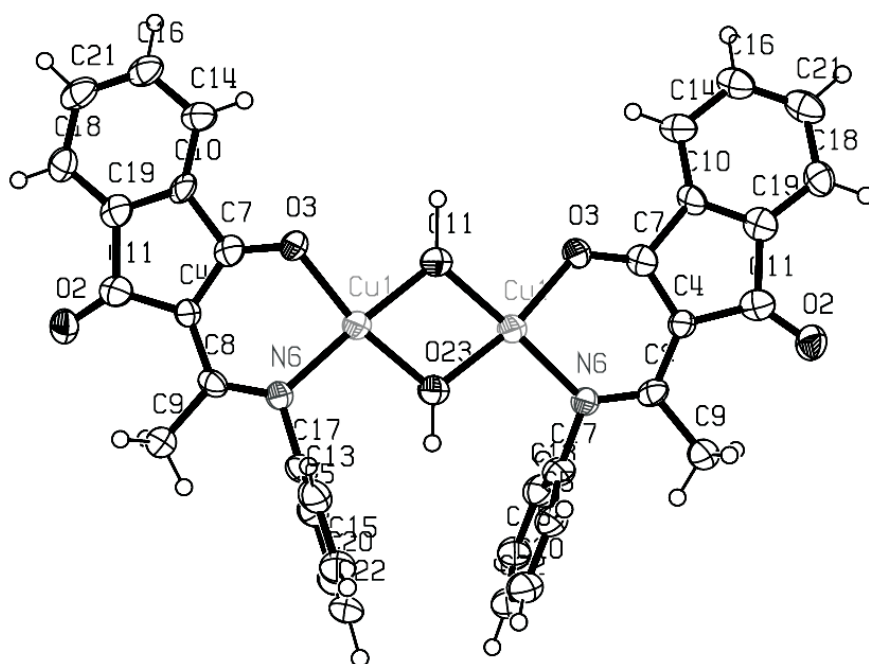
Fig. 5 Crystal structure of the Cu(II) dimer complex, $Cu_2(\mu\text{-OH})_2(EAID)_2$. The solvent molecules and hydrogen atoms numbering are omitted for clarity.
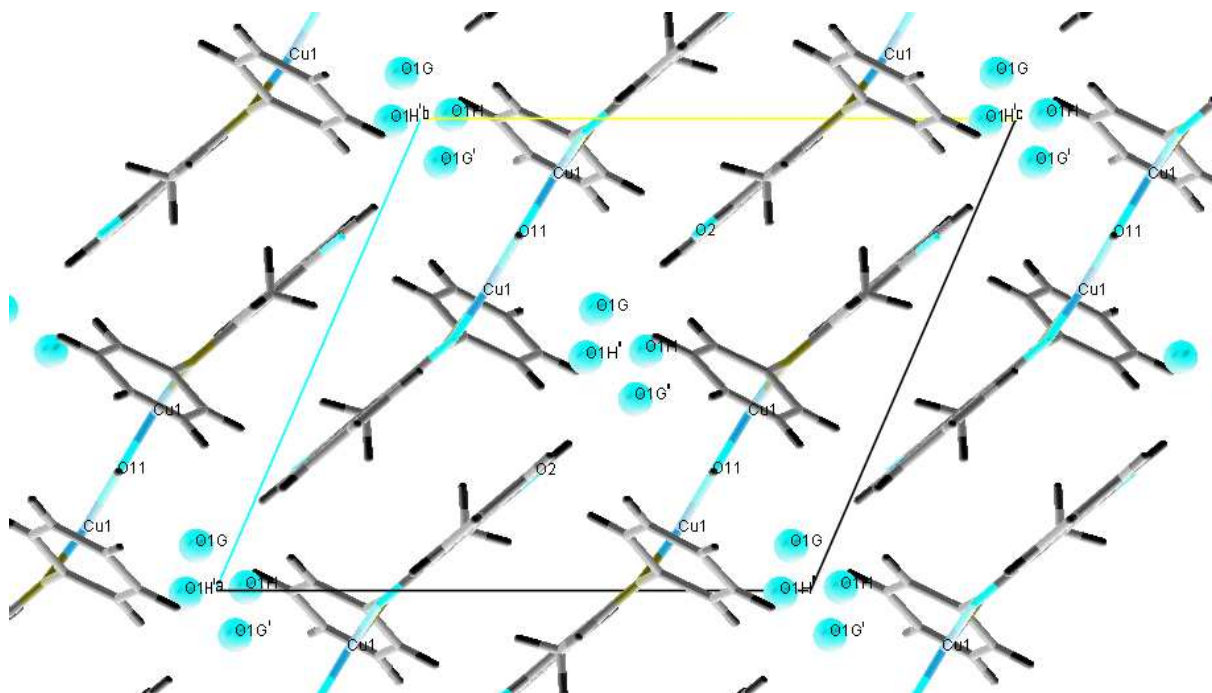

Fig. 6 Crystal packing of $Cu_2(\mu\text{-OH})_2(EAID)_2$ in 0 1 0 plane. O1G and O1H are two different positions of a disordered water molecule.

0.4, respectively). For better visualization of the structural features, described further on, enlarged view of the crystal packing is presented in Figure 7. The O atom in position O1H is very close to one of the copper ions, the O1H-Cu1 distance being 2.639(2) Å. On the

Bond lengths	Å	Angles	°
Cu(1)-O(1)	1.936(3)	O(1)-Cu(1)-N(1)	92.41(12)
Cu(1)-N(1)	2.022(3)	C(1)-O(1)-Cu(1)	120.8(3)
O(2)-C(8)	1.232(5)	C(10)-N(1)-C(12)	116.4(3)
O(1)-C(1)	1.262(5)	C(10)-N(1)-Cu(1)	124.4(3)
N(1)-C(10)	1.324(5)	N(1)-C(10)-C(9)	120.5(4)
N(1)-C(12)	1.439(5)	O(1)-C(1)-C(9)	129.0(4)

Table 2 Selected bond lengths and angles for compound **1**, Cu(EAID)$_2$. For the numberings see Figure 3.

Bond lengths	Å	Angles	°
Cu(1)-O(23)	1.911(5)	O(23)-Cu(1)-O(3)	168.1(2)
Cu(1)-O(3)	1.909(5)	O(23)-Cu(1)-O(11)	78.4(3)
Cu(1)-O(11)	1.935(5)	Cu(1)-O(11)-Cu'(1)	100.8(3)
Cu(1)-N(6)	1.970(6)	Cu'(1)-O(23)-Cu(1)	102.5(4)
Cu(1)-Cu(1)'	2.980(2)	O(3)-Cu(1)-O(11)	90.0(2)
O(2)-C(11)	1.233(9)	O(23)-Cu(1)-N(6)	97.6(3)
O(3)-C(7)	1.254(9)	O(3)-Cu(1)-N(6)	93.9(2)
C(5)-C(17)	1.399(1)	O(11)-Cu(1)-N(6)	174.1(2)
N(6)-C(8)	1.307(8)	C(7)-O(3)-Cu(1)	122.8(5)
N(6)-C(17)	1.449(9)	C(8)-N(6)-Cu(1)	126.5(5)
		C(17)-N(6)-Cu(1)	115.0(4)

Table 3 Selected bond lengths and angles for compound **2**, Cu$_2$(μ-OH)$_2$(EAID)$_2$2H$_2$O. For the numberings see Figure 4.

other hand, it is close to the O atom from the non-coordinated carbonyl group (labeled O2) of an adjacent complex molecule. The latter holds for position O1G of the same water molecule, the corresponding O1G – O2 and O1H – O2 distances are 2.914(2) and 2.792(2) Å, respectively. Besides, position O1G is close to the metal centers of another neighboring molecule of the dinuclear complex (copper – O1G distances are 4.234(1) and 3.867(1) Å) and even closer to the O atom (labeled O11) from the bridging OH group of the same complex molecule, O1G – O11 is 2.909(1) Å. The same description holds for the two positions (labeled O1G' and O1H') of another disordered water molecule, which is symmetry-related to the one already described (symmetry transformations: 2-x, -y, -z).

It seems likely that two complex molecules are competing for the two water molecules, placed between them, and this is mediated by the O2 atom from the non-coordinated carbonyl group from other two complex molecules.
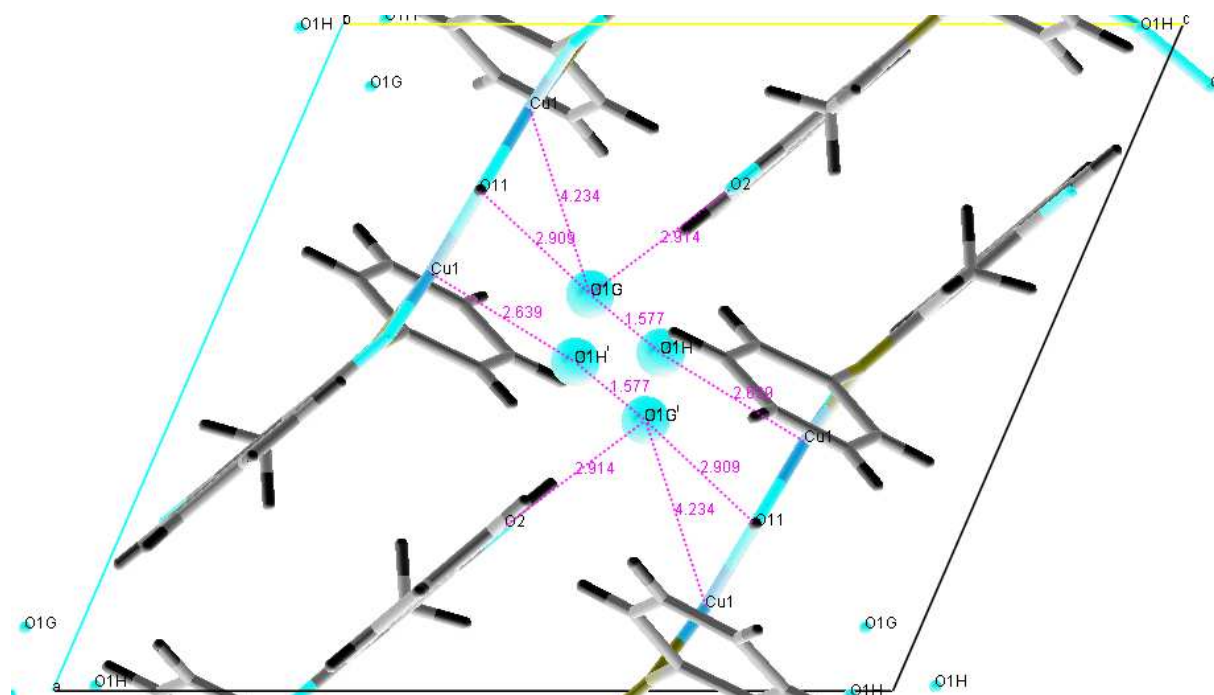
Fig. 7 Magnified view of the crystal packing with some distances.

Acknowledgment

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