

# Tetrahydrated bis(monoaqua-bis(ethylenediamine)copper(II))-diaqua-bis(ethylenediamine)copper(II) dicitrate: preparation, crystal structure, Raman and FTIR spectra and paramagnetic behavior

Andrii Vakulka<sup>a</sup>, Evgeny Goreshnik<sup>b</sup>, Marko Jagodič<sup>c</sup>, Zvonko Jagličič<sup>d</sup> and Zvonko Trontelj<sup>c</sup>

<sup>a</sup>Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia; <sup>b</sup>Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Ljubljana, Slovenia; <sup>c</sup>Institute of Mathematics, Physics and Mechanics, Ljubljana, Slovenia; <sup>d</sup>Institute of Mathematics, Physics and Mechanics & Faculty of Civil and Geodetic Engineering, University of Ljubljana, Ljubljana, Slovenia

## ABSTRACT

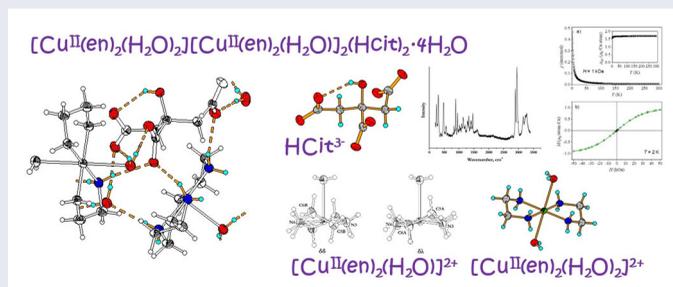
The crystals of the first copper(II) ethylenediamine complex containing citrate anion have been prepared and characterized. Despite the archetypical character of the copper(II) ethylenediamine complexes, some structural peculiarities were found to be interesting since they are quite rare even among the mentioned type of the complex compounds *i.e.* a presence of both mono and diaqua-bis(ethylenediamine)copper(II) cations together in the same crystal structure, intramolecular hydrogen bonding of the citric anion, *cis,trans*-configuration of the citric anion and the disordered C–C bond of the ethylenediamine molecule in the monoaqua-bis(ethylenediamine)copper(II) cation, which in fact is a co-existence of two energetically close  $\delta\delta$  and  $\delta\lambda$  conformers. The Raman as well as FTIR spectra were recorded and discussed. Finally, the magnetic measurements have shown paramagnetic behavior of the prepared complex in a wide range of temperatures.

## ARTICLE HISTORY

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## KEYWORDS

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**CONTACT** Andrii Vakulka  [andrii.vakulka@fs.uni-lj.si](mailto:andrii.vakulka@fs.uni-lj.si)  Faculty of Mechanical Engineering, University of Ljubljana, 1000 Ljubljana, Slovenia.

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## 1. Introduction

One can easily note that a relatively small number of publications are dedicated to copper(II) citrate complexes (less than 10 structures found in CCDC [1]) with any kind of the other ligand, while copper(II) ethylenediamine complexes, without any doubts, could be called “over-investigated” (834 structures found in CCDC [1]). There is a number of different archetypical copper(II) ethylenediamine complexes, for example  $[\text{Cu}(\text{en})(\text{H}_2\text{O})_2]\text{SO}_4$  [2],  $[\text{Cu}(\text{en})_2](\text{NO}_3)_2$  [2],  $[\text{Cu}(\text{en})_2]\text{SO}_4$  [3],  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{OSO}_3)_2(\text{en})_2]\cdot 6\text{H}_2\text{O}$  [4], etc. However, the latest listed crystal structure was found to be not as trivial as it seems to be *i.e.* it contains bis(ethylenediamine)copper(II) sulphate anions as well as water coordinated bis(ethylenediamine)copper(II) cations interconnected with each other by rings of hydrogen bonded water molecules  $R_4^3(10)$ . On the other hand, there are also various more complicated compositions with a  $[\text{Cu}(\text{en})_2]$  motif, for example  $[\text{Cu}(\text{en})_2\text{V}_{10}\text{O}_{28}][\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2\cdot 2\text{H}_3\text{BO}_3\cdot 2\text{H}_2\text{O}$  [5] or  $[\text{Cu}(\text{en})_2][\text{Zn}(\text{NC})_4(\text{CuCN})_2]$  [6]. However, as far as we know, there are no reported copper(II) complexes containing simultaneously copper(II) coordinated ethylenediamine species and the citrate anion in any possible coordination mode. The most important papers related to copper(II) citrate itself or copper(II) citrate complexes may easily be listed and discussed. Practically all early works are related to the water solution chemistry of copper(II) citrate and the 3d-metal cations [7, 8]. It was proposed that even at quite low pH (lower than 3) citrate anion could be coordinated with copper(II) cation in the form of  $\text{cit}^{4-}$ , where the deprotonated OH group is also copper(II) coordinated. Further, 24 years after Parry and DuBois [8], the crystal structure of copper(II) citrate dihydrate was determined and discussed by Donald Mastropaolo and co-workers [9]. The behavior of the citrate anion was confirmed and the formula of the prepared copper(II) citrate was found to be  $\text{Cu}_2(\text{cit})\cdot 2\text{H}_2\text{O}$ . The magnetic susceptibility measurements revealed the strong antiferromagnetism of those copper(II) citrate crystals. Further, the crystal structure of  $\text{Cu}_2(\text{cit})\cdot 2\text{H}_2\text{O}$  was reinvestigated by Zhang *et al.* in 2006 [10]. There is also a monohydrate of copper(II) citrate,  $\text{Cu}_2(\text{cit})\cdot \text{H}_2\text{O}$ , which crystal structure was determined using powder diffraction experiments in 2014 [11]. As for the copper(II) citrate complexes, there are some interesting examples as  $(\text{Gua})_4[\text{Cu}_2(\text{cit})_2]$  [12], supramolecular  $[\text{Cu}_2(\mu\text{-cit})(\text{phen})_4]\cdot 9\text{H}_2\text{O}$  [13], relatively simple  $(\text{NH}_4)_4[\text{Cu}(\text{Hcit})_2]$  [14],  $[\text{Cu}_4(\mu_4\text{-cit})_2(\text{H}_2\text{O})_8]_n$  coordination polymer [15], etc. For example, in the crystal structure of the supramolecular  $[\text{Cu}_2(\mu\text{-cit})(\text{phen})_4]\cdot 9\text{H}_2\text{O}$  complex only one citric anion coordinates two different copper(II) ions with two different carboxylate groups only, while in the structure of the ammonium complex  $(\text{NH}_4)_4[\text{Cu}(\text{Hcit})_2]$  two citrate anions coordinate one copper(II) ion with two carboxylates and one alkoxo group. Thus, depending on the type of complex, the citrate anion may demonstrate different coordination modes as well as different anionic forms ( $\text{cit}^{4-}$ ,  $\text{Hcit}^{3-}$ ,  $\text{H}_2\text{cit}^{2-}$ , etc.), while a non-coordinated citrate anion (isolated and hydrogen bonded only) in a copper(II) complex structure is a rare example and even some simple alkali metal anhydrous citrates contain metal ions chelated with the citrate carboxylate groups (anhydrous tripotassium and trisodium citrates [16, 17]). For this reason, it would be even more interesting to observe the combinations of the citric anion and bis(ethylenediamine)copper(II) cations within the same complex compound.

Herein, we present the synthesis and characterization (crystal structure, Raman as well as FTIR spectrum and magnetic susceptibility) of a new tetrahydrated copper(II) citrate ethylenediamine complex,  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$ .

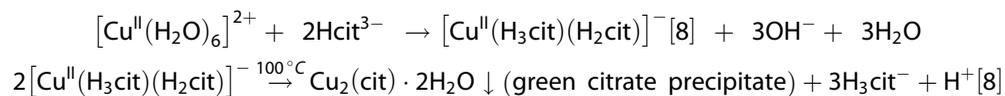
## 2. Experimental

### 2.1. Preparation procedure

All starting reactants were of reagent quality and were not additionally checked or purified.

The discussed copper(II) complex has been prepared in two steps i.e. the powder of copper(II) citrate precursor was prepared and then dissolved in a water solution of ethylenediamine.

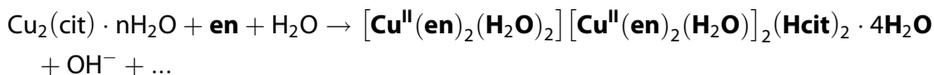
1) 12.03 g (143 mmol) of sodium hydrogen carbonate (Sigma-Aldrich) dry powder was mixed with 10.03 g (47.7 mmol) of citric acid monohydrate crystals (Sigma-Aldrich) and then 20 ml of distilled water was added into the prepared dry mixture, step by step (5 ml on each step) until the evolution of  $\text{CO}_2$  gas stopped. After that, the prepared solution was additionally filtered and evaporated on a water bath at  $100^\circ\text{C}$  until the crystalline hydrated trisodium citrate (most probably  $\text{Na}_3\text{Hcit} \cdot 2\text{H}_2\text{O}$ ) was formed. The prepared white crystals were gently compressed on filter paper sheets and additionally dried over sodium hydroxide pellets in a desiccator. Further, a water solution of copper(II) sulphate was prepared: 5.02 g (20.1 mmol) of copper(II) sulphate pentahydrate (Supelco) was dissolved in 20 ml of distilled water and, as a result, a clear blue solution formed. 3.93 g (13.4 mmol) of trisodium citrate crystals were added directly into the solution of copper(II) sulphate and shaken well until all citrate crystals were dissolved. During the citrate dissolution, the reaction mixture changed from clear blue to blue green and no additional precipitate was formed. After the trisodium citrate was completely dissolved, the mixture was left on a boiling water bath for 10–15 min. After that time, a dense *green* crystalline precipitate of the copper(II) citrate was formed on the bottom and on the walls of the flask. Thus, the crystallization/precipitation was finished and the solution became practically colorless with a pale blue coloring only. The solution was decanted and the *green* copper(II) citrate precursor precipitate was additionally washed with a few portions of distilled water. Finally, the washed wet *green* copper(II) citrate precursor was dried at  $100^\circ\text{C}$ .



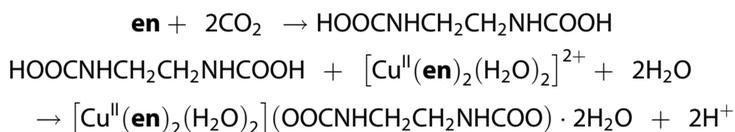
Under drying conditions (at  $100^\circ\text{C}$ ), the *green* copper(II) citrate precursor slowly turned into a *light violet* form; possibly  $\text{Cu}_2(\text{cit}) \cdot 2\text{H}_2\text{O}(\text{green}) \xrightarrow{80-100^\circ\text{C}} \text{Cu}_2(\text{cit}) \cdot (2-n)(\text{light violet}) + n\text{H}_2\text{O}$ , where  $n = 0-2$ . It must be specially noted that the *green* copper(II) citrate precursor should be carefully washed with distilled water (portion by portion) i.e. fresh precipitate of the copper(II) citrate precursor could contain a significant amount of sulphate anions. As a result, instead or together with  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{en})_3]\text{SO}_4$  could be formed, which possesses the same color and a different crystal habit.

Elemental analysis ( $\text{Cu}_2(\text{cit}) \cdot n\text{H}_2\text{O}$ , where  $n=0-2$ ), wt. %: Found: **C** 20.41(3), **H** 2.56(4), **Cu** 32.8(2) in the *green* citrate precursor and **C** 21.45(16), **H** 2.18(3), **Cu** 35.2(2) in the *light violet* citrate precursor. Anal. Calcd.: **C** 20.52, **H** 2.30, **Cu** 36.19 in  $\text{Cu}_2\text{C}_6\text{H}_8\text{O}_9/\text{Cu}_2(\text{cit}) \cdot 2\text{H}_2\text{O}$  and **C** 22.86, **H** 1.28, **Cu** 40.32 in  $\text{Cu}_2\text{C}_6\text{H}_4\text{O}_7/\text{Cu}_2(\text{cit})$ . Yield, g: 2.99; Yield, %: 84.7 (with respect to copper(II) sulphate).

2) 2.37 g (6.75–7.52 mmol of  $\text{Cu}_2(\text{cit}) \cdot n\text{H}_2\text{O}$ , where  $n=0-2$ ) of the prepared *light violet* copper(II) citrate precursor was covered under 2.00 ml of distilled water. 2.00 ml (30.0 mmol) of ethylenediamine (Sigma-Aldrich) was added into the water layer. After that, the color of the mixture turned *dark violet* and the temperature of the mixture raised very quickly to 70–80 °C. After approximately a day in the desiccator over sodium hydroxide pellets, *dark violet* fine crystals of the target complex were formed in the reaction mixture:



It is also important to mark that some long exposure of the solution with ethylenediamine under ambient conditions could also lead to the formation of crystals of a known complex,  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{OOCNHCH}_2\text{CH}_2\text{NHCOO}) \cdot 2\text{H}_2\text{O}$  [18], which is avoidable if using a desiccator with sodium hydroxide pellets:



Elemental analysis  $\text{C}_{24}\text{H}_{74}\text{Cu}_3\text{N}_{12}\text{O}_{22}$ , wt. %: Found: **C** 26.94(9), **H** 7.2(1), **Cu** 16.2(2), **N** 17.0(1). Anal. Calcd.: **C** 26.85, **H** 6.95, **Cu** 17.76, **N** 15.66. The elemental analysis of the prepared copper(II) citrate precursor and  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  (the content of carbon, hydrogen and nitrogen) was performed using a CHNS elemental analyser Vario EL cube (Elementar) operating in the CHNS mode. The copper content was determined separately using a complexometric titration method [19]. Raman bands (single crystal),  $\text{cm}^{-1}$ : 245, 303, 392, 477, 483, 564, 833, 891, 953, 1018, 1050, 1063, 1096, 1140, 1205, 1284, 1300, 1328, 1370, 1400, 1416, 1442, 1464, 1580, 2896, 2948 (very strong), 2992, 3160, 3239, 3275. FTIR bands (polycrystalline sample),  $\text{cm}^{-1}$ : 469 (sharp), 564, 835, 900, 943, 998, 1052, 1110, 1210, 1402, 2895, 2958. Yield, g: 1.66; Yield: 30.8–34.4% (with respect to copper(II) citrate precursor).

## 2.2. Single-crystal diffraction

The diffraction experiment was done on a Gemini + single-crystal diffractometer with an Atlas CCD detector using graphite monochromated Cu-K $\alpha$  radiation. The CrysAlis software suite program package was used for processing of the data gathered [20]. An analytical adsorption correction was applied. The structure was solved using the SHELXT program [21] and refined with SHELXL-2014 [21] implemented in Olex2 crystallographic software [22]. The figures were prepared using DIAMOND 3.2 software [23]. Some experimental data on the diffraction experiment are presented in Table 1.

**Table 1.** Single crystal diffraction data of  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$ .

Tetrahydrated bis(monoaqua-bis(ethylenediamine)copper(II))-diaqua-bis(ethylenediamine)copper(II) dicitrate	
Color and form	Dark violet, irregular
Molecular formula	$\text{C}_{24}\text{H}_{74}\text{Cu}_3\text{N}_{12}\text{O}_{22}$
Molar weight, $\text{g}\cdot\text{mol}^{-1}$	1073.57
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ , Å	8.4676(4)
$b$ , Å	8.7754(5)
$c$ , Å	16.3813(8)
$\alpha$ , °	80.393(5)
$\beta$ , °	83.541(4)
$\gamma$ , °	68.576(5)
$V_{\text{calc}}$ , Å <sup>3</sup>	1115.5(1)
$Z$	1
$D_{\text{calc}}$ , $\text{g}\cdot\text{cm}^{-3}$	1.598
$F(000)$	565
$\mu$ , $\text{mm}^{-1}$	2.455
Crystal size, mm	$0.553 \times 0.128 \times 0.111$
Temperature, K	150.0(1)
Index ranges	$-10 \leq h \leq 10$ , $-11 \leq k \leq 11$ , $-20 \leq l \leq 20$
$\Theta$ min–max, °	2.6990–76.2870
Goodness-of-fit on $F^2$	1.038
$R_1$	0.0389
$wR_2$	0.0859

Weighing scheme:  $w = [\sigma^2 F_0^2 + (0.0404 \cdot P)^2 + 1.2911 \cdot P]^{-1}$ , where  $P = (F_0^2 + 2F_0^2)/3$ .

### 2.3. Raman spectroscopy

The spectrum of the complex was recorded using a Horiba Jobin-Yvon LabRAM HR spectrometer equipped with a He-Ne 17mW LASER, giving rise to the 632.8 nm excitation line. The instrument was additionally calibrated before each measurement was done. A polycrystalline silicon plate was used for the calibration ( $521 \text{ cm}^{-1}$  characteristic band). The spectrum was recorded in a  $200\text{--}3400 \text{ cm}^{-1}$  spectral region.

### 2.4. FTIR spectroscopy

The spectrum of the prepared complex was recorded ( $450\text{--}4000 \text{ cm}^{-1}$ ) on a Spectrum GX FTIR (Perkin Elmer) spectrometer. The spectrum of the solid polycrystalline sample was recorded at  $2 \text{ cm}^{-1}$  resolution using a MTEC Model 300 photoacoustic detector.

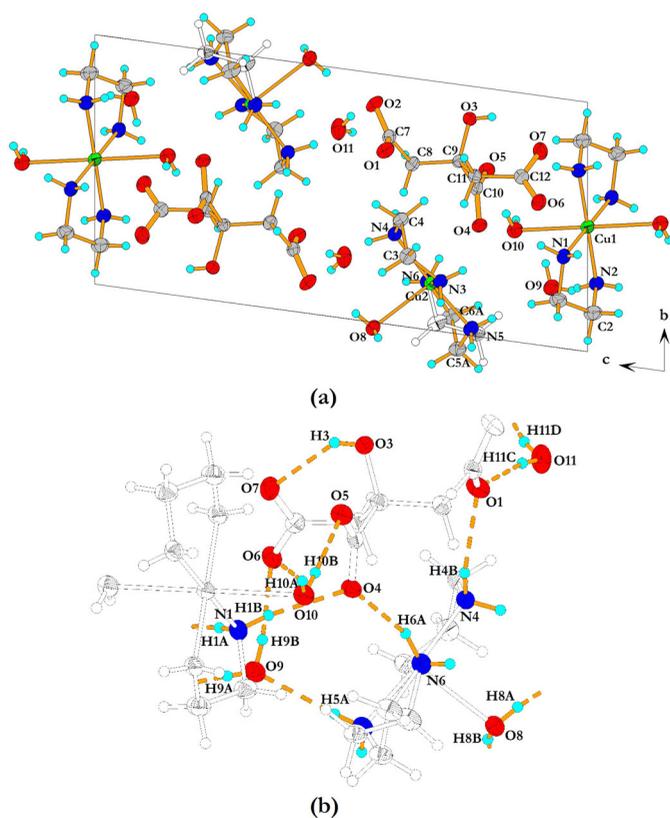
## 3. Results and discussion

### 3.1. Crystal structure

The crystal structure of  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  (Figure 1) could be described as a packing (Figure 2a and 2b) of three types of molecular ions, monoaqua-bis(ethylenediamine)copper(II)  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation, diaqua-bis(ethylenediamine)copper(II)  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation and citrate anion, interconnected via a system of hydrogen bonds including four water molecules per unit cell trapped (hydrogen bonded) in the crystal voids. Interestingly, the monoaqua-bis(ethylenediamine)  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation and the diaqua-bis(ethylenediamine)  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation are both together in the same compound (in a 1 to 2 molar ratio), which is rather rare (only 4 structures in CCDC base [1]).



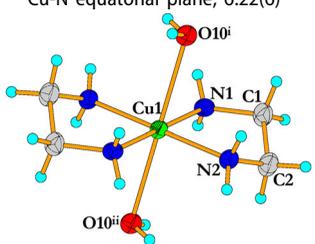
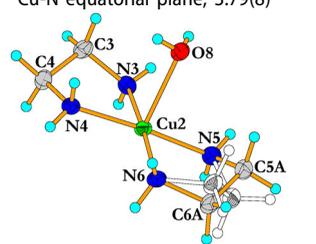
**Figure 1.** The dark violet irregular crystals of  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$ .



**Figure 2.** The dark violet irregular crystals of  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$ . (a) The unit cell projection view along the *a*-crystallographic axis. Thermal ellipsoids are drawn at 50% probability; (b) selected hydrogen contacts (dashed lines) in the structure of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  complex with the shortest  $\text{O} \cdots \text{H}$  distance 1.96(4) Å ( $\text{O6} \cdots \text{H10A}^i \cdots \text{O10}^i$ , Table 5). Symmetry operation:  $i(x - 1, y, z)$ .

**Table 2.** The geometry of two copper(II) coordination centers (pyramidal and octahedral).

Octahedral $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$		Pyramidal $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$	
Cu1-N1, 2.022(2) Å	Mean Cu-N, 2.020(2)	Cu2-N3, 2.002(2) Å	Mean Cu-N, 2.014(2)
Cu1-N2, 2.017(2) Å		Cu2-N4, 2.029(2) Å	
C1-C2, 1.503(5) Å		Cu2-N5, 2.008(3) Å	
Cu1-O10 <sup>i</sup> , 2.545(2) Å		Cu2-N6, 2.016(2) Å	
C1-N1, 1.486(4) Å		Cu2-O8, 2.420(2) Å	
C2-N2, 1.473(4) Å		C5A-C6A, 1.509(6) Å	
O10 <sup>i</sup> -Cu1-O10 <sup>ii</sup>		C3-C4, 1.509(4) Å	
O10 <sup>i</sup> -Cu1-O10 <sup>ii</sup> axis inclination to the normal of the Cu-N equatorial plane, 6.22(6)°		Cu2-O8 axis inclination to the normal of the Cu-N equatorial plane, 3.79(8)°	

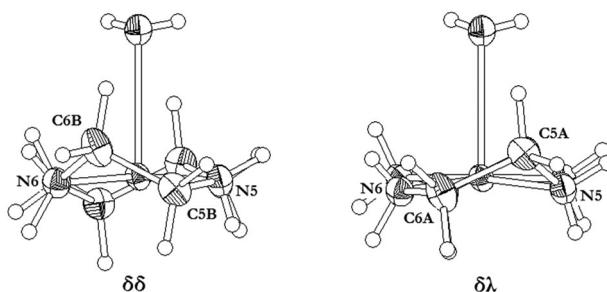



Symmetry operations: i ( $x - 1, y, z$ ), ii ( $1 - x, 1 - y, -z$ ).

**Table 3.** The Cu-N distances in some selected copper(II) complexes containing  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation.

Formula of the complex	Mean Cu-N distance, Å	Literature source
$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_{1.935}]_2[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$	2.016(2)	[25]
$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](4\text{-phenylbenzoate})_2 \cdot 2.66\text{H}_2\text{O}$	2.017	[26]
$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](4\text{-nitrobenzoate})_2$	2.021(2)	[27]
$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}(\text{OSO}_3)_2(\text{en})_2] \cdot 6\text{H}_2\text{O}$	2.015(2)	[4]
$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](\text{OOCCH}_2\text{NHCOO}) \cdot \text{H}_2\text{O}$	2.016(3)	[18]
$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](\text{OOCNH}_2\text{CH}_2\text{NHCOO}) \cdot 2\text{H}_2\text{O}$	2.009(2)	[18]

The coordination polyhedron of the Cu1 ion in the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation is a distorted octahedron ( $\delta\lambda$  diastereoisomeric chelate system with two ethylenediamine molecules in a *gauche* conformation) with two apical water molecules and four nitrogen atoms lying in the equatorial plane (the sum of all N-Cu-N angles in the equatorial plane is  $360.0(1)^\circ$ ). The diaqua cations are expectedly JT distorted (Table 2), although it is quite hard to distinguish between a pure JT distortion (the Tutton salt or  $(\text{NH}_4)_2[\text{Cu}^{\text{II}}(\text{H}_2\text{O})_6](\text{SO}_4)_2$  [24]) effect and some steric effects in the heterogeneous coordination environment. In turn, the metal ion in  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  the monoqua cation possesses a square-pyramidal coordination with a water molecule at the apical position. The most important geometric parameters of both cations are presented in Table 2. One may easily note that the mean value of the Cu-N distances in the diaqua cation (2.020(2) Å, Table 2) is quite common for that type of copper(II) coordination (Table 3). The five-coordinate Cu2 ion found in the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation is maybe less common and could be found in such complexes as  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{diphenylacetate})_2 \cdot 3\text{H}_2\text{O}$  [28] and  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](2,6\text{-dimethylphenolate})_2$  [29]. Similar to that, in the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation, the Cu-O<sub>w</sub> bond in the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation is inclined from the ideal axial position, though the inclination rate is almost twice less (Table 2) than that in the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation. It also worth pointing out that the Cu-O<sub>w</sub> distance in the monoqua cation is shorter than those of the diaqua



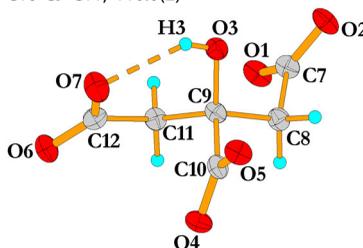
**Figure 3.** Two conformers of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation in the structure of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]_2[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  complex; in the  $\delta\delta$  conformer C6B–C5B angle with respect to the N–Cu–N plane is  $61.5(7)^\circ$  and that of the  $\delta\lambda$  conformer (C6A–C5A) is  $-65.5(3)^\circ$ .

cation (Table 2). This could be supported by some other crystal structure data of the similar  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  containing complexes e.g. the  $\text{Cu}-\text{O}_w$  distance in the monoaqua cation of the  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_2(\text{SeCN})_2]$  complex is equal to  $2.48(1) \text{ \AA}$  [30], which is 2.5% longer than that of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]_2[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  complex. In the similar complex  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})][\text{Cu}_2(\text{CN})_4]$ , the  $\text{Cu}-\text{O}_w$  distance of  $2.441(4) \text{ \AA}$  [31] is only 0.9% longer than that in the complex discussed. The  $\text{Cu}-\text{O}_w$  distance in the monoaqua cation of the  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](2,6\text{-dimethylphenolate})_2$  complex is even shorter,  $2.231(4) \text{ \AA}$  [29] (7.8% shorter than in the present complex). Thus, within the same type of pyramidal  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation the distances  $\text{Cu}-\text{O}_w$  (apical) vary noticeably in different related crystal structures, which is mainly dictated with the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation surrounding (possible hydrogen bonding) as well as crystal packing effects. Thus, the copper(II) coordination in the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation could be better described as  $[4+1]$ . It should be also noted that the 4-coordinate square planar  $[\text{Cu}^{\text{II}}(\text{en})_2]^{2+}$  chromophore itself is a rare particle [32]. At last, the geometry of the  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation could be described with the Addison geometry index  $\tau_5$ , which is equal to 0.023 and in this way indicates nearly perfect square pyramidal surrounding of the copper(II) ion ( $\tau_5 = 0$ —perfectly square pyramidal and  $\tau_5 = 1$ —ideally trigonal bipyramidal geometry [33]).

There is also an interesting feature of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation i.e. the C–C bond in one of the copper(II) coordinated ethylenediamine molecule is disordered and, in fact, the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation is co-existing as two conformers ( $\delta\delta$  enantiomer and diastereoisomeric  $\delta\lambda$  chelate systems, Figure 3). The same type of disorder can be found within other ethylenediamine coordinated copper(II) fragments or cations ( $[\text{Cu}^{\text{II}}(\text{en})\text{Cl}_2]_n$  ribbon [34],  $[\text{Cu}^{\text{II}}(\text{en})_2]^{2+}$  cation [35], etc.), while, as far as we know, it has not been found in similar monoaqua  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cations and there was only one example of the monoaqua cation with a, although C–N, disordering [36] in the ethylenediamine molecule. The inversion between  $\delta\delta$  and  $\delta\lambda$  configurations is proposed to have a low energy barrier ( $\delta\delta$  should be  $\sim 4 \text{ kJ/mol}$  more stable than  $\delta\lambda$  [37]) and very close to the energy of the thermal lattice motion ( $150 \text{ K}$ —temperature of the XRD experiment, each atom  $3kT_{\text{N}_A} = 3 \cdot 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1} \cdot 150 \text{ K} \cdot 6.02 \cdot 10^{23} \text{ mol}^{-1} = 3.74 \text{ kJ/mol}$ ). Thus, both  $\delta\delta$  and  $\delta\lambda$  conformers are energetically very similar, while, as it was shown in a number of structural investigations, the  $\delta\lambda$  configuration of the  $[\text{Cu}(\text{en})_2]^{2+}$  cation could be found more often than the  $\delta\delta$  configuration [37]. At last, the absence

**Table 4.** The most important geometry parameters of the *cis,trans*-configured citric anion.

Selected bonds, Å	Selected angles, °
C7-C8, 1.532(5)	O1-C7-O2, 125.0(3)
C8-C9, 1.533(4)	O4-C10-O5, 126.5(2)
C9-C10, 1.558(4)	O6-C12-O7, 123.7(3)
C9-C11, 1.527(3)	C9-O3-H3, 107(3)
C11-C12, 1.526(4)	C8-C9-C10, 105.1(2)
C7-O1, 1.251(4)	C8-C9-C11, 114.6(2)
C7-O2, 1.255(3)	C10-C9-C11, 110.0(2)
C10-O5, 1.252(3)	
C10-O4, 1.252(3)	
C12-O6, 1.255(3)	
C12-O7, 1.264(3)	
C9-O3, 1.439(3)	
<sup>a</sup> O3-H3...O7, 2.06(3)	



<sup>a</sup>Intramolecular hydrogen bonding.

of effective intermolecular hydrogen bonding between the CH<sub>2</sub> groups of the disordered ethylenediamine molecule is the other important cause of the discussed disordering i.e. H5BA...O9 is the only hydrogen contact between the CH<sub>2</sub> hydrogen atom and the closest neighbor oxygen atom (H<sub>2</sub>O molecule) – 2.418(3) Å. Simply speaking, C-C bond of the coordinated ethylenediamine molecule is not spatially fixed enough with the intermolecular hydrogen bonding.

The citric acid anion Hcit<sup>3-</sup> in the discussed crystal structure adopts the lowest possible symmetry (C<sub>1</sub> point group) and possesses an intramolecular O-H...O hydrogen bonding between the hydrogen atom of the OH group and one of the carboxyl groups (Table 3) [16, 17]. Similar intramolecular hydrogen bonding can also be found in the citric anion of the trisodium citrate crystal structure [17], where the H...O distance indicates significantly stronger interaction (1.805 Å). It is also *cis,trans*-configured about C8-C9 and C9-C11 bonds (Table 4), whereas that of the C8-C9 bond could more precisely be described as a *gauche* conformation with 62.3(3)° of the *synclinal* type torsion C7-C8-C9-C11 angle (citrate anion in trisodium citrate adopts *trans,trans*-configuration [17]). In turn, the conformation of the carbon chain regarding the C9-C11 bond is very close (C8-C9-C11-C12, 174.3(2)°) to a perfectly *antiperiplanar* torsion angle. In the present crystal structure, the citric anions also form a complicated network of intermolecular hydrogen bonds (Figure 2b, Table 5).

### 3.2. Raman and FTIR spectroscopy

Different FTIR and Raman spectral data for the copper(II) ethylenediamine complexes [2, 18, 38] and very detailed Raman spectral data for ethylenediamine itself [39] are quite diverse. However, more specific and accurate FTIR and/or Raman spectral data for the [Cu<sup>II</sup>(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> and [Cu<sup>II</sup>(en)<sub>2</sub>(H<sub>2</sub>O)]<sup>2+</sup> cations as well as the proper assignment in the low-wavenumber region (100–700 cm<sup>-1</sup>) are rather rare. The combination of the Raman spectrum with the FTIR spectrum of the same complex could be

**Table 5.** The intermolecular hydrogen contacts in the structure of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  complex.

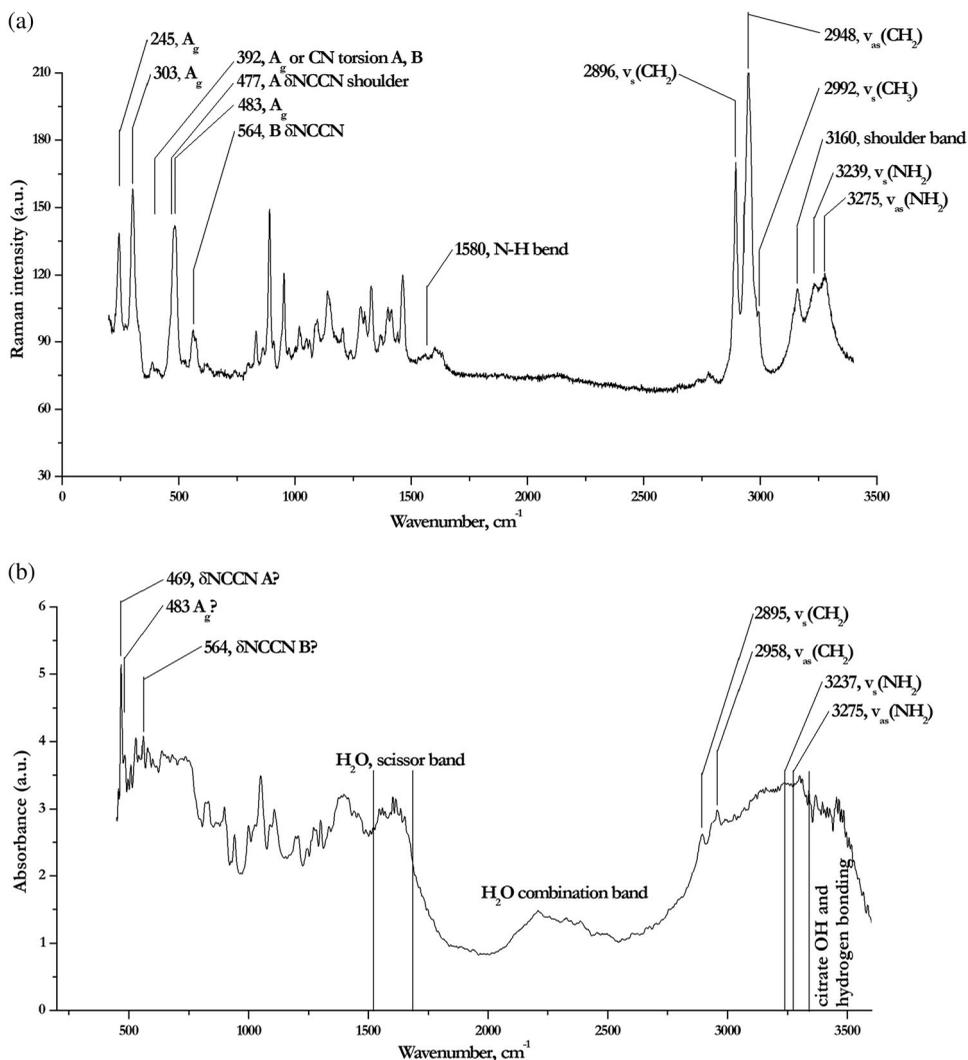
Selected bonds, D—H...A	D—H, Å	H...A, Å	D...A, Å	D—H...A, °
O8—H8A...O2 <sup>iii</sup>	0.73(4)	2.02(4)	2.740(3)	165(4)
O8—H8B...O2 <sup>iv</sup>	0.71(5)	2.08(5)	2.758(3)	158(5)
O3—H3...O7	0.75(3)	2.06(3)	2.674(3)	140(3)
O9—H9A...O7 <sup>ii</sup>	0.68(5)	2.10(5)	2.785(3)	177(5)
O9—H9B...O6	0.80(4)	2.03(4)	2.820(3)	169(4)
O10—H10A...O6	0.80(4)	1.96(4)	2.725(3)	160(4)
O10—H10B...O5 <sup>v</sup>	0.75(4)	1.98(4)	2.734(3)	177(4)
O11—H11C...O1	0.80(4)	1.99(4)	2.788(3)	170(4)
O11—H11D...O8 <sup>vi</sup>	0.78(4)	2.10(4)	2.864(3)	168(4)
N1—H1A...O6 <sup>ii</sup>	0.77(3)	2.24(3)	2.959(3)	158(3)
N5—H5A...O9	0.76(3)	2.23(3)	2.981(4)	167(3)
N6—H6A...O4	0.91(4)	2.11(4)	2.972(3)	157(3)
N4—H4B...O1	0.81(4)	2.18(4)	2.947(3)	157(3)
N1—H1B...O4	0.84(4)	2.14(4)	2.977(3)	171(3)

Symmetry operations: ii (1 - x, 1 - y, -z), iii (1 - x, 1 - y, 1 - z), iv (x + 1, y - 1, z), v (x + 1, y, z), vi (x, y + 1, z).

sometimes very useful especially in the case of the centrosymmetric structures ( $P\bar{1} \equiv C_i^1$  factor group, Table 1).

In general, the recorded spectra (Figure 4a and 4b) are both in line with the crystal structure data presented in the previous section. The whole spectrum, either Raman or FTIR, could be formally divided into three regions, which are mainly due to the fully symmetric  $A_g$  modes (below  $700\text{ cm}^{-1}$ ) of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cations as well as  $\delta\text{NCCN}$ , CC and CN torsion modes, deformation in-plane and out-of-plane vibrations of  $\text{CH}_2$  and  $\text{NH}_2$  together with other citrate anion and ethylenediamine characteristic modes (between  $700$  and  $1700\text{ cm}^{-1}$ ) and, finally, symmetric and asymmetric  $\text{CH}_2$  and  $\text{NH}_2$  stretching vibrations, NH overtone as a shoulder band at  $3160\text{ cm}^{-1}$  (Raman spectrum, Figure 4a) as well as symmetric  $\text{CH}_3$  stretch vibration at  $2992\text{ cm}^{-1}$  (Raman spectrum, Figure 4a), which is a result of some impurities in the crystalline sample (above  $2800\text{ cm}^{-1}$ ). The region between  $1700$  and  $2800\text{ cm}^{-1}$  contains no bands, except for a very weak band at  $2100\text{--}2200\text{ cm}^{-1}$  (Raman and FTIR, Figure 4a and 4b) being a combination  $\text{H}_2\text{O}$  band.

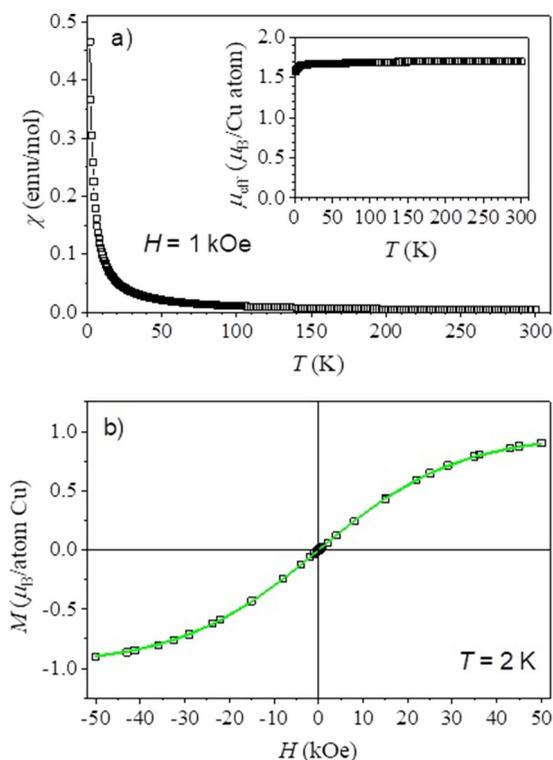
The theoretic group analysis results in the following irreducible representations for the "isolated" copper(II) containing cations:  $\Gamma_{\text{vib}}(C_2 \delta\delta) = 4A + 2B$  or  $\Gamma_{\text{vib}}(C_s \delta\lambda) = 4A' + 2A''$  for  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ ,  $\Gamma_{\text{vib}}(C_{2h}) = 4A_g + A_u + 2B_u$  for  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ . However, the site symmetry of the centrosymmetric  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation is  $C_i$  and that of the pyramidal  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation is  $C_1$ , which correlation with the  $C_i^1$  factor group gives rise to two types of non-degenerated modes only i.e.  $A_g$  and  $A_u$ . In the Raman scattering experiment, only fully symmetric  $A_g$  modes would be active, while in the FTIR spectrum only  $A_u$  modes are active (Mutual Exclusion Rule). Thus, within the low-wavenumber region of the recorded Raman spectrum the intense bands at  $245$ ,  $303$ ,  $392$  and  $483\text{ cm}^{-1}$  could be associated with  $A_g$  normal modes of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  centrosymmetric and pyramidal  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation. The intense band at  $483\text{ cm}^{-1}$  could not be found in the recorded FTIR spectrum (Figure 4b) and therefore it could be associated with a so-called "breathing" vibration of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  centrosymmetric cation. In turn, the Raman spectrum of a known  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{OSO}_3)_2(\text{en})_2] \cdot 6\text{H}_2\text{O}$  complex [4] contains this "breathing"



**Figure 4.** (a) The Raman spectrum of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  complex recorded in the  $200\text{--}3400\text{ cm}^{-1}$  spectral range. (b) The FTIR spectrum of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  complex recorded in the  $450\text{--}4000\text{ cm}^{-1}$  spectral range.

band of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  cation at  $480\text{ cm}^{-1}$  and it is practically not shifted as for that of the citrate complex. There are also deformation  $\delta\text{NCCN}$  modes and torsion CC and CN modes in the recorded Raman spectrum as well as deformation modes in the FTIR spectrum (Figure 4a and 4b). These deformation and torsion bands could correspond either to the copper(II) coordinated **en** or/and liquid **en**, which water solution was possibly presented on the surface of the crystalline sample used in the Raman and FTIR measurements.

All bands corresponding to the citrate anion characteristic modes as well as  $\text{CH}_2$  and  $\text{NH}_2$  deformation modes could be found within a so-called “fingerprint region” ( $400\text{ to }1500\text{ cm}^{-1}$ ) in both Raman and FTIR spectrum. There is also a characteristic



**Figure 5.** (a) Temperature dependent susceptibility of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2](\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  crystals and effective magnetic moment per copper ion (inset); (b) Isothermal magnetization at 2 K. The solid line is a Brillouin function for a magnetic moment with a spin  $S = 1/2$ .

group of bands at  $1500\text{--}1700 \text{ cm}^{-1}$  in the FTIR spectrum (Figure 4b), which could be associated with the scissor vibration modes of  $\text{H}_2\text{O}$  presented on the surface of the crystalline sample. The scissor bands are also overlapped with the NH bend band of the  $\text{NH}_2$  group.

The  $\nu(\text{NH}_2)$  symmetric and asymmetric stretching modes would be also interesting to discuss. The corresponding bands could be found in the recorded Raman spectrum above  $3100 \text{ cm}^{-1}$  as closely packed into a wide line with three distinctive peaks at  $3160$ ,  $3239$  and  $3275 \text{ cm}^{-1}$  with a characteristic distribution of the intensities. The band at  $3160 \text{ cm}^{-1}$  is a “shoulder” band being an overtone of the NH bend vibration found in the Raman at  $1580 \text{ cm}^{-1}$ . Those of the  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{OSO}_3)_2(\text{en})_2] \cdot 6\text{H}_2\text{O}$  complex are only slightly shifted [4] e.g. the “shoulder” band at  $3159 \text{ cm}^{-1}$  and the  $\nu_s(\text{NH}_2)$  band at  $3244 \text{ cm}^{-1}$ . It is interesting that the Raman spectrum of the solid **en** [39] possesses the  $\nu_s(\text{NH}_2)$   $A_g$  band at  $3170 \text{ cm}^{-1}$ , which directly depends on whether the  $\text{NH}_2$  group is copper(II) coordinated or not and could be a benchmark for the energy of the Cu-N coordination bonding. In turn, the symmetric and asymmetric  $\text{CH}_2$  stretching modes could easily be found either in the Raman spectrum at  $2896$  and  $2948 \text{ cm}^{-1}$  or in the FTIR spectrum at  $2895$  and  $2958 \text{ cm}^{-1}$ . Finally, in the FTIR spectrum all bands corresponding to  $\text{CH}_2$ ,  $\text{CH}_3$  and  $\text{NH}_2$  stretch vibrations as well as OH and hydrogen bond vibration modes are merged into a wide peak at  $2750\text{--}3500 \text{ cm}^{-1}$  (Figure 4b).

### 3.3. Magnetic susceptibility measurements

Temperature dependent magnetic susceptibility of  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  is shown in Figure 5(a). It monotonically increases with decreasing temperature. An effective magnetic moment per Cu ion, calculated as  $\mu_{\text{eff}} = T/3$  [40], where factor 3 is for 3 Cu ions per molecular unit, is practically constant in the whole measured temperature range. It acquires a value of 1.70  $\mu\text{B}$ , close to the theoretical value of 1.73  $\mu\text{B}$  of divalent copper ion with spin  $S = 1/2$  and no orbital contribution ( $L = 0$ ) [41]. A slightly smaller value than the theoretical one is possibly due to the small amount of diamagnetic water absorbed by the sample. The isothermal magnetization measured at 2 K (Figure 5b) follows the Brillouin function for spin  $S = 1/2$  conforming to a paramagnetic behavior of Cu(II) magnetic moments. Due to the large distances between Cu(II) ions (Cu1-Cu2, 6.1105(5) Å) there is no significant magnetic interaction between them.

## 4. Conclusion

The prepared  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]_2(\text{Hcit})_2 \cdot 4\text{H}_2\text{O}$  tetrahydrate is a first example of the copper(II) ethylenediamine complex containing archetypical  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_1 \text{ or } 2]^{2+}$  cations together with a citrate anion. It is even more interesting due to the presence of both diaqua  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  and monoqua  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cations together (in 1 to 2 molar ratio) in the same crystal structure, which was found to be a quite rare example (there were only several examples of such complexes in the CCDC data base). In turn, the monoqua cation possesses a disordered C-C bond of the ethylenediamine group and a slightly shorter (in comparison to that of the diaqua cation) Cu-O<sub>w</sub> bond distance (nearly 5% shorter). Since, the C-C bond is disordered, there are in fact two types of monoqua cations in the structure i.e.  $\delta\delta$  and  $\delta\lambda$  conformers. On the other hand, the citrate anion is practically isolated being hydrogen bonded only, which is also quite rare. In other words, the discussed structure is in fact a packing of three types of ions as well as hydrogen bonded (trapped in the crystal voids) water molecules.

The Raman and FTIR spectra of the discussed complex are a combination of three representative regions i.e. below 700  $\text{cm}^{-1}$ , between 700 and 1700  $\text{cm}^{-1}$  and above 2800  $\text{cm}^{-1}$ . A so-called "fingerprint" region (400–1500  $\text{cm}^{-1}$ ) was found to be the most informative towards citrate anion and coordinated ethylenediamine molecules. The region below 700  $\text{cm}^{-1}$  contains a group of some sharp bands corresponding to A<sub>g</sub> modes of the copper(II) containing cations as well as NCCN deformations, torsion CC and CN modes being in that way comparable to the previously reported  $[\text{Cu}^{\text{II}}(\text{en})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{II}}(\text{OSO}_3)_2(\text{en})_2] \cdot 6\text{H}_2\text{O}$  complex.

Finally, the prepared complex is paramagnetic in the wide range of temperatures, which is affected with a low exchange interaction of distant coordinated copper(II) centers (the closest Cu-Cu contact is Cu1-Cu2, 6.1105(5) Å). This allows no long-range spin ordering even at very low temperatures.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

## References

- [1] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.*, **72**, 171 (2016).
- [2] V. Manríquez, M. Campos-Vallette, N. Lara, N. González-Tejeda, O. Wittke, G. Díaz, S. Diez, R. Muñoz, L. Kriskovic. *J. Chem. Crystallogr.*, **26**, 15 (1996).
- [3] M. Kajňaková, A. Orendáčová, M. Orendáč, A. Feher, M. Malárová, Z. Trávníček. *Acta Phys. Pol. A*, **113**, 507 (2008).
- [4] A. Vakulka, E. Goreschnik, M. Jagodič, Z. Jagličić, Z. Trontelj. *Z. Trontelj. J. Mol. Struct.*, **1210**, 128002 (2020).
- [5] L. An, X. Liu, J. Zhou, F. Hu, L. Zhu. *Z. Naturforsch.*, **67b**, 860 (2012).
- [6] L. Ouyang, P.M. Aguiar, R.J. Batchelor, S. Kroeker, D.B. Leznoff. *Chem. Commun.*, **7**, 744 (2006).
- [7] B.F. Terrence, J.L. McCourt, W.A.E. McBryde. *Can. J. Chem.*, **52**, 3119 (1974).
- [8] R.W. Parry, F.W. DuBois. *J. Am. Chem. Soc.*, **74**, 3749 (1952).
- [9] D. Mastropaolo, D.A. Powers, J.A. Potenza, H.J. Schugar. *Inorg. Chem.*, **15**, 1444 (1976).
- [10] G. Zhang, G. Yang, J.S. Ma. *Cryst. Growth Des.*, **6**, 375 (2006).
- [11] A. Palčić, I. Halasz, J. Bronić. *Powder Diffr.*, **29**, 28 (2014).
- [12] D.M. Boghaei, M.M. Najafpour. *Anal. Sci.*, **23**, 123 (2007).
- [13] S. Sarkar, D. Deb, A. Sarkar, S. Chattopadhyay, B. Dutta, S. Khanra. *Indian J. Chem.*, **57A**, 469 (2018).
- [14] R.C. Bott, D.S. Sagatys, D.E. Lynch, G. Smith, C.H.L. Kennard, T.C.W. Mak. *Aust. J. Chem.*, **44**, 1495 (1991).
- [15] E. Çiftçi, M. Kaya, M. Arıcı, O.Z. Yeşilel. *J. Mol. Struct.*, **1220**, 128695 (2020).
- [16] A. Rammohan, J.A. Kaduk. *Acta Crystallogr. E Crystallogr. Commun.*, **72**, 1159 (2016).
- [17] A. Rammohan, J.A. Kaduk. *Acta Cryst.*, **E72**, 793 (2016).
- [18] L.A. Kovbasyuk, I.O. Fritsky, V.N. Kokozay, T.S. Iskenderov. *Polyhedron*, **16**, 1723 (1997).
- [19] R. Pribil. *Applied Complexometry*, Pergamon Press, Oxford (1982).
- [20] CrysAlisPro, Agilent Technologies, Version 1.171.37.31 (release 14-01-2014 CrysAlis171.NET) (2014).
- [21] G.M. Sheldrick. *Acta Crystallogr. A Found. Adv.*, **71**, 3 (2015).
- [22] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Crystallogr.*, **42**, 339 (2009).
- [23] Crystal Impact GbR, Bonn, Germany 2004–2005 DIAMOND v3.1.
- [24] B.N. Figgis, A.N. Sobolev, C.J. Simmons, M.A. Hitchman, H. Stratemeier, M.J. Riley. *Acta Crystallogr. B Struct. Sci.*, **56**, 438 (2000).
- [25] J. Kuchár, J. Černák, W. Massa. *Acta Crystallogr. C*, **60**, m418 (2004).
- [26] J.A. Fernandes, A.I. Ramos, P. Silva, S.S. Braga, P. Ribeiro-Claro, J. Rocha, F.A. Almeida Paz. *Acta Crystallogr. Sect. E Struct. Rep. Online*, **66**, m626 (2010).
- [27] W.T.A. Harrison, A.M.Z. Slawin, R.P. Sharma, B. Sharma, S. Bhamu. *Acta Crystallogr. E Struct. Rep. Online*, **63**, m178 (2007).
- [28] R.P. Sharma, A. Saini, S. Kumar, J. Kumar, P. Venugopalan, V.S. Gondil, S. Chhibber, T. Aree. *Polyhedron*, **123**, 430 (2017).
- [29] P.J. Baesjou, W.L. Driessen, J. Reedijk, A.L. Spek. *Inorg. Chim. Acta*, **306**, 237 (2000).
- [30] V. Vrabel, J. Garaj, L. Kutschabsky. *Acta Crystallogr. B Struct. Crystallogr. Cryst. Chem.*, **35**, 357 (1979).
- [31] R.J. Williams, A.C. Larson, D.T. Cromer. *Acta Crystallogr. B Struct. Crystallogr. Cryst. Chem.*, **28**, 858 (1972).
- [32] H.-K. Fun, Q. Hao, J. Wu, X. Yang, L. Lu, X. Wang, S. Chantrapromma, I.A. Razak, A. Usman. *Acta Crystallogr. C*, **58**, m87 (2002).

- [33] A.W. Addison, N.T. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
- [34] M. Zabel, V.I. Pawlowski, A.L. Poznyak. *J. Struct. Chem.*, **47**, 585 (2006).
- [35] B.-S. Kang, Y.-X. Tong, K.-B. Yu, C.-Y. Su, H.-X. Zhang. *Acta Crystallogr. C Cryst. Struct. Commun.*, **56**, 40 (2000).
- [36] S.-Y. Ke, C.-T. Yeh, C.-C. Wang, G.-H. Lee, H.-S. Sheu. *Z. Anorg. Allg. Chem.*, **643**, 657 (2017).
- [37] G. Wilkinson, R.D. Gillard, J.A. McCleverty. *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties & Applications of Coordination Compounds*, Vol. 2, 1st edn, p. 31, Pergamon Press, Oxford, England, New York (1987).
- [38] J. Sharma, Z. Jiang, A. Bhutani, P. Behera, D.P. Shoemaker. *Cryst. Eng. Commun.*, **21**, 2718 (2019).
- [39] M.G. Giorgini, M.R. Pelletti, G. Paliani, R.S. Cataliotti. *J. Raman Spectrosc.*, **14**, 16 (1983).
- [40] F.E. Mabbs, D.J. Machin. *Magnetism and Transition Metal Complexes*, Chapman and Hall, London (1973).
- [41] N.W. Ashcroft, N.D. Mermin. *Solid State Physics*, Saunders College Publishing, USA (1976).