

Synthesis, Spectral and Thermal Properties, and Crystal Structure of Bis(ethylenediamine)(aqua)copper(II) (Bis)syringate Ethylenediamine Dihydrate $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$

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The complex $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$ has been synthesized and characterized by its electronic and vibrational spectra. The molecular structure of the complex has been determined by X-ray diffraction methods. The complex crystallizes in the orthorhombic space group *Pnma* with unit-cell parameters $a = 10.7236(5)$, $b = 20.4660(10)$, $c = 14.4523(11)$ Å and $Z = 4$. In the cation, the Cu(II) ion has a distorted square pyramidal coordination with two bidentate (en) ligands forming the basal plane and a H_2O molecule in the apical position. The complex cations and syringate anions constitute chains along the *b* axis in –A–B–A– fashion. The members of the chains are linked by through N–H···O hydrogen bonds. The (en) molecules are responsible for connecting adjacent layers.

Key words: Syringic Acid, Ethylenediamine, Copper (II) Complex, Thermal Properties

Introduction

Major types of natural antioxidants are the phenolic acids which are derivatives of benzoic and cinamic acids [1]. There is a definite relationship between the structures of the phenolic acids and their antioxidant activities. The inhibitory effectiveness of monophenols is substantially increased by one or two methoxy groups. Syringic acid, 4-hydroxy-3,5-dimethoxybenzoic acid [syH], is one of the most active antioxidants with two methoxy groups [2, 3]. Furthermore, syringic acid has been identified as an active ingredient which contributes to the prevention of cancer, inhibiting tumour initiation, promotion and progression and heart disease [3, 4]. The salts of 4-hydroxy-3,5-dimethoxybenzoic acid with various cations and mixed ligand complexes of *d*-block elements have not been studied. Ethylenediamine is an N-donor chelator and has been studied intensively, both structurally and spectroscopically for many years [5, 6]. Therefore, we selected syringic acid as primary ligand and prepared Cu(II) ethylenediamine complexes and examined their thermal stability in air, IR spectral characteristics and crystal

structure. In this study, we report the preparation and structural characterization of the new square pyramidal Cu(II) complex $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$.

Results and Discussion

Spectral and magnetic properties

The coordination sphere of the complex can be treated in terms of C_{2v} molecular symmetry. In the IR spectrum, the region of the NH_2 stretching vibrations is relatively broadened by partial superposition with the O–H vibrations of the coordinated and uncoordinated water molecules. The bands at 3370 and 3050 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the NH_2 groups of the coordinated and uncoordinated en ligands. The vibrational frequencies of the CH_2 groups of the en ligands appear at 800 cm^{-1} . This is in agreement with literature data [7, 8]. The Cu–N stretching frequency was observed at 750 cm^{-1} . In the IR spectrum of free syringic acid there is a strong absorption band at 1700 cm^{-1} for the COOH group, which is absent for the complex, and the bands due to the asymmetric and symmetric stretching of carboxylate groups occur at 1575 and 1373 cm^{-1} , respectively [9]. The bands of the C–H asymmetric stretching

Syringic acid = 4-hydroxy-3,5-dimethoxybenzoic acid.

Table 1. Crystal data and structure refinement parameters for $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$.

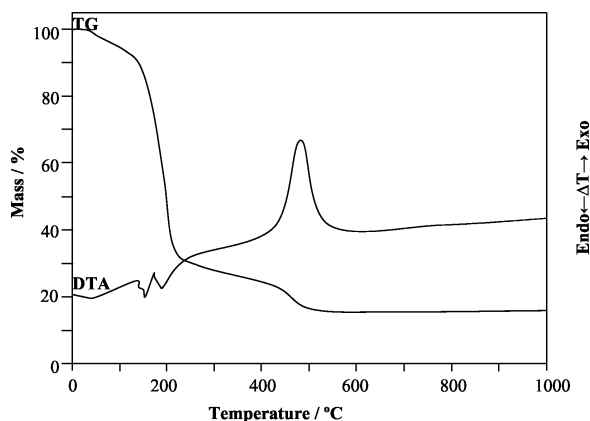
Empirical formula	$\text{C}_{24}\text{H}_{48}\text{CuN}_6\text{O}_{13}$
Formula weight	692.22
Temperature [K]	296
Wavelength [Å]	0.71073 Mo-K α
Crystal system	orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions [Å]	
<i>a</i> ,	10.7236 (5),
<i>b</i> ,	20.466 (1),
<i>c</i>	14.452 (1)
<i>V</i> [Å ³]	3171.8 (3)
<i>Z</i>	4
Absorption coefficient [mm ⁻¹]	0.760
<i>D</i> _{calcd.} [Mg m ⁻³]	1.450
Crystal size [mm ³]	0.310 × 0.180 × 0.060
Theta range for data collection [deg]	1.41–27.14
Measured reflections	38715
Independent reflections	3575
Absorption correction	Integration
Refinement method	Full-matrix least-squares on <i>F</i> ²
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.043, <i>wR</i> ₂ = 0.078
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.112, <i>wR</i> ₂ = 0.092
Goodness-of-fit on <i>F</i> ²	0.810
Largest difference peak and hole (e Å ⁻³)	0.420; –0.573

Table 2. Selected bond lengths (Å) and bond angles (°) for $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$.

Bond lengths (Å)			
Cu1–N1	2.014 (3)	Cu1–O1	2.285 (3)
Cu1–N2	2.012 (3)	O6–C11	1.255 (4)
O5–C11	1.266 (4)		
Bond angles (°)			
N2–Cu1–O1	92.00 (11)	N1–Cu1–O1	95.35 (12)
N2–Cu1–N1	84.10 (12)	N2'–Cu1–N1	171.55 (15)

Symmetry Code ⁱ *x*, 1/2 – *y*, *z*.Table 3. Hydrogen bonds (Å, °) for $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$.

D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
N1–H1⋯O6 ⁱ	0.93 (3)	2.06 (4)	2.960 (4)	165 (3)
N2–H8⋯O2 ⁱⁱ	0.89 (3)	2.11 (4)	2.996 (4)	174 (3)
O7–H23⋯O6 ⁱⁱⁱ	0.83 (3)	1.84 (3)	2.663 (3)	167 (3)
N4–H10⋯O2 ^{iv}	0.914 (17)	1.860 (19)	2.740 (3)	161 (3)
N4–H10⋯O4 ^{iv}	0.914 (17)	2.40 (3)	3.007 (2)	124 (3)
N3–H11⋯O2 ^v	0.865 (17)	1.90 (2)	2.730 (4)	160 (3)
O1–H9⋯O5	0.92 (4)	1.85 (4)	2.762 (3)	175 (4)
O8–H24⋯O5	0.98 (5)	2.02 (5)	2.853 (3)	141 (5)
O2–H22⋯O3	0.820	2.207	2.659 (3)	114.89
O2–H22⋯N3 ^v	0.820	1.973	2.730 (4)	153.30

Symmetry codes: ⁱ *x*, 1/2 – *y*, *z*; ⁱⁱ 3/2 – *x*, *y* – 1/2, 1/2 + *z*; ⁱⁱⁱ *x* – 1/2, *y*, 1/2 – *z*; ^{iv} 3/2 – *x*, 1 – *y*, *z* – 1/2; ^v 1 – *x*, 1 – *y*, 1 – *z*.Fig. 1. TG and DTA curves of the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$ complex.

of the CH_3 groups appear at similar frequencies as in free syringic acid (2850 cm^{-1}).

The electronic *d-d* transition spectrum of $\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$ is compatible with the distorted square pyramidal configuration. The maximum absorption is at 567 with $\epsilon = 61.0\text{ Lmol}^{-1}\text{cm}^{-1}$. This band is assigned to the $a_1 \rightarrow b_1$ *d-d* transition [10–14]. The band observed around 299 nm ($\epsilon = 1362\text{ Lmol}^{-1}\text{cm}^{-1}$) is attributed to MLCT. The mag-

netic moment value of the complex is 1.22 BM corresponding to one unpaired electron.

Thermal properties

The crystals contain water of crystallization and copper-coordinated water. The thermal dehydration occurred in two steps with endothermic effects at 40 °C and 132 °C (Fig. 1). One mole of coordinated water and two moles of crystallization water are removed at these stages (exp. 8.89%; calcd. 7.81%). A color change from black to brown was noted on removal of the water molecules. Further heating causes evaporation of one of the ethylenediamine molecules, resulting in an endothermic DTA peak at 154 °C (exp. 12.89%; calcd. 12.18%). The product is very unstable and undergoes further decomposition by release of the remaining ethylenediamine and decomposition of the syringiato ligands. The exothermic peak at 481 °C can be explained by the burning of the organic residue formed in the previous stages. The final solid product of thermal decomposition was identified as CuO (exp. 86.85%; calcd. 88.50%).

Crystal structure

The crystallographic analysis confirmed that the complex consists of discrete $[\text{Cu}(\text{en})_2\text{H}_2\text{O}]^{2+}$ cations,

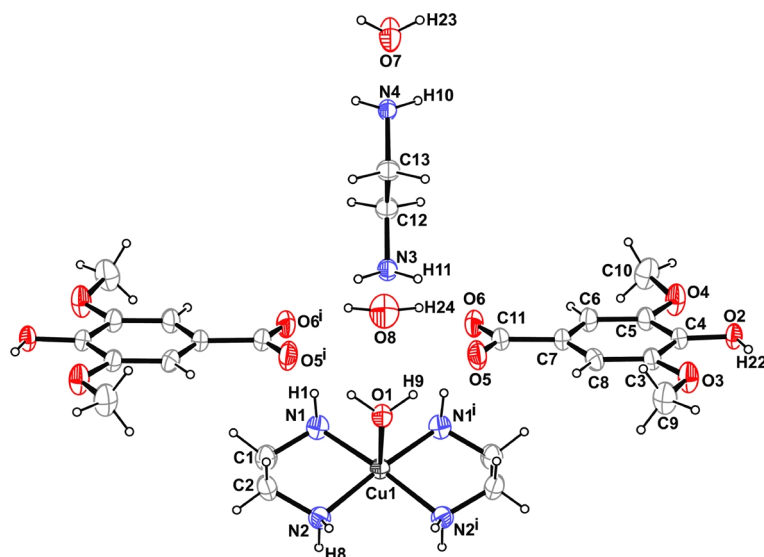


Fig. 2. Perspective view and atom labeling scheme of $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$. Atomic displacement ellipsoids are drawn at the 50% probability level. Symmetry transformation used to generate equivalent atoms (i) $x, -y + 1/2, z$.

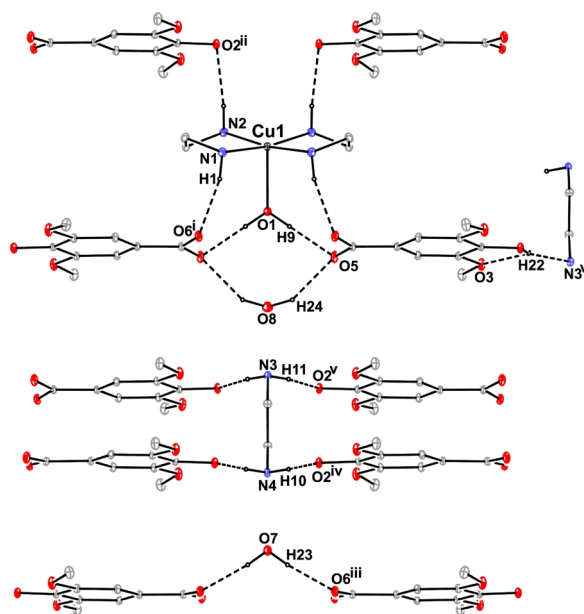


Fig. 3. A view of the complex, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$, normal to (100), showing different types of hydrogen bonding interactions responsible for the layered structure. Refer to Table 3 for symmetry codes.

two deprotonated syringate anions, one neutral (en) molecule and two water molecules of solvation. The Cu(II) ion has a distorted square-pyramidal coordination. The basal coordination plane is formed by two symmetry-related, chelating (en) groups. The coordination is completed by a water molecule located at the pyramid apex (Fig. 2).

One of the interesting features of the structure is that the en molecules exhibit chemically different functions. While in one form they coordinates to metal cation, in the other form they are molecules of solvation (Fig. 3). In the latter, they provide bifurcated (three-centered) hydrogen bonds (Table 3). The syringate anions $[\text{sy}]^-$ do not act as ligands, but are incorporated into the crystal structure by hydrogen bonds. The bond distances in the carboxylate group of deprotonated $[\text{sy}]^-$ are nearly equal (Table 2). This is responsible for the shifting and splitting of the vibrational bands of the carboxylate group.

The Cu–N distances are 2.014(3) and 2.012(3) Å, similar to those found in related structures [15–17]. The *trans* angles N–Cu–N at the Cu(II) ion deviate from linearity with a value of $171.55(15)^\circ$. The Cu1–O1 distance is 2.285(3) Å, and thus in agreement with the reported values for square pyramidal structures [18–20]. It is found that the apical Cu–O bond is larger than the basal Cu–N bonds. This is because the short Cu–N bonds prevent the water molecules from approaching the copper atom, and keep it at a distance of 2.285 (3) Å. The (en) chelate ring (Cu1 N2 N1 C2 C1) is close to planar, with an r. m. s deviation of 0.1918 Å. The Cu(II) cation departs from the mean plane defined by the four nitrogen atoms of the pyramidal basis by 0.0358(18) Å towards the axial water ligand.

The packing in the crystal is stabilized by strong and moderate hydrogen bonding. These intermolecular interactions are depicted in Fig. 3, and are included in

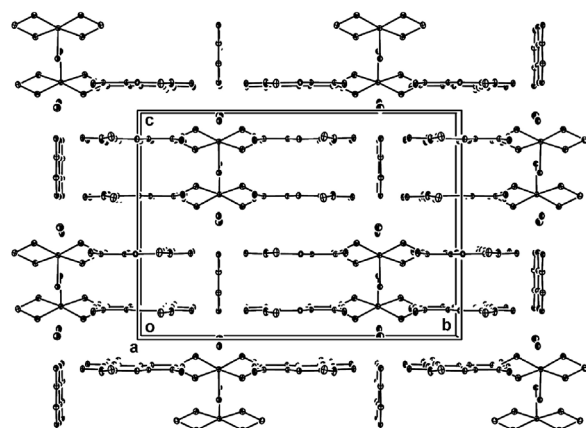


Fig. 4. The unit-cell packing of the complex, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})](\text{sy})_2(\text{en})(\text{H}_2\text{O})_2$, normal to (100).

Table 3. As shown in Fig. 4, $[\text{Cu}(\text{en})_2\text{H}_2\text{O}]^{2+}$ complex cations and $[\text{sy}]^-$ anion constitute a chain which is repeated along the b axis in a $-A-B-A-$ fashion, with a dihedral angle of $24.14 (10)^\circ$ between the (en) chelate ring (Cu1 N2 N1 C2 C1) and the (C3 C4 C5 C6 C7 C8) plane. The neighbouring chains are linked by uncoordinated en ligands through $\text{N3}-\text{H11}\cdots\text{O2}^{\text{v}}$ ($v: 1-x, 1-y, 1-z$) and $\text{N4}-\text{H10}\cdots\text{O2}^{\text{iv}}$ ($iv: 3/2-x, 1-y, z-1/2$) hydrogen bonds (Fig. 3). This arrangement leads to a layered structure. It can be seen from Fig. 4 that the uncoordinated en and water molecules form bridges between the layers through inter-molecular hydrogen bonds. The aqua ligands are linking adjacent $[\text{sy}]^-$ anions through $\text{O1}-\text{H9}\cdots\text{O5}$ hydrogen bonds, and are effective in forming a layered structure.

Experimental Section

Materials and measurements

All chemicals used were analytical reagent products. Copper(II)acetatetetrahydrate and ethylenediamine were obtained from Merck. Syringic acid was purchased from ACROS Organics. The elemental analysis for C, H and N were carried out at TÜBİTAK Marmara Research Centre. The magnetic susceptibility measurement at room temperature was performed using a Sherwood Scientific MXI model Gouy magnetic balance. The UV/vis spectrum was obtained for the aqueous solutions of the complexes with a Unicam UV2 spectrometer in the range 900–190 nm. The IR spectrum was recorded in the 4000–400 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. Thermal analysis curves (TG and DTA) were recorded simultaneously in a static air atmosphere with a Rigaku TG8110 thermal analyzer. The heating rate was $10^\circ\text{C min}^{-1}$.

Synthesis of Cu (II) syringate

The complex was prepared by mixing an aqueous solution of Cu(II) acetate (1 mmol) with a methanolic solution of syringic acid (2 mmol). The reaction mixture was stirred overnight at 50°C and the brown product was isolated by filtration, washed with cold distilled water and diethyl ether and dried in air.

Synthesis of the Cu(II) syringate ethylenediamine complex

A solution of ethylenediamine (2 mmol) in distilled water (20 ml) was added dropwise with stirring to a solution of Cu(II) syringate (1 mmol) in distilled water (40 ml). The solution was heated and stirred for 5 h at 70°C and then the mixture was cooled to room temperature. The black crystals were filtered and washed with 10 ml of cold distilled water and acetone and dried *in vacuo*. UV/vis (H_2O): $\lambda_{\text{max}}\epsilon = 567 \text{ nm} (4.11)$. –IR (KBr): $\tilde{\nu} = 3370$ and 3050 cm^{-1} (NH_2). $-\text{C}_{24}\text{H}_{48}\text{CuN}_6\text{O}_{13}$ (692.2): calcd. C 41.64, H 6.94, N 12.14; found C 41.05, H 7.43, N 12.82.

X-ray structure determination

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by direct methods using the program SHELXS97 [21]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [SHELXL-97]. Hydrogen atoms attached to C9, C10 and O2 were placed in geometrically idealized positions and refined as riding atoms. Therefore, the standard uncertainty (s.u) values for $\text{O2}-\text{H22}\cdots\text{O3}$ and $\text{O2}-\text{H22}\cdots\text{N3}^{\text{v}}$ hydrogen bondings is not included in Table 3. All other H atoms were located in a difference map, and their coordinates and $U_{\text{iso}}(\text{H})$ values were refined freely. The relevant crystal data and experimental conditions along with the final parameters are summarised in Table 1. Data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [21]; program(s) used to refine structure: SHELXL97 [22]; molecular graphics: ORTEP-3 for Windows [23]; software used to prepare material for publication: WinGX [24].

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 271102. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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