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ORIGINAL PAPER

Synthesis, Spectral, Thermal and Structural Study of Monoaquabis(Acetylsalicylato-κO)bis(Nicotinamide-κN)Copper(II)

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Abstract The compound has been formed by mononuclear $[Cu(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)]$ units in which the metal ion as well as the water ligand lies on a twofold symmetry axis, so that only one acetylsalicylate ligand and one nicotinamide ligand are independent. The distortion from ideal five-coordinate geometries can be described best by the degree of trigonality τ. For a regular square-pyramidal (SQP) geometry the trigonality parameter is 0 and for a trigonal–bipyramidal (TBP) structure it increases to 1. The copper coordination geometry is that of a square pyramid ($\tau = 0.23$), with the N atoms from nicotinamide ligands and the bonded carboxylate O atoms from acetylsalicylate ligands defining the quasi-planar square base. The apical site is occupied by the aqua ligand, a bond which coincides with the twofold symmetry axis and is thus exactly perpendicular to the basal plane. The thermal decomposition takes place in four steps: removing of moisture, dehydration of aqua ligand, the elimination of the nicotinamide (na) ligand and the decomposition of acetyl-groups and oxidation of salicylate ion ligands. In complex, all ligands are coordinated to the metal ion as monodendate. The IR spectra of the intermediate products showed similar results.

Keywords Mixed ligand complexes · Thermal decomposition · Transition metal complexes · Crystal structure · Nicotinamide · Acetylsalicylate

Introduction

In the last years, research in bioinorganic chemistry has revealed the important role of metal ions in most biological processes. The carboxylates play an important role in inorganic chemistry, and then still many metal cations in a great number of various biological processes, especially six-membered ring system, are components of several vitamins and drugs [1]. Also some carboxylate compounds (e.g. benzoates) are known to have antibacterial activity. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment for fungal skin diseases [2, 3]. Metal complexes of biologically important ligands are sometimes more effective than the free ligands [4]. It is well documented that heterocyclic compounds play a significant role in many biological systems. Therefore, it is not surprising that many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms [5–15].

In this work, Cu(II) with aspirin-nicotinamide complexes have been synthesized and both single crystal X-ray diffraction studies end thermal decomposition results have been presented. The decomposition pathways of the investigated complexes are discussed in connection with the available spectroscopic data.

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Experimental

Materials and Instrumentation

All chemicals used were analytical reagent products. $CuSO_4 \cdot 5H_2O$, acetylsalicylic acid (asa) and nicotinamide (na) (Fig. 1) were obtained from Merck (Darmstadt, Germany). Elemental analysis (C, H, N) were carried out by standard methods (Tubitak Marmara Research Center). Magnetic susceptibility measurements were performed at room temperature by using a Sherwood Scientific MXI model Gouy magnetic balance. IR spectra were recorded in the 4000–400 cm^{-1} region with a Perkin Elmer Spectrum One FT-IR spectrophotometer using KBr pellets. Thermal analyses (TGA, DTA) were performed by the Shimadzu DTG-60H system, in dynamic nitrogen atmosphere (100 mL/min) at a heating rate of 10 °C/min, in platinum crucibles as sample vessel, using α-Al_2O_3 as reference. Electronic spectra was recorded by a Schimadzu 3600/UV–VIS–NIR Spectrophotometer. Mass spectrum data were recorded Agilent Technologies 5973 spectrophotometer using DIP-MS method.

Preparation of Cu(II)-Acetylsalicylate-Nicotinamide Complex

In the first step, acetylsalicylic acid sodium salt was prepared at room temperature according to the following equation. All of the reactions were carried out in water media.

$$2\ C_9H_8O_4 + 2NaHCO_3 \rightarrow 2\ C_9H_7O_4Na + 2CO_2 + 2\ H_2O$$

In the second step, metal acetylsalicylic acid salts were synthesized from Na(asa) salt by the following substitution reaction:

$$2\ C_9H_8O_4Na + CuSO_4 \cdot nH_2O \rightarrow Cu(C_9H_7O_4)_2 \cdot nH_2O + Na_2SO_4$$

Finally, the solution of nicotinamide (2 mmol) in distilled water (30 mL) was added dropwise to a stirred solution of $Cu(asa)_2(H_2O)n$ (1 mmol) in hot distilled water (50 mL). The resulting solution was left 15–17 days for crystallization at room temperature. The crystals formed were filtered and washed with cold water and acetone and dried in vacuo. The mixed ligand complexes were prepared according to the following equations:

$$Cu(C_9H_7O_4)_2(H_2O)_n + 2\ C_6H_6N_2O \rightarrow [Cu(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)]$$

The yield of compound is about 76%.

Calc. for $C_{30}H_{28}N_4O_{11}Cu$: C, 52.63; H, 4.10; N, 8.19. Found: C, 52.12; H, 4.38; N, 8.27.

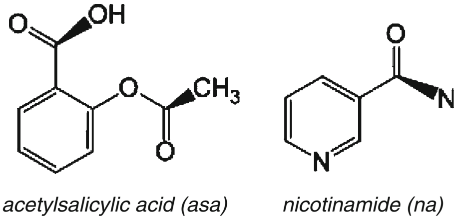


Fig. 1 Molecule structure of ligands

Results and Discussion

The effective magnetic moment of Cu(II) ion is 1.52 BM and compatible with literature values for similar complexes [8, 10, 12]. According to analytical results per mole formula unit of complex contain 2 moles of acetylsalicylate-nicotinamide ligands and 1 mole aqua.

The square pyramidal coordination of the metal ion is completed by two carboxylic oxygen atoms from two acetylsalicylate and two nitrogen atoms from two nicotinamides and aqua oxygen atom. According to the magnetic susceptibility results, the metal complexes are paramagnetic.

The electronic spectrum of the complex was taken in the solid state because of the low solubility of the complexes. The electronic spectra showed multiple absorbsition band at about 11130–16140 cm^{-1} in the Cu(II) complex but they are overlapped. It was to be taken notice of top of the peak as absorption band and d–d transition at about 13150 cm^{-1} ($^2E_g \rightarrow {}^2T_{2g}$) for Cu(II) complex. The UV–visible peaks corresponding to the the $\pi \rightarrow \pi^*$ transitions in the ligands were observed at 265 and 316 nm [16, 17]. The copper coordination geometry is that of a square pyramidal with the N atoms from nicotinamide ligands and the bonded carboxylate O atoms from acetylsalicylate ligands defining the quasi-planar square base.

FT-IR Spectra

The absorption bands in the range of 3500–3150 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of water molecules. The peaks for the N–H stretching of primary amides are strong in the range of 3150–3225 cm^{-1}. Also N–H bending vibrations appear approximately in the range of 1515 cm^{-1}. The asa-na mixed ligand complexes give rise to strong bands responsible from the C=O stretching. Conjugation between the carbonyl group and the amide nitrogen causes small frequency shifts. The strong bands observed at around 1587 cm^{-1} are assigned to this mode. This band remained almost in the same range as the amide group of the free na ligand, indicating that the na ligand does not coordinate through amide group. Pyridine ring vibration of free nicotinamide at 1565 cm^{-1} shifts to 1480 cm^{-1} in the complexes indicating that the pyridine ring is coordinated. The main difference in the spectrum of acetylsalicylic acid is that the C=O stretching vibration of the carboxyl group at 1718 cm^{-1} shifts to lower frequency in all metal complexes. The carboxylate peak in the metal complex appear in the range of 1587 cm^{-1}. This shows that the coordination takes place through the carboxyl group [18].

The –OH bending peak for the acetylsalicylic acid remained almost in the same position at around 1270 cm^{-1} in all metal complexes. The low intensity bands in the region of 600–400 cm^{-1} are attributed to M–N and M–O vibrations [10–15].

Thermal Analysis

$[Cu(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)]$

The TG-DrTGA/DTA and curves for the Cu(II) complex are given in Fig. 2. The moisture remove at 44 °C of DTA peak. The structure is stable in air up to 95 °C. Further heating causes releasing of 1 mole of water an accompanying endothermic effect with the DTA curve at 104 °C. The anhydrous complex begins to decompose with melting at 193 °C (DTA curve). Two moles of neutral nicotinamide ligands are removed from the structure with endothermic effect. At the same time, 2 moles of acetyl-groups of acetylsalicylic acid ligands are broken off and decomposed. The next consecutive three steps are considered decomposition of salicylate ligands by an accompanying endothermic effect with the DTA curve at 354, 402 and 540 °C. A number of undefined processes take place in this range ended by production of CuO. The mass lost is observed at 840 °C (DTA curve) that is belong to conversion of CuO to Cu_2O. This conversion was appeared similar Cu(II) complexes in literature [19–22].

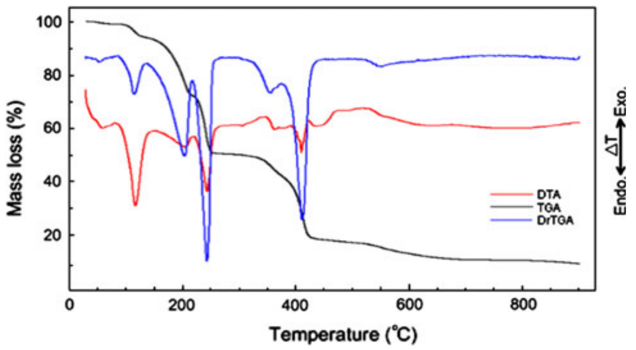


Fig. 2 TG-DrTGA/DTA-curves of the Cu(II)-complex

Crystallography

Diffraction data for $C_{30}H_{28}CuN_4O_{11}$ were collected at 296 K using a STOE IPDS-II diffractometer; in all these cases graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) was employed. Other details of cell data, data collection and refinement are summarized in Table 1.

The structure was solved by direct-methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [23] from within the WINGX [24] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. H atoms of water were located in different maps and refined subject to a DFIX restraint of O–H = 0.83(2) Å, and with $U_{iso}(H) = 1.5\ U_{eq}(O)$. All other H atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.97 Å, O–H distances of 0.82 Å and N–H distances of 0.86 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(C, N, O)$. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [25]. Details of hydrogen-bond dimensions are given in Table 2.

Table 1 Experimental details of the compound

Crystal data	
Chemical formula	$C_{30}H_{28}CuN_4O_{11}$
M_r	684.10
Cell setting, space group	Monoclinic, C2/c
Temperature (K)	296
a, b, c (Å)	26.2960 (14), 5.9539 (2), 20.8568 (11)
α, β, γ (°)	90.00, 111.976 (4), 90.00
V ($Å^3$)	3028.2 (3)
Z	4
D_x (Mg m^{-3})	1.501
μ (mm^{-1})	0.79
Crystal form, colour	Needle, blue
Crystal size (mm)	0.48 × 0.30 × 0.05
Absorption correction	Integration
T_{min}	0.851
T_{max}	0.981
No. of measured, independent and observed reflections	11635, 2984, 2245
Criterion for observed reflection	$I > 2\sigma(I)$
R_{int}	0.065
θ_{max} (°)	26.0
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.107, 1.02
No. of reflections	2984
No. of parameters	213
$(\Delta/\sigma)_{max}$	<0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e$Å^{-3}$)	0.30, −0.56

Table 2 Hydrogen-bond parameters (Å,◦)

D–H···A	D–H	H···A	D···A	D–H···A	Chain	Motif	Direction
N2–H2A···O5^{i}	0.86	2.05	2.889(3)	166	C(12)	$R^{2}_{2}(8)$	[101]
N2–H2B···O2^{ii}	0.86	2.29	3.133(3)	165	C(10)	–	[010]
O6–H6A···O2^{iii}	0.83(4)	1.95(2)	2.763(3)	171(5)	C(6)	$R^{2}_{2}(10)$	[010]
C9–H9A···O4^{iv}	0.96	2.56	3.461(4)	157	C(16)	$R^{2}_{2}(8)$	[001]
C3–H3···O5^{iv}	0.93	2.55	3.441(5)	160	C(12)	$R^{2}_{2}(24)$	[001]
C13–H13···O4^{v}	0.93	2.32	3.247(4)	171	C(12)	$R^{2}_{2}(24)$	[001]
C5–H5···Cg1^{vi}	0.93	2.79	3.530(4)	137	–	–	[100]

Cg1 = C1–C6; Cg2 = C14–C19; Cg3 = C21–C26. Symmetry codes: (i) $-x + 1/2, -y + 3/2, -z$; (ii) $-x + 1, y + 1, -z + 1/2$; (iii) $x, y + 1, z$; (iv) $-x + 1, -y + 1, -z$; (v) $-x + 1, -y, -z$; (vi) $3/2 - x, 1/2 + y, 1/2 - z$; (vii) $x - 1, y, z$; (viii) $x + 1, y, z$; (ix) $x + 1, y, z - 1$; (x) $x - 1, y, z + 1$; (xi) $x, y, z + 1$; (xii) $x, y, z - 1$

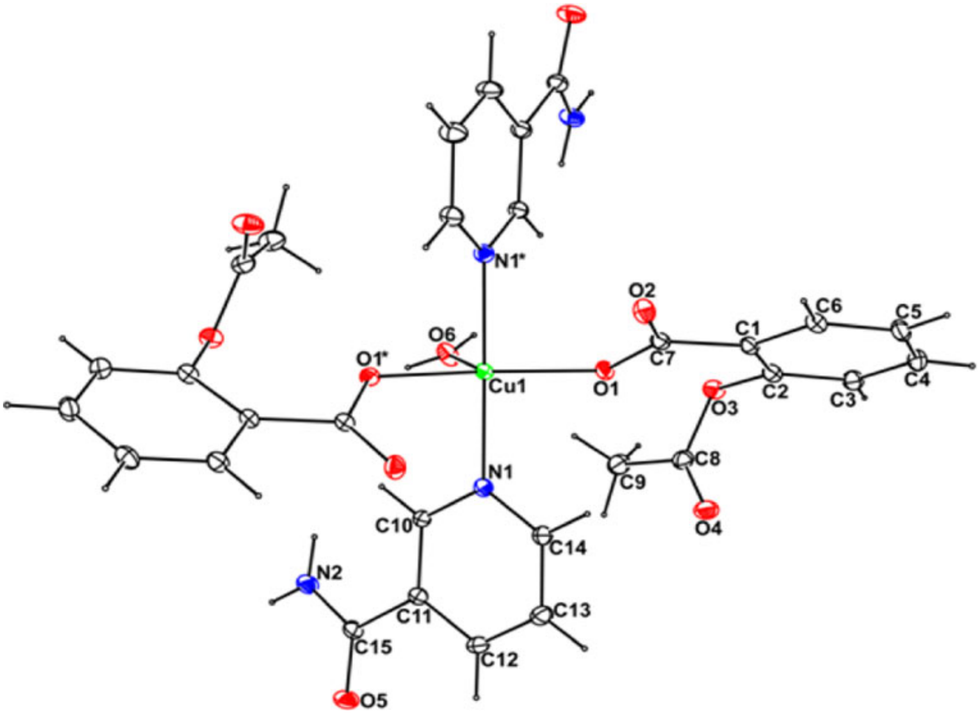


Fig. 3 The molecule of Cu(II)-complex showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and the atoms marked with '*' are at the symmetry position (1 − *x*, *y*, ½ − *z*)

The compound of monoaquabis(acetylsalicylato-κO) bis(nicotinamide-κN)copper(II) (Fig. 3) crystallizes with Z′ = 1/2 in the space group C2/c, and the molecules are linked into a three-dimensional framework of considerable complexity by means two N–H···O hydrogen bonds, three C–H···O hydrogen bonds, one O–H···O hydrogen bond and a C–H···π(arene) hydrogen bond (Table 2); aromatic π···π stacking interactions are, however, absent. In the simplest of the three sub-structures, atom N2 in the reference molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, via H2A, to atom O5 in the molecule at (1/2 − *x*, 3/2 − *y*, −*z*), so forming a C(12)[$R^{2}_{2}(8)$] [26] chain of rings running parallel to the [101] direction and centrosymmetric $R^{2}_{2}(8)$ rings centred at (n/2 + 1/4, 3/4, n/2) (n = zero or integer) (Fig. 4).

The second sub-structure is generated by the N–H···O and O–H···O hydrogen bonds; atom O6 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, via H6A, to atom O2 in the molecule at (*x*, *y* + 1, *z*), so forming a C(6) chain running parallel to the [010] direction and atom N2 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, via H2B, to atom O2 in the molecule at (1 − *x*, 1 + *y*, 1/2 − *z*), so forming a C(10) chain running parallel to the [010] direction and

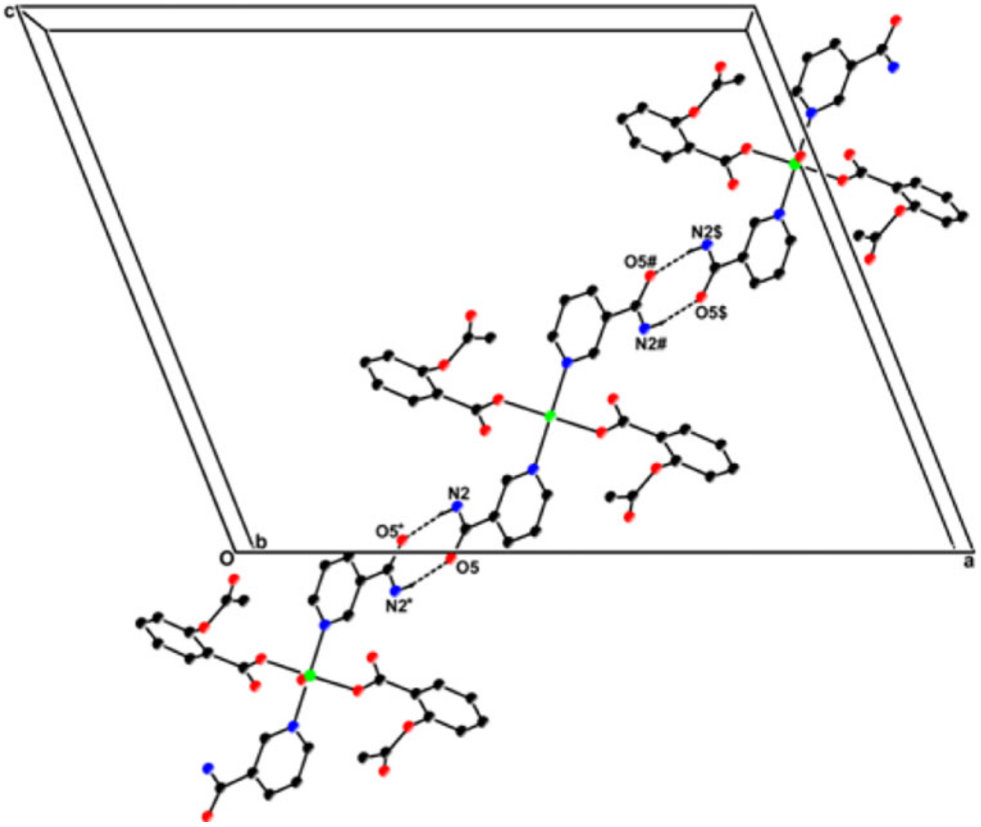


Fig. 4 Part of the crystal structure of Cu(II)-complex showing the formation of a chain edge-fused centrosymmetric $R_2^2(8)$ rings along [101]. For the sake of clarity the H atoms not involved in the motif shown have been omitted. The atoms marked with '*', '#' or '$' are at the symmetry positions (1/2 − *x*, 3/2 − *y*, −*z*), (1 − *x*, *y*, 1/2 − *z*) and (1/2 + *x*, 3/2 − *y*, 1/2 + *z*), respectively

generated by the c-glide plane at $y = 1/2$. The combination of the C(6) and C(10) chains along [010] generate a C(6)C(10)[$R_2^2(10)$][$R_2^1(10)$][$R_2^1(10)$] chain of rings (Fig. 5).

In the final sub-structure, atom C13 in the reference molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O4 in the molecule at (1 − *x*, −*y*, −*z*), so forming a C(12)[$R_2^2(24)$] chain of rings running parallel to the [001] direction and centrosymmetric $R_2^2(24)$ rings centered at (1/2, 0, n/2) (n = zero or integer) (Fig. 6). At the same time, atom C9 in the reference molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O4 in the molecule at (1 − *x*, 1 − *y*, −*z*), so forming a C(16)[$R_2^2(8)$] chain of rings running parallel to the [001] direction and centrosymmetric $R_2^2(8)$ rings centered at (1/2, 1/2, n/2) (n = zero or integer) and atom C3 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O5 in the molecule at (1 − *x*, 1 − *y*, −*z*), so forming a C(12) chain running parallel to the [001] direction. The combination of the C(12) and C(16) chains along [001] generates a chain of edge-fused $R_2^2(20)$ rings (Fig. 7).

In compound, amino atom N2 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, via atoms H2A and H2B, respectively, to atom O5 at (1/2 – *x*, 3/2 − *y*, −*z*) and atom O2 at (1 − *x*, 1 + *y*, 1/2 − *z*). Propagation by inversion and translation of these two interactions generates a chain of edge-fused rings running parallel to the [010] direction, with $R_2^2(8)$ ring centred at (1/4, 3/4, 0) and $R_4^4(24)$ rings centred at (1/4, n + 5/4, 0) (n = zero or integer) (Fig. 8). The combination of the C–H···O and O–H···O hydrogen-bonds produce $R_3^2(20)$ and $R_4^4(32)$ rings (Fig. 9).

In the structure of Cu(II)-complex there is also a strong C–H···π interaction between the two symmetry-related benzene rings of neighbouring molecules. The C5 atom in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to the benzene ring C1–C6 in the molecule at (3/2 − *x*, 1/2 + *y*, 1/2 − *z*), so forming a chain running parallel to the [100] direction (Fig. 10). The combination of the chains along [100], [101], [010] and [001] suffices to generate a three-dimensional structure of considerable complexity.

Mass Spectra

The thermal decomposition pathway of the [$Cu(asa)_2(na)_2(H_2O)$] complex mass spectrum was recorded (Fig. 11) using direct insertion probe pyrolysis mass spectrometry method. The molecular ion peak is detected at 681 *m/z* in the mass spectrum recorded. The mass spectrum obtained is relatively complex and exhibits a large number of peaks that extend to *m/z* value bigger than 720. Beside the most abundant peaks, much fewer abundant peaks observed on the spectrum depend probably on the nature of ligands.

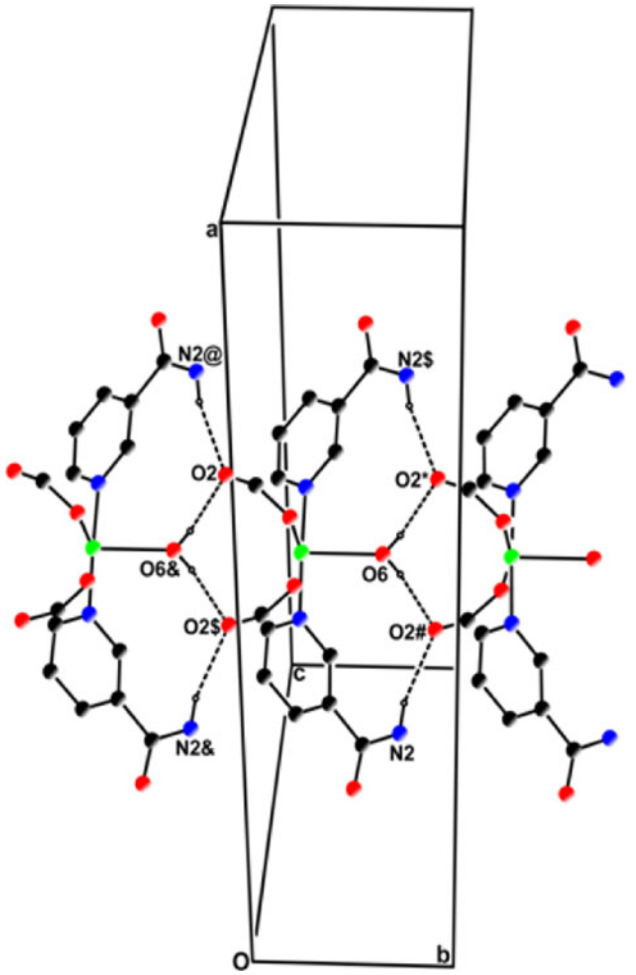


Fig. 5 Part of the crystal structure of Cu(II)-complex showing the formation of a chain rings along [010] generated by N–H···O and O–H···O hydrogen bonds. For the sake of clarity the H atoms not involved in the motif shown have been omitted. The atoms marked with '*', '#', '$', '&' or '@' are at the symmetry positions (x, $y + 1$, z), ($1 - x$, $1 + y$, $1/2 - z$), ($1 - x$, y, $1/2 - z$), (x, $y - 1$, z) and ($1 - x$, $-1 + y$, $1/2 - z$), respectively

Conclusion

The thermal decomposition takes place in four steps: removing of moisture, dehydration of aqua ligand, the elimination of the nicotinamide (na) ligand and the decomposition of acetyl-groups and oxidation of salicylate ion ligands. The complex lose moisture at 45 °C with endothermic DTA peak (1.52%). Then, at 104 °C, endothermic DTA peak is belong to dehydration of 1 mole aqua ligand (exp. 3.81%; calc. 2.65). After the dehydration process, decomposition stages of the anhydrous complexes are related to the release of nicotinamide and partial decomposition of acetylsalicylate ligands with removing of acetyl-groups (exp. 46.67%; calc. 47.6%). Other step is considered as the decomposition of residue of salicylate ions to coordinated of Cu(II) metal by the release of CO_2 (exp. 40.85%; 40.06%). Previous studies showed that the benzoate metal complexes decompose by releasing of CO_2 [19–22]. Finally, at 870 °C, Cu_2O metal oxide molecule turn to stable CuO product of thermal decomposition (exp. 11.04%; calc. 10.45%). According to the results, releasing of the nicotinamide ligand is an endothermal process and resembles to the thermal decomposition of nicotinamide complexes reported by the previous investigators [7, 8].

Early releasing of the nicotinamide than that of acetylsalicylate ligand by volatilisation may be due to the non-ionic bonding to metal ion.

In complex, all ligands are coordinated to the metal ion as monodendate. The IR spectra of the intermediate products showed similar results. The $(\mathrm{COO}^-)_{\mathrm{sym.}}$ peak is located at 1587 cm^{-1} for Cu(II)-complex. The $(\mathrm{COO}^-)_{\mathrm{asym.}}$ peak is observed at 1385 cm^{-1}. The shift (Δ) between of the $\nu_{\mathrm{asym.}}$ and $\nu_{\mathrm{sym.}}$ bands of COO^- group is 202 cm^{-1} for the complex higher than for the sodium salt acetylsalicylic acid (159 cm^{-1}) in which monodentate carboxylate group exists [9–11]

The compound is formed by mononuclear $[\mathrm{Cu(C_9H_7O_4)_2(C_6H_6N_2O)_2(H_2O)}]$ units, in which the metal ion as well as the water ligand lies on a twofold symmetry axis, so that only one acetylsalicylate ligand and one nicotinamide ligand are independent. The distortion from ideal five-coordinate geometries can be described best by the degree of trigonality τ [27]. For a regular square-pyramidal (SQP) geometry the trigonality parameter is 0 and for a trigonal–bipyramidal (TBP) structure it increases to 1. The copper coordination geometry is that of a square pyramid ($\tau = 0.23$), with the N atoms from nicotinamide ligands [Cu1–N1 = 2.010(2) Å] and the bonded carboxylate O atoms from acetylsalicylate ligands [Cu1–O1 = 1.9571(19) Å] defining the quasi-planar square base. The apical site is occupied by the aqua ligand [Cu1–O6 = 2.326(3) Å], a bond which coincides with the twofold symmetry axis and is thus exactly perpendicular to the basal plane. The Cu1–O6 distance is longer than the corresponding distances in related structures. This elongation can be attributed to the static Jahn–Teller effect.

The bond valences around the $\mathrm{Cu^{II}}$ atom in both structures were computed according to Brown [28] and O'Keeffe and Brese [29] as $\upsilon_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$, where R_{ij} is the bond-valence parameter (in the formal sense, it is the single-bond length between the i and j atoms) and d_{ij} is the observed bond length. In the present structures, the application of this correlation allows one to compare the relative importance of Cu–L bonds of Cu polyhedra, and to check the valence-sum rule for the $\mathrm{Cu^{II}}$ atom [30]. According to Shields et al. [31, 32], $R_{\mathrm{Cu–N}}$ and $R_{\mathrm{Cu–O}}$ were taken as 1.705 and 1.652 Å. The estimated

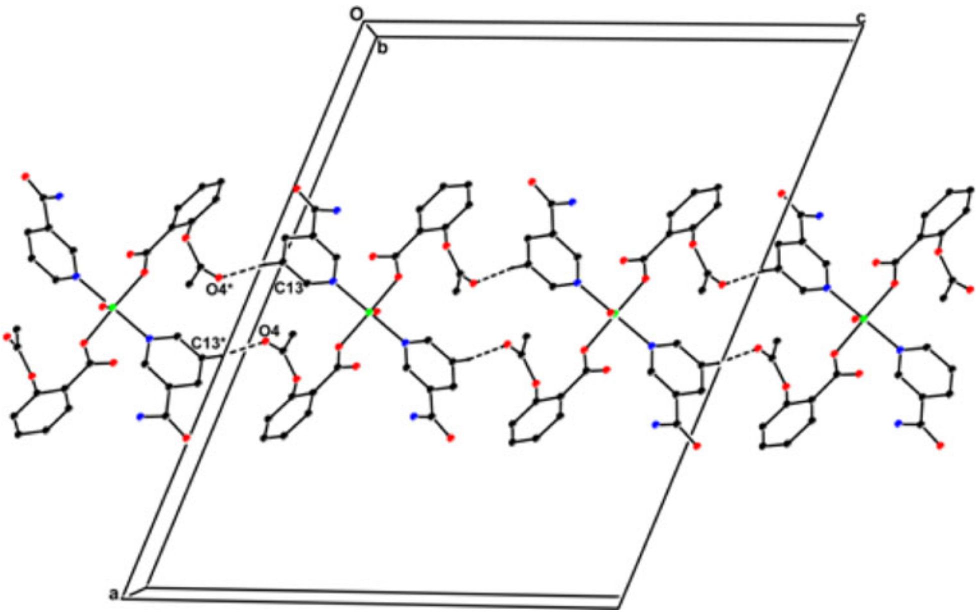


Fig 6 Part of the crystal structure of Cu(II)-complex showing the formation of centrosymmetric $R_2^2(24)$ rings along [001]. For the sake of clarity the H atoms not involved in the motif shown have been omitted. The atoms marked with '*' are at the symmetry position (1 − *x*, −*y*, −*z*)

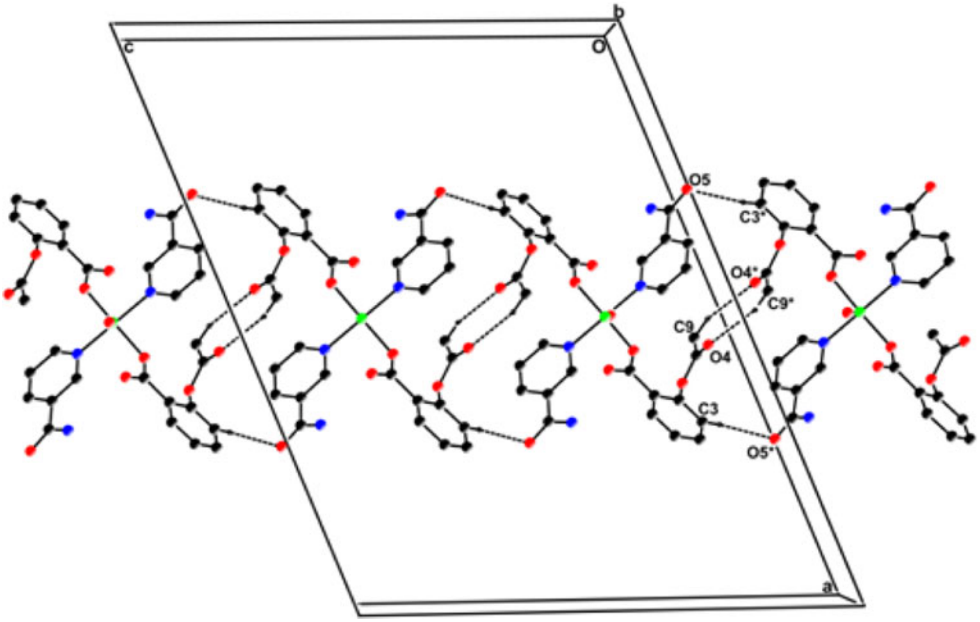


Fig. 7 Part of the crystal structure of Cu(II)-complex showing the formation of $R_2^2(8)$ and $R_2^2(20)$ rings along [001]. For the sake of clarity the H atoms not involved in the motif shown have been omitted. The atoms marked with '*' are at the symmetry position (1 − *x*, 1 − *y*, −*z*)

bond valences of the Cu^{II} ion show that, in both structures, the equatorial Cu–N bonds are identical with the equatorial Cu–O bonds [$\upsilon_{Cu-N} = 0.438$ valence units (v.u.) and $\upsilon_{Cu-O} = 0.438$ v.u. in Cu(II)-complex]. The valence of the axial Cu–O$_{aqua}$ bonds are 0.161 v.u for Cu(II)-complex. Finally, the valences of the five-coordinate Cu atoms are consistent with the valence-sum rule ($V_i = \Sigma\upsilon_{ij}$), which gives $V_{Cu} = 1.913$ for Cu(II)-complex.

According to mass spectrum, The 44, 78, 95, 106, 120, 136, 163, 178, 242 etc. peaks are belong to decomposition products of complex and ligands [8, 10, 11, 14]. The mass spectrum shows the fragmentation pattern and the most fragile points of the molecule.

Supplementary Material

CCDC 755284 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fig. 8 Part of the crystal structure of Cu(II)-complex showing the formation of an [010] chain of edge-fused $R_2^2(8)$ and $R_4^4(24)$ rings. For the sake of clarity the H atoms not involved in the motif shown have been omitted. The atoms marked with '*', '#', '$', '&' or '@' are at the symmetry positions (1 − *x*, 1 + *y*, 1/2 − *z*), (*x*, 1 + *y*, *z*), (1/2 − *x*, 5/2 − *y*, −*z*), (−1/2 + *x*, 3/2 − *y*, −1/2 + *z*) and (1/2 − *x*, 3/2 − *y*, −*z*), respectively

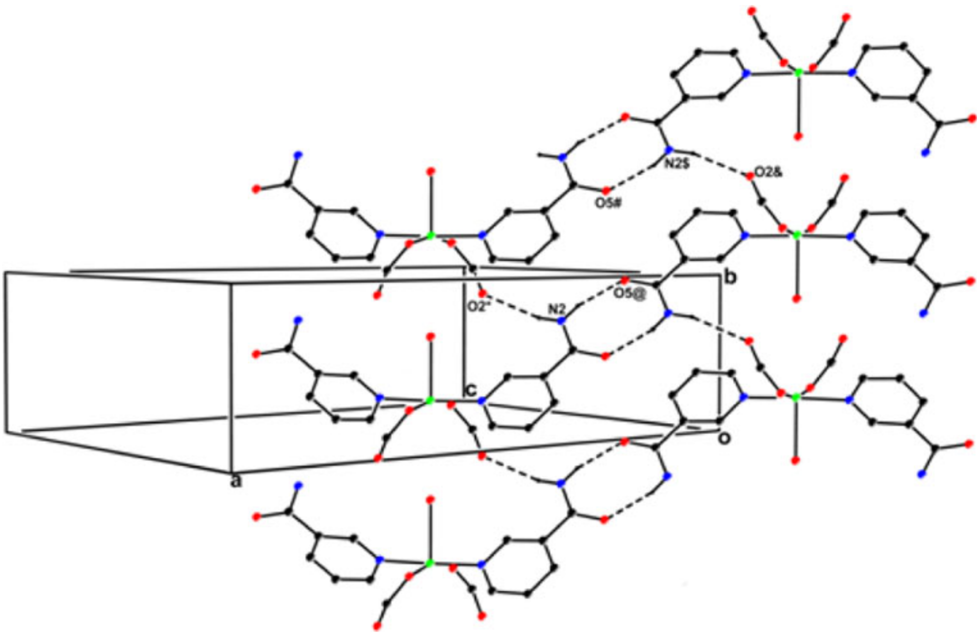


Fig. 9 Part of the crystal structure of Cu(II)-complex showing the formation of $R_3^2(20)$ and $R_4^4(32)$ rings. The atoms marked with '*', '#', '$', '&', '%' or '@' are at the symmetry positions (1 − *x*, *y*, 1/2 − *z*), (*x*, 1 − *y*, 1/2 + *z*), (1 − *x*, 1 + *y*, 1/2 − *z*), (*x*, 1 + *y*, *z*), (1 − *x*, 1 − *y*, −*z*) and (1 − *x*, 2 − *y*, −*z*), respectively

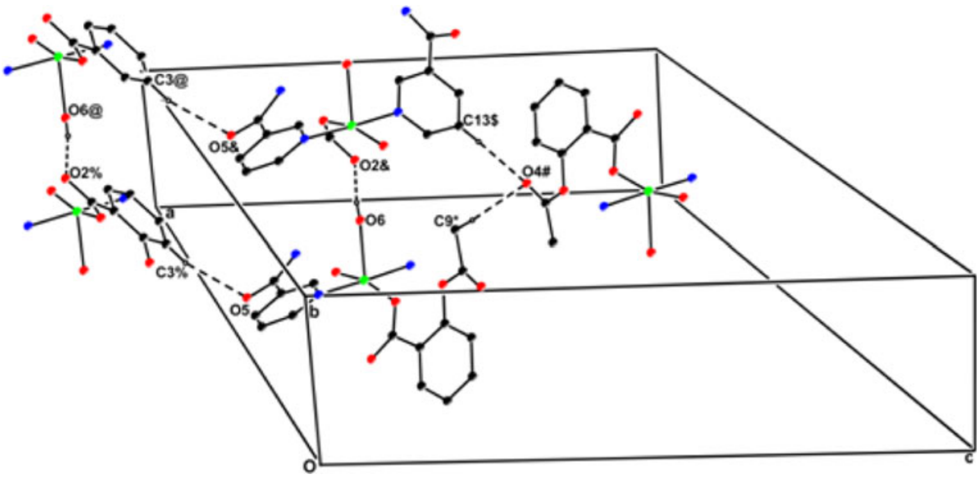
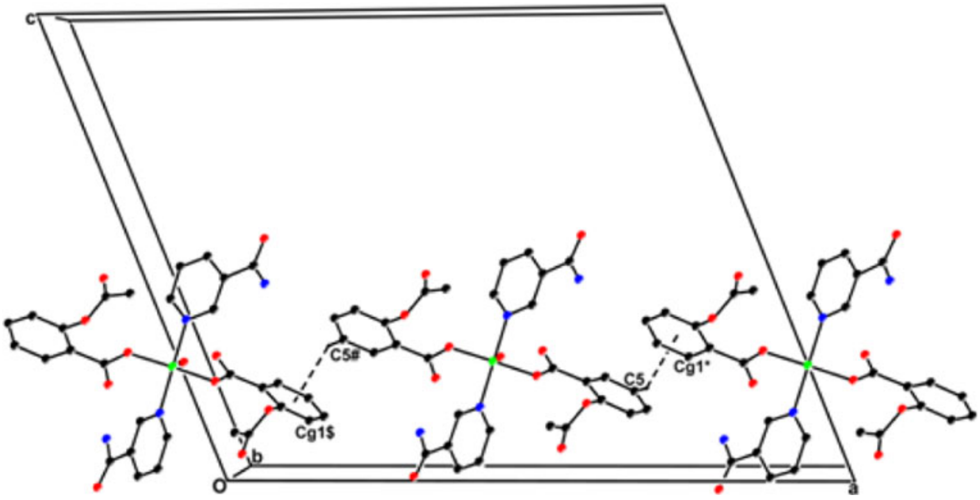


Fig. 10 Part of the crystal structure of Cu(II)-complex showing the formation of a chain along [100] generated by the C–H···π(arena) hydrogen bonds. For the sake of clarity the H atoms not involved in the motif shown have been omitted. The atoms marked with '*', '#' or '$' are at the symmetry positions (3/2 − *x*, 1/2 + *y*, 1/2 − *z*), (1 − *x*, *y*, 1/2 − *z*) and (−1/2 + *x*, 1/2 + *y*, *z*), respectively



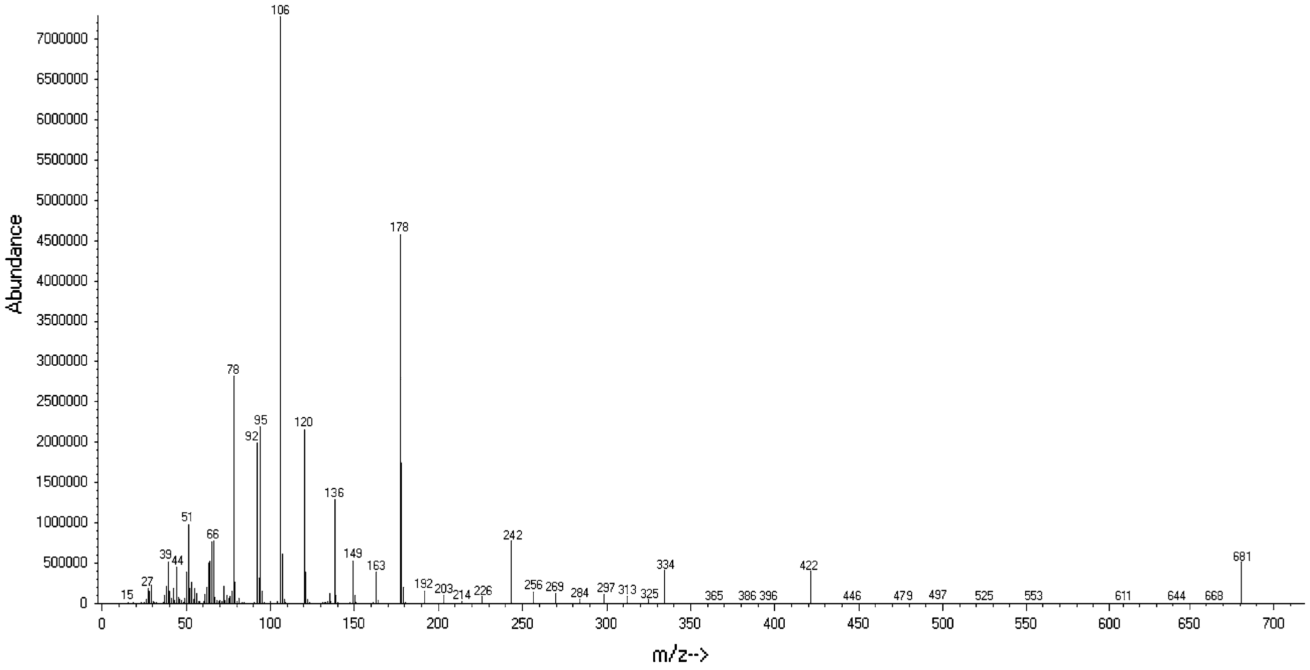


Fig. 11 Mass spectrum of [Cu(*asa*)$_2$(*na*)$_2$(H$_2$O)] complex

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