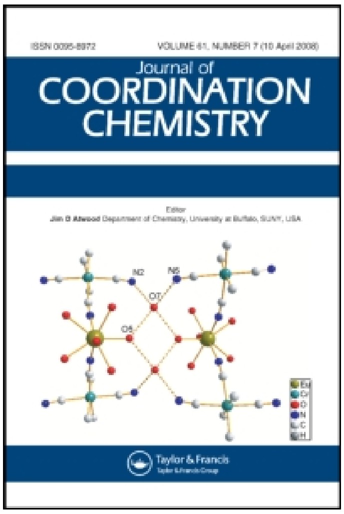

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Bis(saccharinato)copper(II) complexes with 2-aminomethylpyridine and 2-aminoethylpyridine: Syntheses, crystal structures, spectral and thermal characterizations of *trans*-[Cu(sac)$_2$(ampy)$_2$] and [Cu(sac)$_2$(aepy)(H$_2$O)] (ampy = 2-aminomethylpyridine and aepy = 2-aminoethylpyridine)

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Bis(saccharinato)copper(II) complexes with 2-aminomethylpyridine and 2-aminoethylpyridine: Syntheses, crystal structures, spectral and thermal characterizations of *trans*-[Cu(sac)$_2$(ampy)$_2$] and [Cu(sac)$_2$(aepy)(H$_2$O)] (ampy = 2-aminomethylpyridine and aepy = 2-aminoethylpyridine)

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Two bis(saccharinato)copper(II) complexes with 2-aminomethylpyridine (ampy) and 2-aminoethylpyridine (aepy) have been prepared and characterized by elemental analyses, IR and electronic spectroscopy, magnetic measurements and single-crystal X-ray diffraction. The copper(II) ion in *trans*-[Cu(sac)$_2$(ampy)$_2$] has -1 site symmetry and is octahedrally coordinated by two neutral ampy and two anionic sac ligands, whereas the copper(II) ion in [Cu(sac)$_2$(aepy)(H$_2$O)] is five-coordinate with a distorted square-pyramidal coordination geometry. Both ampy and aepy behave as bidentate (N,N') chelating ligands, while the saccharinate anion (sac) in the title complexes is N-coordinated. IR spectra of both complexes display typical absorption bands of bidentate aminopyridines and N-bonded sac ligands. Thermal decomposition behavior of the complexes is described in detail.

Keywords: 2-Aminomethylpyridine; 2-Aminoethylpyridine; Copper(II) complex; Crystal structure

1. Introduction

Saccharin ($C_7H_5NO_3S$, also named 1,2-benzoisothiazol-3(2*H*)-one-1,1-dioxide or *o*-benzosulfimide) is currently the most widely used noncaloric artificial sweetener in the world [1], available commercially as water-soluble alkali salts. Saccharin is one of the most studied components of food ingredients because of its potential harmfulness and especially its suspected carcinogenic nature [2–6]. Although there was controversy

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over its safety when bladder tumors were found in some male rats fed high doses of saccharin in the past, it is now thought that saccharin is safe at human levels of consumption. However, the coordination chemistry of saccharin was found to be interesting. The corresponding deprotonated saccharinate anion [sac = $(C_7H_4NO_3S)^-$] behaves as a polyfunctional ligand and coordinates to metals by means of its imino nitrogen, carbonyl oxygen or sulfonyl oxygen atoms. The most common coordination mode of sac is ligation through the negatively charged nitrogen atom, usually observed in the aqua bis(saccharinato) complexes of metal(II) [7–12].

Our current interest is to prepare a series of metal-sac complexes with chelating ligands, containing in particular hydroxyalkyl and hydroxyamine groups. As an extension of these studies, we describe here the synthesis, spectral, thermal and structural characterizations of two copper(II) complexes of sac with 2-aminomethylpyridine (ampy) and 2-aminoethylpyridine (aepy).

2. Experimental

2.1. *Materials*

All reagents were purchased from commercial sources and used as supplied. The starting complex $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ was prepared according to the literature method [12].

2.2. *Preparation of the complexes*

The ampy ligand (0.216 g, 2.0 mmol) was added dropwise to an aqueous solution of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ (0.58 g, 1 mmol) (25 cm^3) and stirred for 30 min at 60°C. The blue crystals were dissolved in a water–EtOH mixture (1 : 1) and X-ray quality blue crystals of $[Cu(sac)_2(ampy)_2]$ were obtained by slow evaporation of the solution at room temperature after 2 days. Yield 70%; mp 230°C. Anal. Calcd. for $C_{26}H_{24}N_6O_6S_2Cu$(%): C, 48.5; H, 3.7; N, 13.0; S, 10.0. Found: C, 48.2; H, 3.8; N, 13.1; S, 9.8.

A solution of the aepy ligand (0.12 g, 1.0 mmol) in MeOH (20 cm^3) was added to an aqueous solution of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ (0.58 g, 1 mmol) (25 cm^3) with continuous stirring at 60°C. Blue crystals of $[Cu(sac)_2(aepy)(H_2O)]$ were obtained by slow evaporation at room temperature after 1 month. Yield 40%; dp 132°C. Anal. Calcd. for $C_{21}H_{20}N_4O_7S_2Cu$(%): C, 44.4; H, 3.6; N, 9.9; S, 11.3. Found: C, 44.3; H, 3.6; N, 10.0; S, 11.1.

2.3. *Physical measurements*

IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets in the frequency range 4000–300 cm^{-1}. Electronic spectra of the aqueous solutions were measured on a Unicam UV2 in the 200–900 nm range. Elemental analyses (C, H, N and S) were performed on a Vario EL instrument. Room-temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Evans magnetic balance. Thermal analysis curves, using thermogravimetry (TG) and differential thermal analysis (DTA), were obtained using a Rigaku TG8110 instrument in a static air atmosphere. A sample size of 5–10 mg was used.

Table 1. Crystallographic data for $[Cu(sac)_2(ampy)_2]$ and $[Cu(sac)_2(aepy)(H_2O)]$.

	$[Cu(sac)_2(ampy)_2]$	$[Cu(sac)_2(aepy)(H_2O)]$
Empirical formula	$C_{26}H_{24}N_6O_6S_2Cu$	$C_{21}H_{20}N_4O_7S_2Cu$
M_r	644.18	568.07
T (K)	293(2)	293(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Unit cell dimensions		
a (Å)	7.8072(16)	13.2772(7)
b (Å)	8.4205(17)	7.4351(4)
c (Å)	11.336(2)	23.3628(12)
α (°)	96.54(3)	90
β (°)	95.52(3)	97.089(1)
γ (°)	106.38(3)	90
V (Å^3)	703.9(2)	3046.4(6)
Z	1	4
D_c (g/cm^3)	1.520	1.649
μ (mm^{-1})	0.976	1.189
$F(000)$	331	1164
Crystal size (mm^3)	$0.47 \times 0.43 \times 0.16$	$0.36 \times 0.34 \times 0.09$
θ range (°)	1.82–27.50	1.76–27.52
Index range (h, k, l)	–10/10, –10/8, –14/14	–17/16, –6/9, –30/30
Reflections collected	6093	17456
Independent reflections (R_{int})	3199 (0.014)	5253 (0.0768)
Absorption correction	Multiscan	Multiscan
Min. and max. transmissions	0.657 and 0.860	0.674 and 0.901
Data/restraints/parameters	3199/0/184	5253/0/325
Goodness-of-fit on F^2	1.041	1.129
Final R indices [$I > 2\sigma(I)$]	0.0422	0.1109
R indices (all data)	0.0487	0.1475
Largest diff. peak and hole (e Å^{-3})	0.589 and –0.411	2.795 and –0.853

2.4. *X-ray structure determination*

Intensity data for the title compounds were collected using a Bruker Smart 1000 CCD area detector diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods using SHELXS-97 [13] and refined by a full-matrix least-squares procedure using SHELXL-97 [14]. Non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms attached to N were located in difference maps and refined by riding on their parent atom in their as-found positions. H atoms attached to C were included using a riding model in idealized positions. In $[Cu(sac)_2(aepy)(H_2O)]$, the copper and water O atoms are significantly disordered and this resulted in comparatively high R-factors. Moreover, all attempts at location of the water H atoms failed. Details of data collection, refinement and crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

trans-Bis(2-aminomethylpyridine)bis(saccharinato)copper(II), $[Cu(sac)_2(ampy)_2]$, and aqua(2-aminoethylpyridine)bis(saccharinato)copper(II), $[Cu(sac)_2(aepy)(H_2O)]$, were

Table 2. Selected IR spectral data for [Cu(sac)$_2$(ampy)$_2$] and [Cu(sac)$_2$(aepy)(H$_2$O)].

Assignment	[Cu(sac)$_2$(ampy)$_2$]	[Cu(sac)$_2$(aepy)(H$_2$O)]
νOH)	–	3310m
νNH)	3209m, 3121m	3261m
ν(CH)	3055vw, 2937vw, 29128vw	3085vw, 2951vw
νCO)	1651vs, 1626vs	1655vs, 1630vs
ν(CN)	1609m	1607m
ν(CC)	1583s	1588vs
ν(CC)	1490m	1487s
ν_s(CNS)	1330m	1378s
ν_{as}(SO$_2$)	1271s, 1250vs	1305vs, 1296vs
ν_s(SO$_2$)	1170vs, 1146vs	1163vs, 1148vs
ν_{as}(CNS)	953s	950vs
γ(CH) (py)	640m	644m

Frequencies in cm^{-1}. vw, very weak; vs, very strong; s, strong; m, medium.

synthesized by the direct reaction of the ampy and aepy ligands with [Cu(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O in aqueous solution. In [Cu(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O, the two sac ligands occupy the *trans* positions of the coordination octahedron around the copper(II) ion. All aqua ligands in [Cu(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O have been substituted by two ampy ligands, resulting in [Cu(sac)$_2$(ampy)$_2$]. However, in the case of the aepy ligand, a five-coordinate copper(II) complex consisting of one aqua, one aepy and two sac ligands were obtained. These observations suggest that the complexation mechanisms of both complexes are different. [Cu(sac)$_2$(ampy)$_2$] is soluble in water, MeOH and warm EtOH at room temperature, whereas [Cu(sac)$_2$(aepy)(H$_2$O)] is soluble in warm water and MeOH. The complexes are nonhygroscopic and stable and retain their structural integrity at room temperature indefinitely. [Cu(sac)$_2$(ampy)$_2$] melts at 230°C, while [Cu(sac)$_2$(aepy)(H$_2$O)] decomposes at 132°C.

3.2. *Spectral and magnetic properties*

Selected IR bands of both complexes are listed in table 2. The absorption bands of the NH$_2$ groups in both complexes are observed in the frequency range 3120–3260 cm^{-1}, and are significantly shifted to lower frequency compared to the free ligands [15]. The NH absorption band of [Cu(sac)$_2$(ampy)$_2$] was found to be a doublet, whereas the corresponding vibration appears as a single band at 3261 cm^{-1} in [Cu(H$_2$O)(aepy)(sac)$_2$]. This may be due to differences in hydrogen bonding of both hydrogens of the amine groups in the complexes, as discussed later. The band at 3310 cm^{-1} characterizes the coordinated water molecule in [Cu(sac)$_2$(aepy)(H$_2$O)]. The relatively weak bands between 2928 and 3085 cm^{-1} are assigned to the ν(CH) mode of the ethylene groups. The absorption bands of the carbonyl group of sac in the complexes are observed as two split bands at *ca* 1650 and 1625 cm^{-1}. The bands around 1608 cm^{-1} correspond to the ν(C=N) vibrations of the aminopyridines; the bands occurred at around 1590 cm^{-1} in the free ligands, suggesting that the electron density of the C=N bond increased upon coordination. The symmetric and asymmetric absorption bands of the CNS moiety of sac in [Cu(sac)$_2$(ampy)$_2$] are observed at *ca* 1330 and 950 cm^{-1}, respectively, at but notably higher frequencies in [Cu(sac)$_2$(aepy)(H$_2$O)]. The ν_{as}(SO$_2$) and ν_s(SO$_2$) vibration bands of sac appear as clearly separated doublets, although the S–O distances in both complexes are almost identical.

The electronic spectrum of aqueous solutions of both complexes display distinct absorption bands at 586 nm ($\varepsilon = 68\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) for [Cu(sac)2(ampy)2] and 603 nm ($\varepsilon = 42\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) for [Cu(sac)2(aepy)($H_2O$)], assigned to d–d transitions. A band with smaller intensity at 377 nm ($\varepsilon = 9\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) is due to the Jahn-Teller effect in [Cu(sac)$_2$(ampy)$_2$]. The absorption bands below 300 nm are due to intraligand transitions of ampy and aepy.

The room-temperature magnetic moment measurements show that the mononuclear complexes are paramagnetic with a μ_{eff} of 1.6 BM, in satisfactory agreement with the expected μ_{eff} value of 1.73 BM for a spin-only d^9 system.

3.3. *Thermal analysis*

The thermal behavior of the copper(II) complexes was followed up to 800°C in a static air atmosphere. [Cu(sac)$_2$(ampy)$_2$] melts at 230°C and then begins to decompose. This compound shows a continuous mass loss, indicating a multistep decomposition of the complex. It is therefore almost impossible to calculate mass loss values for each step; however, the DTA curve exhibits a small endothermic peak at 400°C, probably due to removal of two ampy ligands, and one large exothermic peak at 490°C, assigned to consumption of the sac moiety. The decomposition process ends at 540°C. The total experimental mass loss of 88.5% agrees well with the calculated mass loss of 90.1% for the process [Cu(sac)$_2$(ampy)$_2$] $\rightarrow$ CuO + gaseous products, suggesting that the grey–black product is copper oxide.

[Cu(sac)$_2$(aepy)(H_2O)] decomposes in three stages. The first stage between 132 and 185°C corresponds to the endothermic dehydration of the complex with a mass loss of 3.5% (calcd. 3.2%). The relatively high dehydration temperature indicates that the water molecule is strongly coordinated to the copper(II) ion. In the second stage, elimination of an aepy molecule takes place in the temperature range 190–317°C with an endothermic peak at 300°C. The experimental mass loss of 20.8% agrees well with the calculated mass loss of 21.5%. The solid residue consisting of mainly copper and sac decomposes between 320 and 500°C with an extremely exothermic DTA peak at 470°C to give a grey–black end-product of CuO (found 61.2%, calcd. 61.3%).

3.4. *Description of the crystal structure of [Cu(sac)$_2$(ampy)$_2$]*

The molecular structure of [Cu(sac)$_2$(ampy)$_2$] with the atom labelling is shown in figure 1. Selected bond lengths and angles together with the hydrogen bonding geometry are listed in table 3. The structure consists of individual molecules of [Cu(sac)$_2$(ampy)$_2$], in which the copper(II) ion sits on a center of symmetry, coordinated by two ampy and two sac ligands, forming an octahedral CuN_6 chromophore. Both ampy and sac ligands occupy the *trans* positions of the coordination octahedron. Each ampy ligand is bidentate, chelating through the two N atoms and forming a five-membered chelate ring around copper(II), while each sac ligand is N-bonded. Some of the carbon atoms (C9–C12) in the phenyl rings of the sac ligands are disordered over two positions with essentially equal occupancy.

The Cu–N_{ampy} bond distances are 2.000(2) and 2.025(2) Å, similar to other reported copper(II) complexes of ampy [16–18]. The Cu–N_{sac} bond distance of 2.662(2) Å is

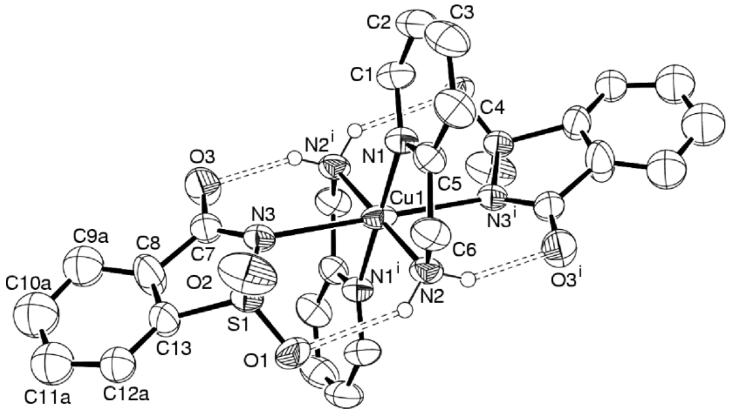

Figure 1. Molecular structure of [Cu(sac)$_2$(ampy)$_2$] with the atom labelling scheme and 50% thermal ellipsoids. Only one orientation of the disordered sac phenyl ring is shown and all the C–H hydrogen atoms are omitted for clarity. Symmetry code (i): $-x$, $-y$, $-z$.

Table 3. Selected bond lengths (Å), angles (°) and hydrogen bonding geometry for [Cu(sac)$_2$(ampy)$_2$].

Cu(1)–N(1)	2.025(2)	N(1)–Cu(1)–N(3)	93.99(8)
Cu(1)–N(2)	2.000(2)	N(1)–Cu(1)–N(3)^i	86.01(8)
Cu(1)–N(3)	2.662(2)	N(2)–Cu(1)–N(3)	93.15(8)
N(1)–Cu(1)–N(2)	82.42(9)	N(2) (1)–Cu–N(3)^i	86.85(8)
N(1)–Cu(1)–N(2)^i	97.58(9)		

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(2)–H(1)···O(1)	0.90	2.39	3.139(3)	140
N(2)–H(1)···O(1)^{ii}	0.90	2.32	3.034(3)	137
N(2)–H(2)···O(3)^i	0.90	2.08	2.897(3)	151
C(2)–H(2A)···O(2)^{iii}	0.93	2.56	3.422(4)	154
C(12)–H(12B)···O(3)^{iv}	0.93	2.44	3.313(7)	156

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

significantly longer than those found for other N-coordinated sac complexes [9,19–26]. The Cu–N$_{sac}$ bonds are also much longer than the two Cu–N$_{ampy}$ bonds, and this results in formation of an elongated octahedral geometry along the N$_{sac}$ atoms. The distortion in the copper(II) complex is a consequence of the Jahn–Teller effect as also observed in the electronic spectra. Significant distortion from octahedral is also evident from the angles in the coordination polyhedron, especially at the bite angle of ampy of 82.42 (9)°.

Both the sac and ampy ligands are essentially planar with root-mean-square (rms) deviations from the best least-squares planes of 0.095 and 0.024 Å, respectively. The dihedral angles between the ampy ring and disordered sac planes are 59.78(11)° for sac(a)-ampy and 45.91(12)° for sac(b)-ampy. The N2 atom of ampy deviates by 0.461(4) Å from the best plane of the ampy ring. The packing diagram of [Cu(sac)$_2$(ampy)$_2$] is presented in figure 2. The amine hydrogen atoms of the ampy ligands form intra- and intermolecular hydrogen bonds with the carbonyl or sulfonyl O atoms of the adjacent sac ligands. One of the amine hydrogen atoms (H1) of ampy forms a bifurcated intra/intermolecular hydrogen bond. Furthermore, some of

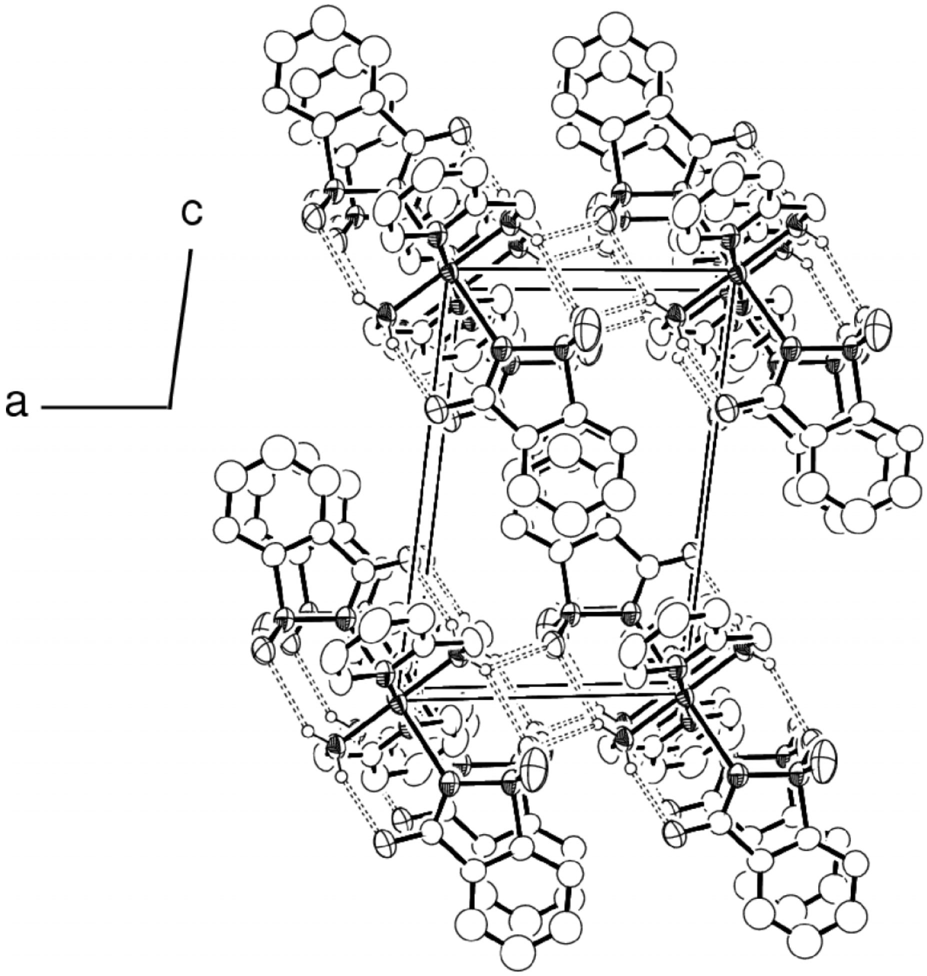

Figure 2. Packing diagram of [Cu(sac)$_2$(ampy)$_2$] viewed down *b*. Only one orientation of the disordered sac phenyl ring is shown. All C–H hydrogen atoms are omitted for clarity and hydrogen bonds are indicated by broken lines.

the ring hydrogen atoms of sac and ampy are involved in relatively weak C–H$\cdots$O interactions with the carbonyl or sulfonyl O atoms of the sac ligands. π–π stacking interactions involving the pyridine rings (atoms N1, C1–C5) result in [0 1 0] chains of molecules [Cg$\cdots$Cg^i 3.637(2) Å, (i) $= -x, 1-y, -z$]. Probable π–π stacking interactions between the disordered sac phenyl rings (atoms C8–C13 with C9, C10, C11, C12 disordered over two sites) result in $(1, 0, -1)$ pseudo-sheets that are cross-linked by the N–H$\cdots$O hydrogen bonds, resulting in a three-dimensional network.

3.5. *Description of the crystal structure of [Cu(sac)$_2$(aepy)(H$_2$O)]*

The molecular structure of [Cu(sac)$_2$(aepy)(H$_2$O)] consists of neutral molecules as shown in figure 3. Selected bond lengths and angles together with the hydrogen bonding

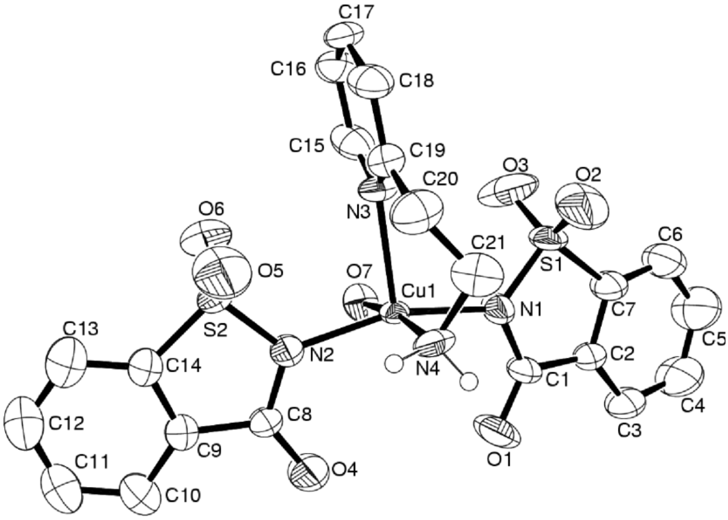

Figure 3. Molecular structure of $[Cu(sac)_2(aepy)(H_2O)]$ with the atom labelling scheme and 50% thermal ellipsoids. The Cu and water O atoms are strongly disordered and, as a result, the H atoms attached to O7 were not found. All C–H hydrogen atoms are omitted for clarity.

Table 4. Selected bond lengths (Å), angles (°) and hydrogen bonding geometry for $[Cu(sac)_2(aepy)(H_2O)]$.

Cu(1)–N(1)	2.058(6)	N(1)–Cu(1)–O(7)	84.2(3)
Cu(1)–N(2)	2.049(6)	N(2)–Cu(1)–N(3)	98.7(2)
Cu(1)–N(3)	2.260(5)	N(2)–Cu(1)–N(4)	94.4(3)
Cu(1)–N(4)	1.886(8)	N(2)–Cu(1)–O(7)	84.9(3)
Cu(1)–O(7)	2.014(7)	N(3)–Cu(1)–N(4)	95.1(2)
N(1)–Cu(1)–N(2)	158.5(2)	N(3)–Cu(1)–O(7)	96.3(3)
N(1)–Cu(1)–N(3)	100.9(2)	N(4)–Cu(1)–O(7)	168.5(3)
N(1)–Cu(1)–N(4)	92.7(3)		

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(4)–H(4A)···O(1)^i	0.90	2.31	3.007(9)	134
N(4)–H(4B)···O(4)^i	0.90	2.21	2.972(9)	142

Symmetry operations: (i) $1/2 - x$, $y - 1/2$, $1/2 - z$.

geometry are collected in table 4. The copper(II) ion is coordinated by one aqua, one aepy and two sac ligands, exhibiting a distorted square-pyramidal configuration of the CuN_4O type. The aepy molecule acts as a bidendate donor via two nitrogen atoms, creating a six-membered chelate ring, while the sac ligands are N-coordinated. The copper and water O atoms are strongly disordered over two adjacent sites with occupancy factors 0.762(5) for Cu1 and O7 and 0.238(5) for Cu1a and O7a.

The Cu–N_{aepy} bond distances are 1.886(8) and 2.260(5) Å, while the Cu–N_{sac} bond distances of 2.049(6) and 2.058(6) Å are comparable to those reported for the corresponding mononuclear copper(II) complexes of sac [9,19–26]. The bond angle values for N(4)–Cu1–O(7) and N(1)–Cu1–N(2) indicate a significant distortion in the coordination polyhedron around the copper(II) ion. The calculated structural index parameter (τ) of 0.17 reflects a significantly distorted square-pyramidal geometry ($\tau = \alpha - \beta/60$, where α and β correspond to two angles showing tendency to linearity).

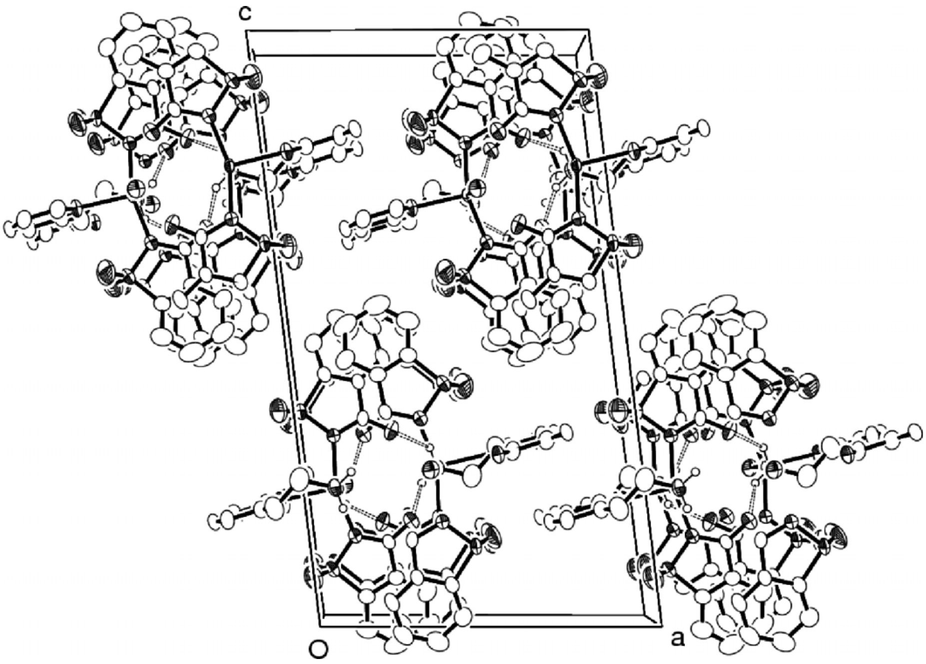

Figure 4. Packing diagram of [Cu(sac)$_2$(aepy)(H$_2$O)] viewed down *b*. All C–H hydrogen atoms are omitted for clarity and N–H$\cdots$O hydrogen bonds are indicated by broken lines.

The τ-values of square-based-pyramidal and trigonal-bipyramidal extremes are 0 and 1, respectively [27].

The ring systems of the sac and ampy ligands are essentially planar. The rms deviations for sac1 with the N1 atom, and for sac2 with the N2 atom and aepy are 0.026, 0.057 and 0.005 Å, respectively. The C21 atom of the aminomethyl group of ampy deviates from the py ring of ampy by 0.749(16) Å. The sac1–sac2, sac1–aepy and sac2–aepy dihedral angles are 26.17(9), 73.1(2) and 80.7(2)°, respectively.

A packing diagram of [Cu(sac)$_2$(aepy)(H$_2$O)] is shown in figure 4. The amine hydrogen atoms (H4A and H4B) of ampy form intermolecular hydrogen bonds with the carbonyl O atoms of the neighboring sac ligands. Furthermore, there are weak π–π interactions between the phenyl rings of the sac ligands [$Cg\cdots Cg^{i}$ 3.906(2) Å, (i): $1/2-x$, $y-1/2$, $1/2-z$)]. Thus, individual molecules are held together by the hydrogen bonds and aromatic π–π stacking interactions, forming a structure with significant one-dimensional character.

Supplementary material

Crystallographic data for the structures reported here have been deposited at the CCDC as supplementary data, CCDC Nos 237619 and 237620 for [Cu(sac)$_2$(ampy)$_2$] and [Cu(sac)$_2$(aepy)(H$_2$O)], respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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