Synthesis, Spectral, Thermal and Structural Characterization of the Copper(II) Saccharinato Complex of 2–Aminopyrimidine, [Cu(sac–O)$_2$(ampym–N)$_2$(H$_2$O)$_2$]·2ampym

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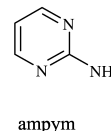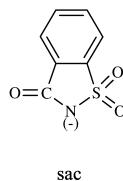Reprint requests to Dr. O. Z. Yeşilel. Fax.: +90 0222 239 3578. E-mail: yesilel@ogu.edu.tr

Bis(2-aminopyrimidine-N)diaquabis(saccharinato-O)copper(II) di(2-aminopyrimidine), [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$] · 2ampym was synthesized and characterized by means of elemental analysis, IR and UV-vis spectroscopy, magnetic susceptibility, simultaneous TG, DTG, DTA techniques, and X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/c$ [$a = 7.4697(5)$, $b = 10.1679(5)$, $c = 22.743(2)$ Å, $\beta = 92.844(5)$, $Z = 2$, $R = 0.0275$, $wR = 0.0757$, $V = 1725.26(19)$ Å^3]. The copper atom is bonded to two ampym N atoms and two sac O atoms as well as to two water O atoms in *trans* positions in the geometry of a distorted octahedron. There are also two ampym moieties as solvate molecules in the unit cell. The crystal structure is stabilized by N–H···O, O–H···N and C–H···O type hydrogen bonding interactions. Intermolecular $\pi - \pi$ interactions between the phenyl rings of ampym groups and C–H···π interactions also support the packing of the molecules. The thermal decomposition of the complex has been studied.

Key words: Copper(II) Complex, Saccharinato Complex, 2-Aminopyrimidine, Thermal Studies

Introduction

Saccharin (3H-benzisothiazol-3-one 1,1-dioxide or *o*-benzosulfimide) is a well known artificial sweetener. The molecule is readily deprotonated to form the corresponding saccharinato anion (sac), which is a versatile polyfunctional ligand [1]. Because of the biological significance of saccharin, there has been increased interest in metal complexes, especially with first-row transition metals. Saccharin, or its anion, may bond to metals by means of their imino nitrogen, carbonyl oxygen, or sulfonyl oxygen atoms. The first systematic syntheses and structural studies of aqua complexes of metal saccharinates were reported by the groups of Haider [2, 3] and Cotton [4, 5]. In the last two decades, the synthesis and spectroscopic properties [6 – 9], particularly vibrational properties [10 – 12], of the metal saccharinates and metal complexes including saccharin and various *N*-donor ligands (mono- or bidentate) have been intensively studied by many investigators, but less so far *O*-donor ligand. A number of crystal structures and the thermal properties of metal saccharinato and mixed-ligand complexes have been studied [13 – 31].

Scheme 1. Structures of the ligands: sac = deprotonated saccharin; ampym = 2-aminopyrimidine.

In the present paper, we report the synthesis, UV/vis and IR spectra, thermal behaviour, and molecular structure of bis(2-aminopyrimidine-N)diaqua−bis(saccharinato-O)copper(II) di(2-aminopyrimidine), [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$] · 2ampym. The structures of the ligands are shown in Scheme 1.

Results and Discussion

The complex was synthesized in good yields (72%) and with high purity. The compound includes two saccharinato ligands, four ampym molecules, and two water molecules, based on elemental analyses. The presence of aqua ligands was confirmed also by IR spectra and the endothermic weight loss in the temperature range of 72 – 104 °C in the TG and DTA analy-

ses. X-ray single crystal studies showed that the complex has a distorted octahedral geometry with two 2-aminopyrimidine molecules coordinated to the Cu(II) ion through one N atom of each pyrimidine ring, two monodentate saccharinato ligands coordinated to the metal ion through a carbonyl oxygen atom and two aqua ligands in *trans* positions.

UV/vis spectra

The λ_{max} value of [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$] · 2ampym is 563 nm, and this value was assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition. The Δ_o value for the complex was calculated as 17,760 cm^{-1}, since there is only one transition for d^9 complexes. The complex exhibits an experimental magnetic moment value of 1.62 BM corresponding to one unpaired electron.

IR spectra

In IR spectra of the [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$] · 2ampym complex, the strong and broad absorption band at 3411 cm^{-1} is attributed to the ν(OH) vibrations of the aqua ligands. The doublet bands at 3563 and 3505 cm^{-1} are attributed to the ν(NH$_2$) modes of ampym. The stretching modes of the carbonyl and sulfonyl groups are used most frequently for structural studies of various saccharinates [8, 9, 30]. In the IR spectrum of the complex, the coordination of saccharinato ligand through the carbonyl oxygen atom shifts the ν(C=O) band by 26 cm^{-1} from 1642 cm^{-1} (free sac) down to 1616 cm^{-1}. The CNS moiety of sac is observed at 1351 and 935 cm^{-1}. The stretching vibrations of ν_{asym}(SO$_2$) and ν_{sym}(SO$_2$) appear characteristically at 1303 and 1166 cm^{-1}, respectively, as very strong bands. The weak bands at 543 and 480 cm^{-1} may be attributed to Cu-O and Cu-N vibrations, respectively.

Thermal properties

The first process, in the temperature range of 72 – 104 °C, corresponds to the loss of two moles of aqua ligands in a single stage (exp. 5.15; calcd. 4.27%). In several consecutive stages, the TG curve of the anhydrous Cu(II) complex shows that the mass loss in the temperature range of 105 – 201 °C, is attributed to the endothermic loss of ampym molecules (DTG$_{max}$ = 126, 130, 176 °C). On further heating, endothermic removal of the other ampym molecules and two sac lig-
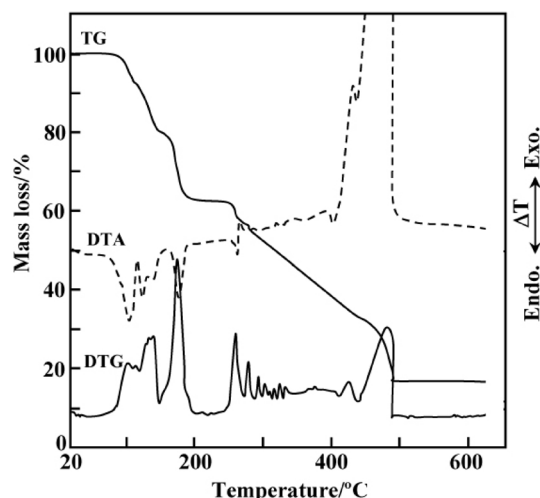

Fig. 1. TG, DTG and DTA curves of [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$] · 2ampym.

ands take place in the 280 – 405 °C range (DTG$_{max}$ = 292, 386 °C). In the last stage, a strong exothermic peak on the DTA curve (DTG$_{max}$ = 492 °C) is associated with burning of the organic residue, leading to CuO (Fig. 1). The overall mass loss (exp. 89.38; calcd. 90.58%) is in agreement with this stoichiometry. The final decomposition product, CuO, was identified by IR spectroscopy with corresponding spectra obtained under the same conditions for the pure oxide.
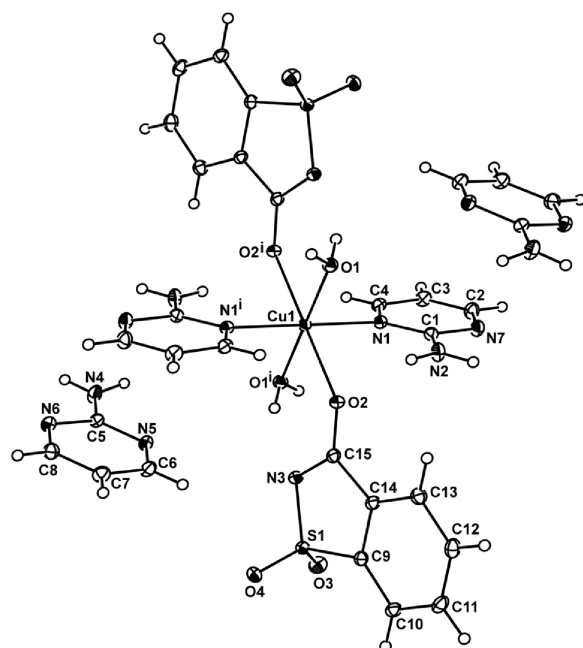
Crystal structure

The crystallographic analysis reveals that the complex consists of two sac ions and two water ligands along with ampym moieties being coordinated to the metal in *trans* positions. There are two more ampym molecules which are not coordinated (Fig. 2). The crystallographic data are summarized in Table 1. The geometry around the copper(II) ion is a distorted octahedron, with the bond distances and angles as given in Table 2. The equatorial plane (N1–O1–N1^i–O1^i) is formed by heterocyclic N atoms of two *trans* ampym ligands and oxygen atoms of two aqua ligands while the axial positions are occupied by carbonyl O atoms of sac ligands.

The Cu1–N1 distance is 2.071(1) Å and the Cu1–O1 distance 1.993(1) Å. These values are comparable to those observed in other mixed-ligand copper complexes [32, 33]. The sac ligands are weakly bonded to copper, Cu1–O2/O2^i = 2.412(1) Å, through the carbonyl O atoms although N-coordination is usu-

Table 1. Crystal data and structure refinement parameters for [Cu(sac-*O*)$_2$(ampym-*N*)$_2$(H$_2$O)$_2$]·2ampym.

Empirical formula	C$_{30}$H$_{32}$CuN$_{14}$O$_8$S$_2$
Formula weight	844.36
Temperature (K)	296
Wavelength (Å)	0.71073 Mo-K$_\alpha$
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a, b, c [Å]	7.4697(5); 10.1679(5); 22.743(2)
β [°]	92.844(5)
V [Å^3]	1725.26 (19)
Z	2
Absorption coefficient [mm^{-1}]	0.828
D_{calc} [Mg m^{-3}]	1.625
Crystal size (mm)	0.430 × 0.393 × 0.370
Theta range for data collection [°]	1.88 – 26.0
Measured reflections	17331
Independent reflections	3395
Absorption correction	Integration
Refinement method	Full-matrix least-squares on F^2
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0275$, $wR_2 = 0.0757$, $R_1(all\ data) = 0.0304$
Goodness-of-fit on F^2	1.072
Largest difference peak and hole [e Å^{-3}]	0.269; −0.545

Table 2. Selected bond lengths and bond angles for [Cu(sac-*O*)$_2$(ampym-*N*)$_2$(H$_2$O)$_2$]·2ampym.

Bond lengths (Å)

Cu1–N1	2.071(1)	S1–O3	1.437(1)
Cu1–O1	1.993(1)	S1–O4	1.440(1)
Cu1–O2	2.412(1)	O2–C12	1.243(2)

Bond angles (°)

O1–Cu1–N1	86.98(5)	O1^i–Cu1–O2	91.07(5)
O1–Cu1–O2	88.93(5)	C15–O2–Cu1	126.36(11)
N1–Cu1–O2	92.93(5)	N1^i–Cu1–O2	87.07(5)
O1^i–Cu1–N1	93.03(5)		

Symmetry code: [(i)] $2-x, -y, -z$.

Fig. 2. The molecular structure of [Cu(sac-*O*)$_2$(ampym-*N*)$_2$(H$_2$O)$_2$]·2ampym, together with the atomic numbering system [Symmetry transformation: (i) $2-x, -y, -z$].

ally preferred by this ligand in the first row transition metal complexes; and the Cu–O2 distance is longer than corresponding values in the related structures [34, 35]. This axial elongation can be attributed to the static Jahn-Teller effect [36]. The carbonyl C–O [1.243(2) Å] and sulphonyl S–O distances [1.440(1) Å and 1.437(1) Å] of the sac ligand are consistent with previously reported values [34, 35, 37–39]. The torsion angles of the C12–C13–C14–C15 [176.4(2)°], C13–C14–C15–N3 [179.3(2)°] and C13–C14–C9–S1 [179.3(1)°] planes suggest that the sac groups are essentially planar. The dihedral angle between the equatorial plane and the mean plane of the sac ligand is 71.8(3)°. The ampym ligands are planar with an r.m.s deviation of 0.0023 Å. The individual bond lengths of the ampym molecules correspond well to those reported for this ligand in other complexes [40–43]. The dihedral angle between the mean plane through the sac and ampym moieties is 81.9(4)°, that is, the saccharinate anion lies nearly perpendicular to the ampym molecule.

The crystal structure is mainly stabilized by strong and moderate hydrogen-bonding interactions. The $\pi \cdots \pi$ interactions between the ampym rings together with $\pi \cdots$ ring interactions between the hydrogen atoms of ampym and the sac rings are also effective in the molecule packing (Fig. 3). It can be seen from Fig. 4(a) that the phenyl hydrogen atoms of the sac ligands are involved in intermolecular hydrogen bonding with the sulfonyl O atoms of the sac ligands of neighbouring molecules. The C13–H10$\cdots$O3^i and C10–H7$\cdots$O4^v distances are 2.40 and 2.47 Å, respectively. This weak hydrogen bonding has also been previously reported [39, 44, 45]. The water molecules form O1–H15$\cdots$N5^i and O1–H16$\cdots$N3^{ii} hydrogen bonds with the N atoms of unligated ampym molecules and sac anions. While the coordinated ampym molecule participates in bifurcated hydrogen bonds [N2–H14$\cdots$O2/O3^i] with the carbonyl and sulfonyl oxygen atoms of sac ligands, the unligated ampym

Table 3. Hydrogen bonds, $\pi\cdots\pi$ and $\pi\cdots$ ring interactions for [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$]·2ampym.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N2–H13···N6[i]	0.89(3)	2.22(3)	3.115(2)	174(2)
N4–H11···N7[ii]	0.86(3)	2.12(3)	2.973(2)	171(2)
O1–H15···N5[iii]	0.88(3)	1.88(3)	2.755(2)	175(3)
O1–H16···N3[iv]	0.77(3)	2.14(3)	2.852(2)	154(3)
N2–H14···O3[i]	0.82(3)	2.56(2)	2.877(2)	105(2)
C13–H10···O3[i]	0.93	2.40	3.327(2)	176.1
C4–H3···O2[iv]	0.93	2.31	2.291(2)	122.9
C10–H7···O4[v]	0.93	2.47	3.241(2)	140.8
N2–H14···O2	0.82(3)	2.07(3)	2.803(2)	148(2)
C8–H6···O3	0.93	2.58	3.243(2)	128.9

Cg(I)	Cg(J)	Cg–Cg (Å)	Perpendicular distance (Å)
Cg(2) [A]	Cg(5) [A^{vi}]	3.7910(9)	3.422
Cg(2) [A]	Cg(5) [A^{vii}]	3.8046(9)	3.533

X···H(I)	Cg(J)	H···Cg (Å)	X–H···Cg (°)
C(2)–H(1)	CgB^{vii}	2.71	165
C(3)–H(2)	CgB^{viii}	2.99	142

Symmetry codes: [(i)] $1+x, y, z$; [(ii)] $x-1, y, z$; [(iii)] $1+x, y-1, z$; [(iv)] $2-x, -y, -z$; [(v)] $1-x, 1/2+y, 1/2-z$; [(vi)] $1-x, 1-y, -z$; [(vii)] $2-x, 1-y, -z$; [(viii)] $x, 1/2-y, -1/2+z$.
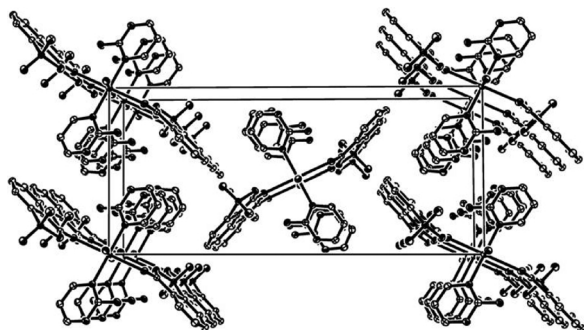
Fig. 3. Packing of the components of [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$]·2ampym in the unit cell, normal to (100).

molecule is hydrogen bonded to the coordinated sac anions and ampym molecules through the bonds C8–H6···O3 and N4–H11···N7[ii], respectively. The details of hydrogen bonding interactions are given in Table 2.

In the extended structure of the complex, shown in Fig. 4(b), there are weak intermolecular $\pi\cdots\pi$ and $\pi\cdots$ ring interactions. The intermolecular $\pi\cdots\pi$ interactions occur between the phenyl rings of ampym groups (hereafter A) of neighbouring molecules. The perpendicular distances between successive rings are 3.422 Å from A to A^{vi} and 3.533 Å from A to A^{vii} (Fig. 4(b)). The distances between the ring centroids are 3.7910(9) and 3.8046(9) Å. The benzene rings of the sac groups (hereafter B) are involved in inter-molecular C–H···π interactions with coordinated ampym molecules. The details of C2–H1···CgB^{vii} and C2–H2···CgB^{viii} interactions are given in Table 3.

Experimental Section

Materials and instrumentation

All chemicals used were analytical reagent products. Elemental analysis for C, H and N was carried out at the TÜBİTAK Marmara Research Centre. 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 solution of the complex (10^{-3} M) 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 IR spectrometer using KBr pellets. A TG8110 thermal analyzer was used to record simultaneously TG, DTG and DTA curves in static air atmosphere at a heating rate of 10 Kmin^{-1} in the temperature range 20–600 °C using platinum crucibles. Highly sintered α-Al$_2$O$_3$ was used as a reference, and the DTG sensitivity was 0.05 mgs^{-1}.

Crystallographic analysis

Data collection were performed on a STOE IPDSII image plate detector using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the θ range 1.88–26.00° at 296 K. Details of crystal structures are given in Table 1. Data collection: Stoe X-AREA [46]. Cell refinement: Stoe X-AREA [46]. Data reduction: Stoe X-RED [46]. The structure was solved by direct-methods using SIR97 [47], and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [48]. All hydrogen atoms except those bound to the O5 (water) atom were positioned geometrically and refined by a riding model with U_{iso} 1.2 times that of the attached atoms. Molecular drawings were obtained using ORTEP-III [49].

Preparation of the [Cu(sac-O)$_2$(ampym-N)$_2$(H$_2$O)$_2$]·2ampym

A solution of ampym (4 mmol, 0.38 g) in ethanol (30 ml) was added dropwise with stirring to a solution of [Cu(sac)$_2$(H$_2$O)$_4$]·2H$_2$O (1.0 mmol, 0.535 g) in hot distilled water (50 ml). The mixture was heated to 60 °C in a temperature-controlled bath and stirred for 4 h. The reaction mixture was then cooled to room temperature. The crystals formed were filtered and washed with 10 ml of cold distilled water and ethanol and dried in air. [Cu(sac-O)$_2$(ampym)$_2$(H$_2$O)$_2$]·2ampym: Analysis for [CuC$_{30}$H$_{32}$N$_{14}$O$_8$S$_2$] (%): calcd. C 42.68, H 3.82, N 23.22; found C 42.74, H 3.91, N 23.55.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Cen-
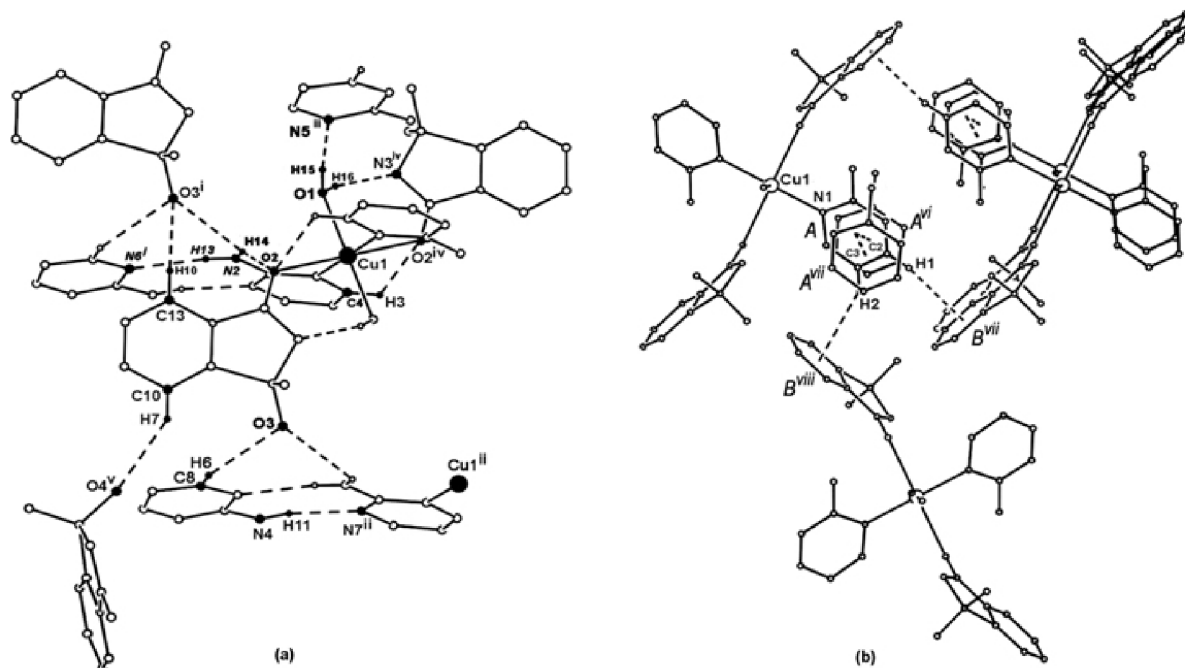
Fig. 4. A view of the organisation of complexes [Cu(sac-*O*)$_2$(ampym-*N*)$_2$(H$_2$O)$_2$] · 2ampym, showing (a) the hydrogen bonding interactions, (b) the $\pi \cdots \pi$ and $\pi \cdots$ ring interactions normal to (100). [Symmetry transformations: (i) $1 + x, y, z$; (ii) $x - 1, y, z$; (iii) $1 + x, y - 1, z$; (iv) $2 - x, -y, -z$; (v) $1 - x, 1/2 + y, 1/2 - z$; (vi) $1 - x, 1 - y, -z$; (vii) $2 - x, 1 - y, -z$; (viii) $x, 1/2 - y, -1/2 + z$].

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