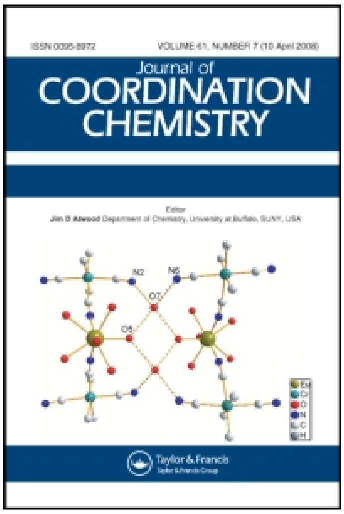

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Synthesis, crystal structure and properties of *trans*-[Cu(sac)$_2$(en)$_2$] (sac = saccharinato and en = ethylenediamine)

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The title complex *trans*-[Cu(sac)$_2$(en)$_2$] (sac = saccharinato, en = ethylenediamine) has been obtained accidentally by the reaction of piperazine (ppz) with [Cu(sac)$_2$(H$_2$O)$_4$]·2H$_2$O in butanol solution. During the reaction, ppz was presumably decomposed to produce en which then coordinated to copper(II) to yield the title complex. *trans*-[Cu(sac)$_2$(en)$_2$] has been characterized by elemental analysis, IR, UV-VIS, magnetic measurements and single crystal X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ (No. 2) and it consists of neutral units linked by bi- and trifurcated N–H···O hydrogen bonds into chains which are further connected by aromatic π–π stacking interactions forming a three-dimensional supramolecular network. The copper(II) ion in [Cu(sac)$_2$(en)$_2$] sits on a inversion centre and is octahedrally coordinated by two neutral en and two anionic sac ligands. An elongated distorted octahedral geometry along the Cu–N$_{sac}$ bonds is a consequence of the Jahn–Teller effect. The en ligand acts as a bidentate (N,N′) chelating ligand, while sac is *N*-coordinated. IR and UV spectra and thermal analysis are in agreement with the crystal structure.

Keywords: Ethylenediamine; Saccharinato; Copper(II) complex; Crystal structure

1. Introduction

Saccharin (C$_7$H$_5$NO$_3$S and also named 1,2-benzoisothiazol-3(2*H*)-on-1,1-dioxide or *o*-benzosulfimide) is best known and widely used as a non-caloric artificial sweetener and is commercially available as water-soluble alkali salts [1]. Due to the suspected carcinogenicity of this compound [2–6], its interaction with some biologically relevant metal ions has received much attention and the studies showed that in the deprotonated form, the saccharinate anion (sac) it is a good complexing agent in coordination

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chemistry acting as a polyfunctional ligand due to the presence of several potential sites such as the imino nitrogen, carbonyl oxygen, or sulfonyl oxygen atoms. Most of the initially prepared complexes were the mixed-aqua saccharinato complexes, in which sac is coordinated through the negatively charged nitrogen atom [7–11]. Metal complexes and coordination modes of sac have been reviewed by Baran [12].

Our own interest is to prepare a series of metal–sac complexes with chelating ligands. As an extension of these studies, we describe the synthesis, spectroscopic, thermal and structural characterization of a copper(II) complex of sac with ethylenediamine (en), *trans*-$[Cu(sac)_2(en)_2]$.

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 [13].

2.2. *Preparation of the complex*

Piperazine (ppz) (0.34 g, 4.0 mmol) dissolved in butanol (15 cm^3) was mixed with a solution of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ (0.54 g, 1 mmol) in butanol (30 cm^3) and stirred for 1 h at room temperature. Pale purple crystals of the title complex suitable for X-ray diffraction were obtained by slow evaporation at room temperature within two days. Yield 86%, m.p. 225°C (Found: C, 39.3; H, 4.5; N, 15.5; S, 11.5; $C_{18}H_{24}N_6O_6S_2Cu$ Calcd: C, 39.4; H, 4.4; N, 15.3; S, 11.7).

2.3. *Physical measurements*

IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets in the frequency range 4000–400 cm^{-1}. Electronic spectra of the aqueous solutions were measured on a Unicam UV2 in the 200–900 nm range. The elemental analyses (C, H, N and S contents) were performed on a Vario EL Elemental Analyser. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Evans magnetic balance. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer with a heating rate of 10°C min^{-1} in a static air atmosphere, using platinum crucibles. A sample size of 5–10 mg was used and sintered α-alumina was used as the reference material.

2.4. *X-ray structure determination*

Intensity data for the title compound were collected using a Nonius Kappa CCD area detector diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å) at 120 K. The structure was solved with SHELXS-97 [14] and refined using SHELXL-97 [15]. All the non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included using a riding model in idealised positions. The details of data collection, refinement and crystallographic data are summarized in table 1.

Table 1. Crystallographic data for $[Cu(sac)_2(en)_2]$.

Compound	$[Cu(sac)_2(en)_2]$
Empirical formula	$C_{18}H_{24}N_6O_6S_2Cu$
M_r	548.10
T (K)	120(2)
Radiation, λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	7.0215(3)
b (Å)	7.9489(4)
c (Å)	11.2929(6)
α (°)	102.668(3)
β (°)	99.411(3)
γ (°)	110.181(3)
V (Å^3)	557.16(3)
Z	1
D_c (g cm^{-3})	1.634
μ (mm^{-1})	1.217
F (000)	283
Crystal size (mm^3)	$0.12 \times 0.08 \times 0.04$
θ range (°)	2.93–27.60
Index range (h, k, l)	$-8/9, -10/10, -14/14$
Reflections collected	11927
Independent reflections (R_{int})	2567 (0.047)
Absorption correction	Multi-scan
Min. and max. transmissions	0.868 and 0.953
Data/restraints/parameters	2574/0/152
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	0.0352
R indices (all data)	0.0440
Largest diff. peak and hole (e Å^{-3})	0.436 and −0.617

3. Results and discussion

3.1. *Synthesis*

The aim of the study was to prepare a mixed-ligand sac complex of copper(II) with a co-ligand ppz. However, the reaction of ppz with $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ in butanol accidentally yielded the title complex *trans*-$[Cu(sac)_2(en)_2]$. The formation of the en molecule may be attributed to decomposition of the ppz molecule to en during the reaction. In fact, ppz is found as an intermediate in the reaction pathways for the catalytic formation of en from ethanolamine [16]. Therefore, conversion of ppz to en or vice versa seems to be possible in the present reaction medium. In the starting $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ complex, the four aqua ligands weakly coordinate to copper(II) and formation of en resulted in the replacement of these aqua ligands by two en ligands, forming a solid complex *trans*-$[Cu(sac)_2(en)_2]$ in over 85% yield. The title complex is not soluble in water, but sparingly soluble in warm MeOH, EtOH and ButOH. The complex is non-hygroscopic and stable in air.

3.2. *Spectral and magnetic properties*

The assignments of the most important IR bands of the copper(II) complex are listed in table 2, together with those of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ for comparison.

Table 2. Selected IR spectral data[a] for $[Cu(sac)_2(en)_2]$ and $[Cu(sac)_2(H_2O)_4] \cdot H_2O$.

Assignment	$[Cu(sac)_2(en)_2]$	$[Cu(sac)_2(H_2O)_4] \cdot H_2O$
ν(OH)	–	3500–3100s, b
ν(NH)	3342m, 3276w	–
ν(CH)	3057w, 2962w	3090w
ν(CO)	1643vs	1610vs
ν(CC)	1581vs	1570vs
ν(CC)	1456m	1479s
ν_s(CNS)	1327s	1354m
$\nu_{as}(SO_2)$	1281sh, 1254vs	1280vs
$\nu_s(SO_2)$	1140vs	1150vs
ν_{as}(CNS)	951vs	942vs

[a] Frequencies in cm^{-1}. b = broad; w = weak; vs = very strong; s = strong; sh = shoulder; m = medium.

The absorption bands between 3342 and 3276 cm^{-1} are characteristic of ν(NH) vibrations of the en ligand. The relatively weak absorption bands in the range 2960–3060 cm^{-1} are assigned to the ν(CH) vibrations. The stretching vibration of the carbonyl group of sac is observed at 1643 cm^{-1} as a very strong absorption band and appears at significantly higher frequency compared to $[Cu(sac)_2(H_2O)_4] \cdot H_2O$ (table 2), in spite of the fact that the sac ligands in both complexes are *N*-bonded. Due to intra- and intermolecular interactions such as hydrogen bonds, the ν(C=O) frequency often does not correlate to the coordination mode of the ligand [17]. The bands with strong intensity around 1580 and 1460 cm^{-1} correspond to the ν(CN) and ν(CC) vibrations of the aromatic ring, respectively. The absorption bands of the CNS moiety of sac occur at ca 1330 and 950 cm^{-1}. The $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$ modes of sac appear as very strong bands at approximately 1280 and 1150 cm^{-1}, respectively. The weak bands located at 447 and 517 cm^{-1} are indicative of Cu–N bonds [18].

The electronic spectrum of the copper(II) complex could not be obtained due to its low solubility. The room-temperature magnetic moment measurements show that the copper(II) complex is paramagnetic with a μ_{eff} of 1.8 BM, in good agreement with the expected μ_{eff} value of 1.73 BM for a spin-only d^9 system.

3.3. *Thermal analysis*

The thermal decomposition behaviour of *trans*-$[Cu(sac)_2(en)_2]$ was followed up to 600°C under atmospheric conditions. The compound does not melt and is thermally stable up to 225°C and then begins to decompose. The elimination of two en molecules takes place in the temperature range 225–365°C with two endothermic DTA peaks at 265 and 307°C. The experimental mass loss of 21.8% agrees well with the calculated mass loss of 21.9%. The solid residue, presumably $[Cu(sac)_2]$, decomposes between 370 and 522°C with two extremely exothermic DTA peaks at 426 and 464°C to give a black end product of CuO (Found 65.8%, Calcd 65.5%) as also confirmed by microanalysis.

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

The molecular structure of *trans*-$[Cu(sac)_2(en)_2]$ with the atom labelling is shown in figure 1. The selected bond lengths and angles together with the hydrogen bonding

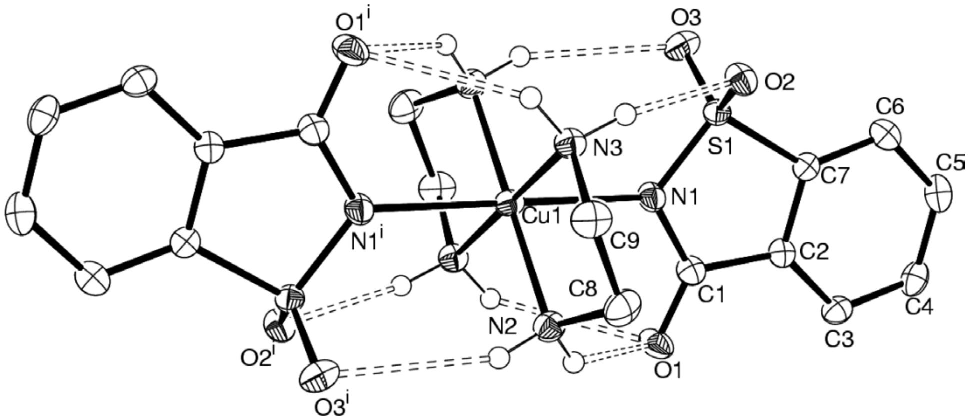

Figure 1. Molecular structure of $[Cu(sac)_2(en)_2]$ with the atom labelling scheme and 40% displacement ellipsoids (arbitrary spheres for the H atoms). All the C–H hydrogen atoms are omitted for clarity. Symmetry code (i) $= -x, -y, -z$.

geometry are listed in table 3. The structure consists of individual molecules of *trans*-$[Cu(sac)_2(en)_2]$, in which the copper(II) ion sits on a inversion centre, coordinated by two en and two sac ligands, creating an octahedral CuN_6 chromophore. Both en and sac ligands occupy the *trans* positions of the coordination octahedron. Each en ligand acts as a bidentate chelating ligand through its N atoms forming a five-membered chelate ring, while each sac ligand is *N*-bonded.

The Cu–N_{sac} bond distance of 2.466(2) Å is significantly longer than the equivalent distances found in the following octahedral complexes: $[Cu(sac)_2(H_2O)_4] \cdot H_2O$ 2.061(2) Å [19], $[Cu(sac)_2(NH_3)_4]$ [20], $[Cu(sac)_2(ea)_2]$ 2.1776(16) Å [21], $[Cu(sac)_2(pym)_2]$ 2.3345(15) Å [22], but much shorter than those found in $[Cu(sac)_2(HydEt\text{-}en)_2]$ 2.5507(14) Å [23] and $[Cu(sac)_2(ampy)_2]$ 2.662(2) Å [24] (ea = ethanolamine, pym = 2-pyridylmethanol, HydEt-en = N-(2-hydroxyethyl)-ethylendiamine and ampy = 2-aminomethylpyridine). The Cu–N_{en} bond distances ranging from 2.007(2) to 2.037(2) Å are similar to those reported for $[Cu(sac)_2(HydEt\text{-}en)_2]$ 2.0210(14) and 2.0562(13) Å [23], and $[Cu(en)_2][V_6O_{14}]$ 1.999(7) and 2.027(6) Å [25].

The larger deviations from regular octahedral geometry in the title complex are characteristic of the Jahn–Teller effect. As shown in table 3, the Cu–N_{sac} bonds occupying the axial positions are much longer than the Cu–N_{en} bonds forming the equatorial plane of the CuN_6 chromophore, resulting in usual elongated tetragonal octahedron around the copper(II) ion. The *cis* bond angles, ranging from 89.27(7) to 94.72(8)°, also show the deviation of these bonds angles from those of a regular octahedron.

The sac ligand is essentially planar with a root-mean-square (rms) deviation from the best least-squares plane of 0.016 Å for atoms C1–C7, N1, O1 and S1. The copper atom is displaced by 0.4086(18) Å from the best plane of sac. The structure of $[Cu(sac)_2(en)_2]$ exhibits an interesting hydrogen bonding scheme as listed in table 3. The amine hydrogen atoms of the en ligands form mono-, bi- and trifurcated intra- and intermolecular hydrogen bonds of the N–H···O type with the carbonyl and sulfonyl oxygen atoms of the adjacent sac ligands. This results in a one-dimensional hydrogen bonded chain (see figure 2). Some of the phenyl and ethylene hydrogen atoms are

Table 3. Selected bond lengths and angles and hydrogen bonding geometry for $[Cu(sac)_2(en)_2]$.[a]

Bond lengths (Å) and angles (°)				
Cu1–N1	2.466(2)		N1–Cu1–N3	90.73(7)
Cu1–N2	2.037(2)		N1–Cu1–N3^a	89.27(7)
Cu1–N3	2.007(2)		N2–Cu1–N3	85.28(8)
N1–Cu1–N2	89.30(7)		N2–Cu1–N3^a	94.72(8)
N1–Cu1–N2^a	90.70(7)			
Hydrogen bonds				
D–H···A	d(D–H)	d(H···11)	d(D···A)	∠(D–H···A)
N2–H9···O3^a	0.92	2.66	3.520(3)	156
N2–H10···O1	0.92	2.32	3.074(3)	139
N2–H10···O2^b	0.92	2.51	3.133(2)	125
N3–H11···O2	0.92	2.20	3.078(3)	159
N3–H12···O3^c	0.92	2.53	3.136(3)	124
N3–H12···O1^a	0.92	2.63	3.356(3)	137
N3–H12···O2^c	0.92	2.66	3.233(3)	121
C6–H4···O1^d	0.95	2.39	3.188(3)	142
C8–H6···O1^e	0.99	2.50	3.484(3)	173

[a] Symmetry operations: (a) $-x, -y, -z$; (b) $x-1, y, z$; (c) $1-x, -y, -z$; (d) $1+x, y, z$; (e) $-x, 1-y, -z$.

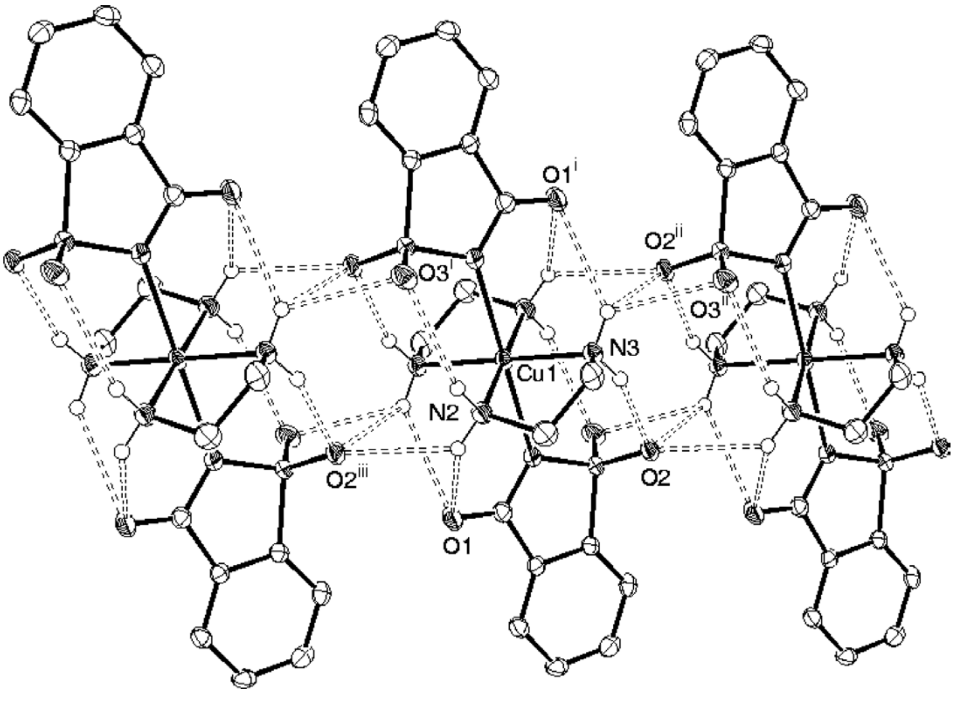

Figure 2. A fragment of a hydrogen bonded chain of $[Cu(sac)_2(en)_2]$ molecules involving bi- and trifurcated hydrogen bonds. Symmetry codes (i) $= -x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $x-1, y, z$.

also involved in relatively weak C–H···O interactions with the carbonyl oxygen atoms of the neighboring sac ligands. As shown in figure 3, the hydrogen bonded chains running along the *a* axis are further connected by weak aromatic π(sac)–π(sac) interactions [$C_g \cdots C_g^i$ 3.7210(14) Å; C_g = centroid of atoms C2–C7; (i): $1-x$, $1-y$, $1-z$)], forming a three-dimensional supramolecular network.

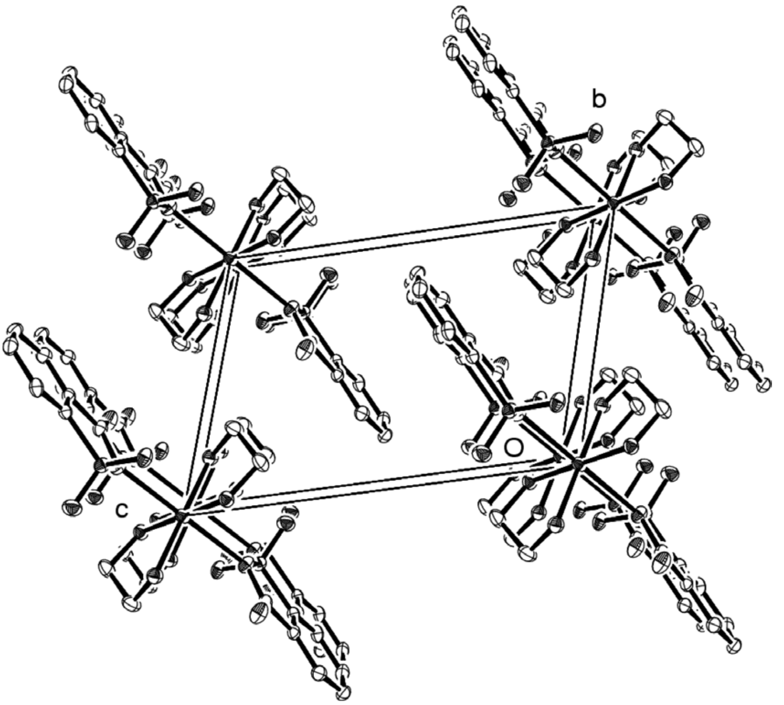

Figure 3. Packing diagram of [Cu(sac)$_2$(en)$_2$] viewed along the *a* axis. All H atoms omitted for clarity.

Supplementary material

Crystallographic data for the structure reported in the article have been deposited at the CCDC as supplementary data, CCDC No. 280023. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk

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