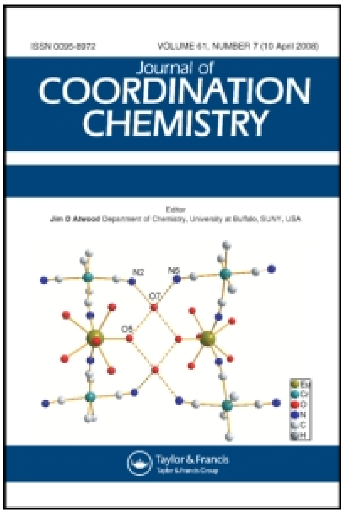

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Synthesis, crystal structure, spectroscopic and thermal properties of *trans*-[Ni(sac)$_2$(aeppz)$_2$] [sac = saccharinate and aeppz = <i>N</i>-(2-aminoethyl)piperazine]

Serkan Guney[a]; Veysel T. Yilmaz[a]; William T. A. Harrison[b]
[a] Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey [b] Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland, UK

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Synthesis, crystal structure, spectroscopic and thermal properties of *trans*-[Ni(sac)$_2$(aeppz)$_2$] [sac = saccharinate and aeppz = *N*-(2-aminoethyl)piperazine]

SERKAN GUNEY†, VEYSEL T. YILMAZ*†
and WILLIAM T. A. HARRISON‡

†Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis
University, 55139 Kurupelit, Samsun, Turkey
‡Department of Chemistry, University of Aberdeen, Meston Walk,
Aberdeen AB24 3UE, Scotland, UK

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A nickel(II) complex of saccharinate (sac) with *N*-(2-aminoethyl)piperazine (aeppz), *trans*-[Ni(sac)$_2$(aeppz)$_2$], has been prepared and characterized by elemental analyses, IR, UV-vis, magnetic measurements and single crystal X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ (No. 2). The nickel(II) ion sits on an inversion centre and is octahedrally coordinated by two neutral aeppz and two anionic sac ligands. The aeppz ligand is bidentate (N,N′) chelating, while sac is O-coordinated through the carbonyl O atom. The IR spectrum of [Ni(sac)$_2$(aeppz)$_2$] displays typical absorption bands of bidentate aeppz and O-bonded sac ligands. Under atmospheric conditions, [Ni(sac)$_2$(aeppz)$_2$] is thermally stable up to 220°C, but at higher temperatures, loses two aeppz ligands between 220 and 317°C and two sac ligands in the temperature range 320–528°C, giving NiO as end product.

Keywords: *N*-(2-Aminoethyl)piperazine; Saccharinate; Nickel(II) complex; Crystal structure

1. Introduction

Saccharin ($C_7H_5NO_3S$, also named 1,2-benzoisothiazol-3(2*H*)-on-1,1-dioxide or *o*-benzosulfimide) is widely used as a non-caloric artificial sweetener [1] and is commercially available as water soluble alkali salts. The presence of several potential sites such as the imino nitrogen, carbonyl oxygen, or sulfonyl oxygen atoms makes it a good candidate as a complexing agent in coordination chemistry. Although no metal complexes of neutral saccharin are known, the corresponding, deprotonated, saccharinate anion (sac) acts as a polyfunctional ligand. The most common coordination mode of sac is ligation through the negatively charged nitrogen atom, usually observed

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*Corresponding author. Email: vtyilmaz@omu.edu.tr

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in aqua bis(saccharinato) complexes of metal(II) [2–6] and O-coordination usually occur in the case of *s*- or *p*-block metals [7–10].

The interest of this study is to prepare a series of metal-sac complexes with a second chelating ligand, especially containing hydroxyalkyl and aminoalkyl groups. As an extension of these studies, the synthesis, spectroscopic, thermal and structural characterization of a nickel(II) complex of sac with *N*-(2-aminoethyl)piperazine (aeppz), *trans*-[Ni(sac)$_2$(aeppz)$_2$] are described.

2. Experimental

2.1. *Materials*

All reagents were purchased from commercial sources and used as supplied. The starting complex [Ni(sac)$_2$(H$_2$O)$_4$] $\cdot$ 2H$_2$O was prepared according to the literature method [11].

2.2. *Preparation of the complex*

The aeppz ligand (0.26 g, 2.0 mmol) was added drop-wise to a solution of [Ni(sac)$_2$(H$_2$O)$_4$] $\cdot$ 2H$_2$O (0.53 g, 1 mmol) in EtOH (30 cm^3) and stirred for 1 h at room temperature. X-ray quality pale blue crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of the resulting solution into ether after 2 days. Yield 90%. decomp. point 220°C (Found: C, 45.6; H, 5.7; N, 16.5; S, 9.3; $C_{26}H_{38}N_8O_6S_2Ni$ calcd: C, 45.8; H, 5.6; N, 16.4; S, 9.4).

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. 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 [thermogravimetric analysis (TGA) and differential thermal analysis (DTA)] were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere. A sample size of 5–10 mg was used.

2.4. *X-ray structure determination*

Intensity data for the title compound were collected using a BRUKER SMART 1000 CCD area detector diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å) at 293 K. The structure was solved with SHELXS-97 and refined using SHELXL-97 [12]. All the non-hydrogen atoms were refined with anisotropic displacement 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. The details of data collection, refinement and crystallographic data are summarized in table 1.

Table 1. Crystallographic data for [Ni(sac)$_2$(aeppz)$_2$].

Compound	[Ni(sac)$_2$(aeppz)$_2$]
Empirical formula	$C_{26}H_{38}N_8O_6S_2Ni$
M_r	681.48
T (K)	293(2)
Radiation, λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	8.4729 (4)
b (Å)	9.3424 (4)
c (Å)	11.5734 (5)
α (°)	93.621 (1)
β (°)	110.280 (1)
γ (°)	116.854 (1)
V (Å^3)	739.76 (6)
Z	1
D_c (g/cm^3)	1.530
μ (mm^{-1})	0.853
F(000)	358
Crystal size (mm^3)	$0.49 \times 0.23 \times 0.22$
θ range (°)	1.94–32.48
Index range (h, k, l)	−9/12, −14/13, −17/15
Reflections collected	9654
Independent reflections (R_{int})	4056 (0.0151)
Absorption correction	Multi-scan
Min and max transmissions	0.680 and 0.835
Data/restraints/parameters	5173/0/196
Goodness-of-fit on F^2	0.967
Final R indices [$I > 2\sigma(I)$]	0.0331
R indices (all data)	0.0462
Largest diff. peak and hole (e Å^{-3})	0.399 and −0.327

3. Results and discussion

3.1. *Synthesis*

The title complex *trans*-[Ni(sac)$_2$(aeppz)$_2$] was synthesized by direct reaction of equimolar quantities of the aeppz ligand and [Ni(sac)$_2$(H$_2$O)$_4$]$\cdot$2H$_2$O in solution. In the starting complex [Ni(sac)$_2$(H$_2$O)$_4$]$\cdot$2H$_2$O, the two sac ligands occupy *trans* positions of the coordination octahedron around nickel(II). The four aqua ligands weakly coordinate to nickel(II); addition of the aeppz ligand resulted in the replacement of these aqua ligands by two aeppz ligands, forming a solid complex [Ni(sac)$_2$(aeppz)$_2$] in good yield. [Ni(sac)$_2$(aeppz)$_2$] is not soluble in common solvents, but sparingly soluble in warm MeOH. The complex is non-hygroscopic and stable in air.

3.2. *Spectral and magnetic properties*

Selected IR bands of the nickel(II) complex, together with their assignments are listed in table 2. For comparative purposes, the IR data for [Ni(sac)$_2$(H$_2$O)$_4$]$\cdot$2H$_2$O are also given [4, 11]. The absorption bands of the NH groups in the nickel(II) complex are observed as a strong band centered at 3300 cm^{-1} and are significantly shifted to lower frequency, compared to the

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

Assignment	$[Ni(sac)_2(aeppz)_2]$	$[Ni(sac)_2(H_2O)_4] \cdot H_2O$
ν(OH)	—	3363s
ν(NH)	3300vs, 3288sh	—
ν(CH)	2981m, 2953w	3117w
ν(CO)	1614vs	1630vs
ν(CN)	1593sh	—
ν(CC)	1570vs	1583vs
ν(CC)	1462s	1471vs
ν_s(CNS)	1367s	1359m
$\nu_{as}(SO_2)$	1286vs	1295vs, 1267vs
$\nu_s(SO_2)$	1159vs	1165vs
ν_{as}(CNS)	943vs	969m

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

free ligand (3415 cm^{-1}). The relatively low frequency of the band is indicative of hydrogen bonding. The relatively weak bands around 3000 cm^{-1} are assigned to the $\nu(CH_2)$ mode of ethylene groups. The absorption band of the carbonyl group of sac in the title complex is observed at 1614 cm^{-1} as a very strong band. The carbonyl vibration frequency of the carbonyl group of sac in $[Ni(sac)_2(aeppz)_2]$ shifts to lower frequency by *ca.* 16 cm^{-1} compared to the starting complex $[Ni(sac)_2(H_2O)_4] \cdot 2H_2O$ with two N-bonded sac ligands, indicating O-coordination of the sac ligand through the carbonyl group in the title complex. The bands between 1580 and 1460 cm^{-1} correspond to the ring ν(CC) vibrations. The symmetric and asymmetric absorption bands of the CNS moiety of sac in $[Ni(sac)_2(aeppz)_2]$ are observed at *ca.* 1365 and 945 cm^{-1}, while the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibrations bands of sac appear as very strong bands centered at 1285 and 1160 cm^{-1}.

The electronic spectrum of the aqueous solution of the nickel(II) complex displays two distinct absorption bands at 369 nm ($\varepsilon = 17\,dm^3\,mol^{-1}\,cm^{-1}$) and at 610 nm ($\varepsilon = 7\,dm^3\,mol^{-1}\,cm^{-1}$) assigned to *d*–*d* transitions. The absorption bands below 300 nm are due to intra-ligand electronic transitions of sac and aeppz.

The room temperature magnetic moment measurements show that the nickel(II) complex is paramagnetic with a μ_{eff} of 2.8 BM, in good agreement with the expected μ_{eff} value of 2.83 BM for a spin-only d^8 system.

3.3. *Thermal analysis*

Thermal behavior of the title compound was followed up to 800°C under atmospheric conditions. It does not melt and the compound is thermally stable up to 220°C and then begins to decompose. The elimination of two aeppz molecules takes place in the temperature range 220–317°C with two exothermic DTA peaks at 252 and 295°C. The experimental mass loss of 37.5% agrees well with the calculated mass loss of 37.9%. The solid residue consisting of mainly nickel and sac decomposes between 320 and 528°C with an extremely exothermic DTA peak at 464°C to give a grey–black end product of NiO (found 54.2%, calcd 53.5%) as also confirmed by microanalysis.

3.4. *Description of the crystal structure of [Ni(sac)$_2$(aeppz)$_2$]*

The molecular structure of [Ni(sac)$_2$(aeppz)$_2$] with the atom labeling is shown in figure 1. The selected bond lengths and angles together with the hydrogen bonding geometry are listed in table 3. The structure consists of individual molecules of [Ni(sac)$_2$(aeppz)$_2$], in which the nickel(II) ion sits on an inversion center, coordinated by two ampy and two sac ligands, thus forming an octahedral NiN$_4$O$_2$ chromophore. Both aeppz and sac occupy the *trans* positions of the coordination octahedron. Each aeppz ligand acts as a bidentate chelating ligand through one of the ring N atoms and the hydroxyamino N atom, forming a five-membered chelate ring around nickel(II), while each sac ligand is O-bonded.

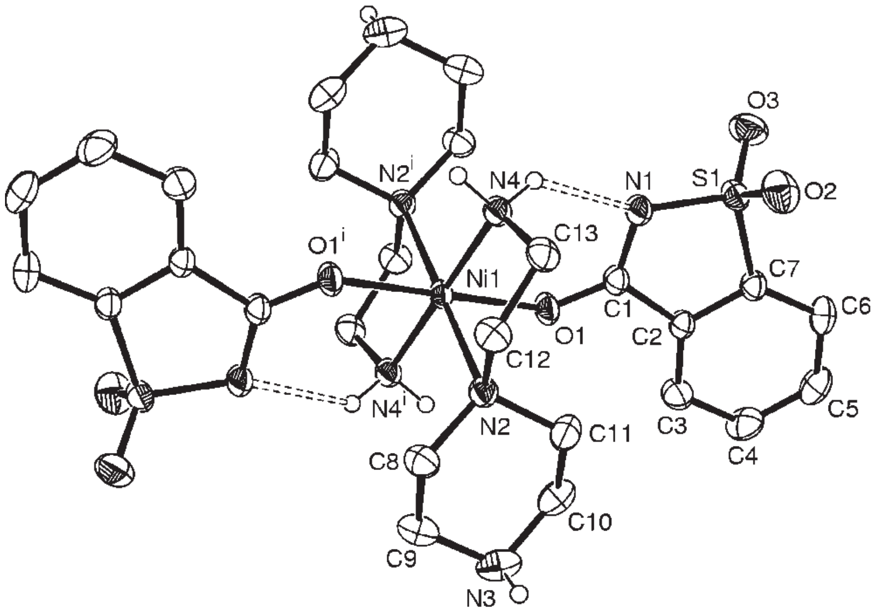

Figure 1. Molecular structure of [Ni(sac)$_2$(aeppz)$_2$] with the atom labeling scheme and 40% thermal ellipsoids (arbitrary spheres for the H atoms). All C–H hydrogen atoms are omitted for clarity. Symmetry code (i) = $-x$, $-y$, $-z$.

Table 3. Selected bond lengths and angles and hydrogen bonding geometry for [Ni(sac)$_2$(aeppz)$_2$]*.

Bond lengths (Å) *and angles* (deg)				
Ni1–O1	2.0932(9)	O1–Ni1–N4	92.48(4)	
Ni1–N2	2.3099(11)	O1–Ni1–N4^{a}	87.52(4)	
Ni1–N4	2.0688(11)	N2–Ni1–N4	82.10(4)	
O1–Ni1–N2	92.26(4)	N2–Ni1–N4^{a}	97.90(4)	
O1–Ni1–N2^{a}	87.74(4)			
Hydrogen bonds				
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(D–H···A)
N4–H18···N1	0.90	2.26	2.9651(16)	135
N4–H19···N3^{b}	0.90	2.39	3.2062(18)	151
N3–H17···O2^{c}	0.90	2.17	3.0519(19)	166
C4–H2···O3^{d}	0.93	2.55	3.382(2)	150
C13–H15···O2^{e}	0.97	2.59	3.4383(19)	147

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

The coordination of sac to the transition metal ions using the donor groups other than the amine nitrogen atom is unusual and the only examples of O-coordination reported previously in mononuclear nickel(II) complexes are $[Ni(sac)_2(py)_4]\cdot 2py$ [13], $[Ni(sac)_2(mpy)_2]$ (mpy = 2-methanolpyridine) [14], $[Ni(sac)_2(pypr)_2]$ (pypr = 2-pyridinepropanol) [15], and $[Ni(sac)_2(aepy)_2]$ (aepy = 2-aminoethylpyridine) [16]. Therefore, the most interesting aspect of the title complex is the O-coordination of the sac ligands via the carbonyl oxygen. Except $[Ni(sac)_2(py)_4]\cdot 2py$ [5], it may be said that the O-coordination of the sac ligands in the title complex and the reported complexes may be attributed to the presence of hydroxyalkyl and hydroxyamino spacers and their steric hindrance, which prevents coordination of sac through the N atom.

The $Ni–O_{sac}$ bond distance of 2.0932(9) Å is comparable to the equivalent distances found in $[Ni(sac)_2(py)_4]\cdot 2py$ [13], $[Ni(sac)_2(mpy)_2]$ [14], $[Ni(sac)_2(pypr)_2]$ [15], and $[Ni(sac)_2(aepy)_2]$ [16]. The $Ni–O_{sac}$ and $Ni–N_{hydoxyamino}$ bond distances are almost identical, but the $Ni–N_{ppz–ring}$ bond distance of 2.3099(11) Å shows that the two $Ni–N_{ppz–ring}$ bonds are significantly longer than the other four bonds around nickel(II), resulting in an elongated octahedron. This may be due to the molecular conformation of the ppz ring. The puckering parameters [17] of the ppz ring system in $[Ni(sac)_2(aeppz)_2]$ are $q = 0.5328(18)$ Å and $\theta = 6.67(19)^\circ$, suggesting that the ppz ring exhibits an essentially "undistorted" (cyclohexane like) chair conformation, so that the sp^3 lone pair on the N2 atom does not completely overlap with the valence orbitals of the nickel(II) ion. The Ni species is axial to the ring atoms. The poor overlap results in lengthening of the $Ni–N_{ppz–ring}$ bonds. The bond angles involving the nickel and N2 atoms are Ni–N2–C8 = 118.24(8)°, Ni–N2–C11 = 115.80(8)° Ni–N2–C12 = 99.05(8)°, which also show deviation from regular tetrahedron. Distortions in the Ni coordination polyhedra from ideal octahedral geometry are also clearly evident from the *cis* angles, which are in the range 82.10(4)°–97.90(4)°. The H atom attached to N3 is in an axial position, which facilitates N3 accepting an intermolecular H bond (table 3).

The sac ligand is essentially planar with root-mean-square (rms) deviation from the best least-squares plane of 0.028 Å for the non-H atoms excluding O2 and O3. The Ni atom deviates from the best plane of sac by 0.6746(14) Å. The packing diagram of $[Ni(sac)_2(aeppz)_2]$ is presented in figure 2. The amine hydrogen atoms of the ampy ligands form intra- and inter-molecular hydrogen bonds with the imino N, carbonyl or sulfonyl O atoms of the adjacent sac ligands. Some of the phenyl and ethylene hydrogen atoms of sac and aeppz are also involved in relatively weak C–H···O interactions with the sulfonyl O atoms of the adjacent sac ligands. Furthermore, the sac ligands form weak π–π interactions with their inversion-symmetry generated partners [$C_g \cdots C_g^i$ 3.906(2) Å; C_g = centroid of atoms C2–C7; (i): $-x$, $-y$, $1-z$)]. Thus, the molecular packing is reinforced by hydrogen bonds and aromatic π–π stacking interactions forming a three-dimensional network as shown in figure 2.

Supplementary material

Crystallographic data for the structure reported in the paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary data, CCDC No. 254840. 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

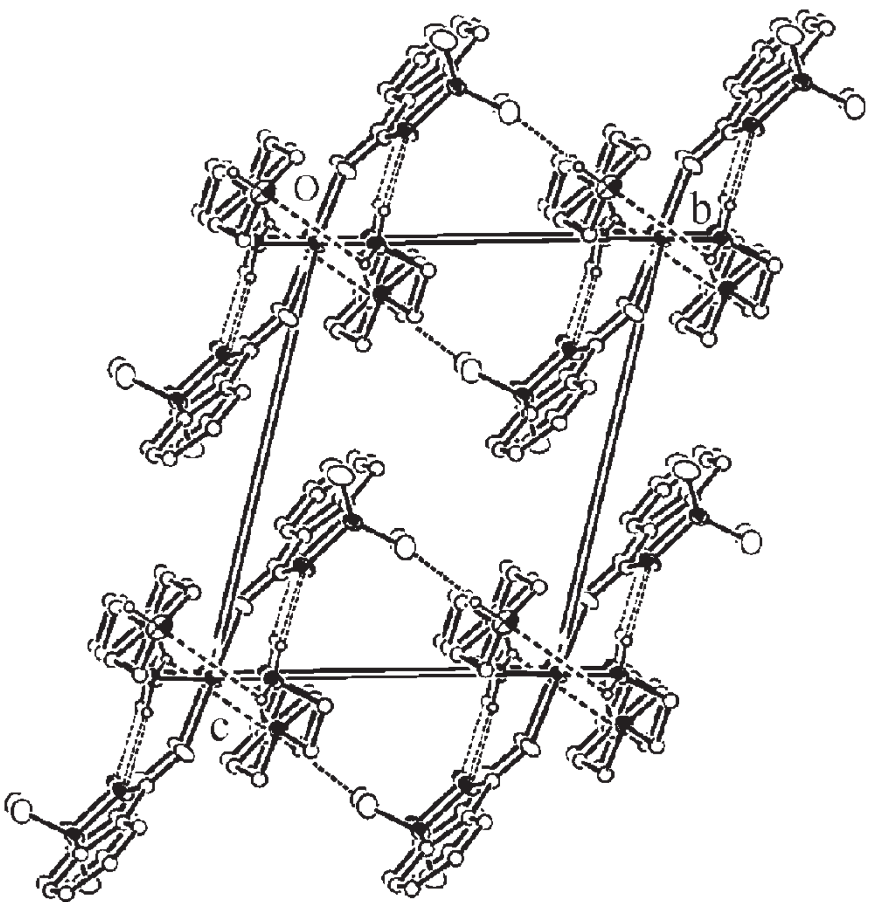

Figure 2. Packing diagram of [Ni(sac)$_2$(aeppz)$_2$] viewed along the *a* axis. All C–H hydrogen atoms are omitted for clarity and hydrogen bonds are indicated by dashed lines.

Acknowledegments

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