

## BIS(*N,N'*-BIS(2-HYDROXYETHYL)ETHYLENEDIAMINE)NICKEL(II) SACCHARINATE: SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE<sup>♦</sup>

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A new nickel(II) saccharinate (sac) complex containing *N,N'*-bis(2-hydroxyethyl)ethylenediamine (bishydeten), [Ni(bishydeten)<sub>2</sub>](sac)<sub>2</sub>, has been synthesized and characterized by elemental analysis, FTIR and single crystal X-ray diffraction. The title complex consists of a [Ni(bishydeten)<sub>2</sub>]<sup>2+</sup> cation and two sac anions. In the complex cation, the nickel(II) ion is coordinated by two neutral bishydeten ligands, leading to a distorted octahedral NiN<sub>4</sub>O<sub>2</sub> coordination, while both sac anions remain outside the coordination sphere. In the crystal, the complex cations and sac anions are connected by an extensive network of N–H⋯N, N–H⋯O, O–H⋯O and C–H⋯O hydrogen bonds into a three-dimensional supramolecular lattice.

**Keywords:** saccharinate; *N,N'*-bis(2-hydroxyethyl)ethylenediamine; nickel(II); crystal structure

## БИС(*N,N'*-БИС(2-ХИДРОКСИЕТИЛ)ЕТИЛЕНДИАМИН)НИКЕЛ(II) САХАРИНАТ: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И КРИСТАЛНА СТРУКТУРА

Со помош на анализа на елементите, Фуриеова трансформна инфрацрвена спектроскопија и рендгенска дифракција на монокристал, е синтетизиран и карактеризиран нов никел(II)сахаринатен (sac) комплекс кој содржи *N,N'*-бис(2-хидроксиетил)етилендиамин (bishydeten), [Ni(bishydeten)<sub>2</sub>](sac)<sub>2</sub>. Изучуваното соединение се состои од катјони на [Ni(bishydeten)<sub>2</sub>]<sup>2+</sup> и два сахаринатни (sac) анјони. Јонот на никел(II) во комплексниот катјон е координиран со два неутрални бидентатни лиганда, постигнувајќи координација на деформиран октаедар од типот NiN<sub>4</sub>O<sub>2</sub>, додека двата сахаринатни (sac) анјона остануваат надвор од координационата сфера. Во кристалот комплексните катјони и сахаринатните (sac) анјони се поврзани преку екстензивна мрежа од водородни врски N–H⋯N, N–H⋯O, O–H⋯O и C–H⋯O, формирајќи притоа тридимензионална супрамолекуларна решетка.

**Клучни зборови:** сахаринат; *N,N'*-бис(2-хидроксиетил)етилендиамин; никел(II); кристална структура

### 1. INTRODUCTION

Saccharin (SacH, 1,2-benzisothiazoline-3-(2H)one 1,1-dioxide or *O*-sulfobenzimide) is a well-known artificial sweetening agent and commercially available as the sodium salt. SacH has a dissociable imine proton and is readily deprotonated in solutions to form the corresponding saccharinate anion (sac). The sac anion contains a

deprotonated imine nitrogen, a carbonyl and two sulfonyl oxygen atoms, and the presence of these donor groups makes it an interesting polyfunctional ligand in coordination chemistry. Sac forms different metal complexes ranging from mononuclear species to coordination polymers and supramolecular assemblies [1]. In most cases, the sac anion is directly bonded to the metal ions via the negatively charged N atom. However, the presence

<sup>♦</sup>Dedicated to Academician Gligor Jovanovski on the occasion of his 70<sup>th</sup> birthday.

of bulky ligands such as triethanolamine [2–5], 2,6-pyridinedimethanol [6, 7] usually prevents the coordination of sac to the metal ions, remaining it outside the coordination sphere as a counter-ion.

As a continuation of our work on the synthesis and structures of metal complexes of sac, in this paper we report the synthesis, characterization and crystal structure of a new nickel(II) saccharinate complex with the *N,N'*-bis(2-hydroxyethyl)ethylenediamine(bishydeten) ligand, namely  $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$ .

## 2. EXPERIMENTAL

### 2.1. Materials and measurements

All chemicals were purchased and used as supplied. The elemental analyses (C, H and N) were performed on a LECO, CHNS-932 elemental analyzer. FTIR spectra were recorded on a Jasco FT/IR 430 FTIR spectrophotometer in the frequency range 4000–400  $\text{cm}^{-1}$ .

### 2.2. Synthesis of $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$

The starting nickel(II) complex of sac,  $[\text{Ni}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  was prepared according to the conventional methods described in the literature [8, 9].  $[\text{Ni}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  (1.0 mmol) was dissolved in water (25 ml) and mixed with a solution of the bishydeten ligand (2.0 mmol) in MeOH (15 ml) with continuous stirring at ca. 70 °C for 30 min. The resulting solution was left to stand at room temperature and allowed to evaporate slowly over a few days for crystallization. The blue prismatic crystals of  $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$  were collected by suction filtration, washed with water and dried in air. Yield 32%, m.p. 170 °C. Anal. for  $\text{C}_{26}\text{H}_{40}\text{S}_2\text{O}_{10}\text{N}_6\text{Ni}$  ( $M_w$  719.41). Found %: C, 43.14; H, 5.41; N, 11.51. Calculated %: C, 43.40; H, 5.60; N, 11.68%. Selected IR data ( $\nu$ ,  $\text{cm}^{-1}$ ), 3403s, 3245m, 2964w, 2923w, 2879vw, 1640vs, 1536s, 1455m, 1338m, 1280s, 1149vs, 948m. UV-Vis  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ): 235 (39260), 256 (16260), 285 (12568), 582 (67).

### 2.3. X-ray crystallography

The intensity data for  $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$  were collected using a Rigaku R-AXIS RAPID-S diffractometer using Mo  $K_\alpha$  radiation (0.71073 Å). The structure was solved by direct methods and refined against  $|F|^2$  with the SHELX-97 program [10]. All non-hydrogen atoms were found from the difference Fourier map and refined

anisotropically, while all hydrogen atoms were placed and refined using a riding model. The details of data collection, refinement and crystallographic data are summarized in Table 1. CCDC 1041136 contains the supplementary crystallographic data reported in this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Table 1

### Crystal data and structure refinement details for $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$

CCDC deposition number	1041136
Empirical formula	$\text{C}_{26}\text{H}_{40}\text{N}_6\text{O}_{10}\text{S}_2\text{Ni}$
Formula mass	719.5
Crystal system	monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	13.1730(5)
<i>b</i> (Å)	9.3860(5)
<i>c</i> (Å)	25.9630(5)
$\beta$ (°)	100.534(5)
<i>V</i> (Å <sup>3</sup> )	3156.01(37)
<i>Z</i>	4
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.514
$\mu$ (mm <sup>-1</sup> )	0.811
<i>F</i> (000)	1512
$\theta$ range (°)	2.3–30.5
Refls. collected	87408
Refls. independent	9637 ( $R_{\text{int}} = 0.0685$ )
Absorption correction	multiscan
GOF on $F^2$	1.070
$R_1$ [ $I > 2\sigma(I)$ ]	0.0455
$wR_2$ (all data)	0.1079

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis and characterization

The title nickel(II) complex was synthesized from the reaction of  $[\text{Ni}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ , with the bishydeten ligand. The aqua ligands in  $[\text{Ni}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  are very labile and readily displaced by neutral ligands. However, the addition of the bulky bishydeten ligand to the solution of the starting complex resulted in the substitution of both two aqua and two sac ligands, and the formation of an air-stable complex of  $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$ . The elemental analysis data confirm the formula of the complex. The complex is soluble in water, DMSO and DMF.

The IR spectrum of the title complex displays characteristic bands of the bishydeten ligands and sac anions. The absorption bands centered at *ca.* 3400 cm<sup>-1</sup> and 3245 correspond to the  $\nu(\text{OH})$  and  $\nu(\text{NH})$  vibrations of the bishydeten ligand, respectively. The  $\nu(\text{C}=\text{O})$  vibration of sac appears at *ca.* 1640 cm<sup>-1</sup> as a very strong band, while the stretching vibrations of  $\nu_{\text{asym}}(\text{SO}_2)$  and  $\nu_{\text{sym}}(\text{SO}_2)$  occur at *ca.* 1280 and 1150 cm<sup>-1</sup>, respectively. Additional absorption bands at *ca.* 1340 and 960 cm<sup>-1</sup> are assigned to the symmetric and asymmetric stretchings of the CNS moiety of the sac anions. The electronic spectrum of the title complex exhibits three relatively sharp bands in the UV region at *ca.* 235, 256 and 285 nm, arising from intraligand transitions of the bishydeten ligand and sac anion. The broad band with very low intensity at 582 nm is assigned to a *d-d* transition.

### 3.2. Description of the crystal structure

The molecular structures of the title complex is shown in Figure 1. Selected bond lengths and angles are listed in Table 2 together with the hydrogen bonding parameters. The complex crystallizes in the monoclinic (*P*2<sub>1</sub>/*c*) crystal system. The present compound consists of a complex cation and two sac anions. In the complex cation, the nickel(II) ion is coordinated by a pair of neutral bishydeten ligands, creating a distorted NiN<sub>4</sub>O<sub>2</sub>

octahedral coordination. Each bishydeten ligand behaves as a tridentate (*N,N,O*) ligand. Although it has four donor sites, one hydroxyl O atom is non-coordinate. In addition, there is no sac in the primary coordination sphere of nickel(II) and therefore, both sac anions act as a counter-ion. The bond parameters involving the anion are similar to those found in the other metal saccharinates such as Na(sac)·2/3H<sub>2</sub>O and Mg(sac)<sub>2</sub>·7H<sub>2</sub>O [11].

The Ni–O bond distances in the complex cation are noticeably longer than the Ni–N bond distances (Table 2). Although a number of metal complexes containing the bishydeten ligand were reported earlier by our research group [12–14], its coordination to nickel(II) has been reported here for the first time.

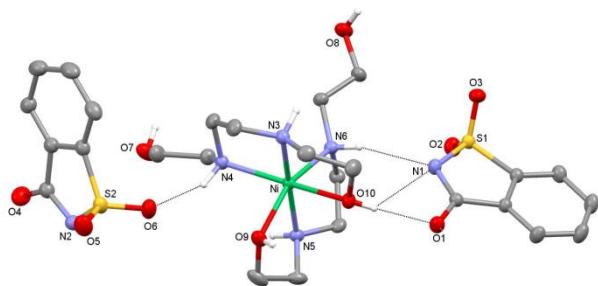
The crystal of the title complex exhibits a number of hydrogen bonds as listed in Table 2. The packing of the complex cations and sac anions is shown in Figure 2. In addition to electrostatic interactions, the cations and anions are connected by strong intermolecular N–H···N, N–H···O and N–H···O hydrogen bonds involving the NH and OH groups of the bishydeten ligands and the carbonyl and sulfonyl groups of the sac anions (Table 2). The hydrogen bonding interactions result in two-dimensional layers at the *a-b* plane (see Fig. 2), which are further connected into a three-dimensional network by weak C–H···O hydrogen bonds.

Table 2

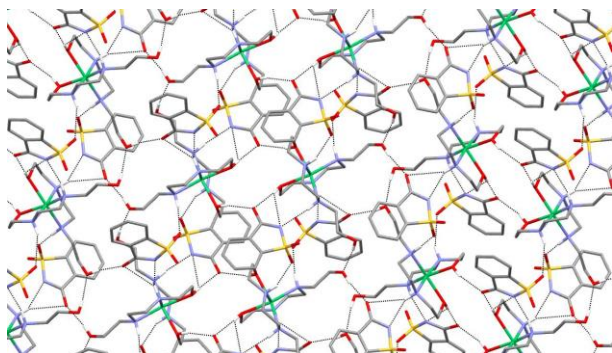
#### Selected bond and hydrogen bonding geometry for [Ni(bishydeten)<sub>2</sub>](sac)<sub>2</sub>

Ni–N3	2.0415(16)	N5–Ni–N6	83.54(7)	
Ni–N4	2.1178(17)	N3–Ni–O9	93.86(7)	
Ni–N5	2.0697(17)	N3–Ni–O10	79.16(7)	
Ni–N6	2.1111(17)	N4–Ni–O9	88.13(7)	
Ni–O9	2.1884(16)	N4–Ni–O10	159.20(6)	
Ni–O10	2.2150(16)	N5–Ni–O9	80.89(7)	
N3–Ni–N4	83.85(7)	N5–Ni–O10	96.10(6)	
N3–Ni–N5	173.46(6)	N6–Ni–O9	161.15(6)	
N3–Ni–N6	100.85(7)	N6–Ni–O10	90.00(7)	
N4–Ni–N5	99.79(7)	O9–Ni–O10	81.19(7)	
N4–Ni–N6	105.00(7)			
Hydrogen bonds				
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N4–H4···O6	0.91	2.22	3.058(3)	153
N3–H3···N2 <sup>i</sup>	0.91	2.25	3.010(3)	140
N5–H5···O3 <sup>ii</sup>	0.91	2.29	3.136(3)	155
N6–H6···N1 <sup>iii</sup>	0.91	2.33	3.188(3)	157
O7–H7···O4 <sup>iv</sup>	0.82	1.85	2.658(3)	170
O8–H8···O7 <sup>i</sup>	0.82	1.89	2.675(3)	161
O9–H9···O1 <sup>v</sup>	0.78	2.00(3)	2.758(3)	164(3)
O10–H10···O1 <sup>ii</sup>	0.80	1.93(3)	2.715(3)	169(3)

Symmetry codes: (i) *x*, –1+*y*, *z*; (ii) 1–*x*, 1–*y*, –*z*; (iii) 1–*x*, –*y*, –*z*; (iv) 1–*x*, –1/2+*y*, 1/2–*z*; (v) –1+*x*, *y*, *z*.



**Fig. 1.** A molecular view of  $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$ . All C-bound hydrogen atoms are omitted for clarity



**Fig. 2.** Packing of molecules of  $[\text{Ni}(\text{bishydeten})_2](\text{sac})_2$  viewed down  $c$ .

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