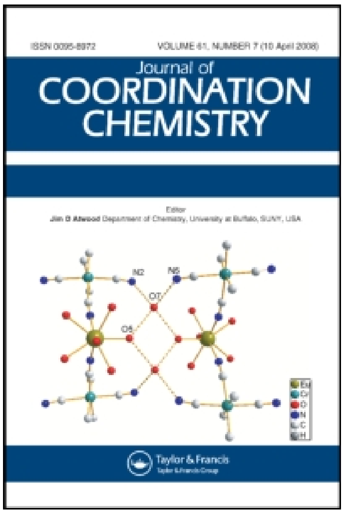

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Saccharin complexes of zinc(II) with phenanthroline and 2,9-dimethyl-1,10-phenanthroline: synthesis and characterization

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To cite this Article Raad, Afshin T. , Boghaei, Davar M. and Reza Khavasi, Hamid(2010) 'Saccharin complexes of zinc(II) with phenanthroline and 2,9-dimethyl-1,10-phenanthroline: synthesis and characterization', Journal of Coordination Chemistry, 63: 2, 273 — 283, First published on: 29 October 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903380786

URL: http://dx.doi.org/10.1080/00958970903380786

Journal of Coordination Chemistry
Vol. 63, No. 2, 20 January 2010, 273–283

Saccharin complexes of zinc(II) with phenanthroline and 2,9-dimethyl-1,10-phenanthroline: synthesis and characterization

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(*Received 10 May 2009; in final form 12 August 2009*)

The saccharinato complexes [Zn(phen)$_2$(sac)(H$_2$O)]sac (**1**) and [Zn(sac)(dmp)(H$_2$O)](sac) (**2**), where phen = 1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline, and sac = saccharinato ion/ligand, were synthesized by the reaction of [Zn(sac)$_2$(H$_2$O)$_4$] $\cdot$ 2H$_2$O with ligands and have been characterized by elemental analysis, IR, and ^{1}H NMR spectroscopies. Conductivity of complexes was measured in DMSO. Compound **1** is characterized by single crystal X-ray diffraction and compared with some isomorphous zinc-saccharinate complexes reported previously. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $Z = 2$, and consists of alternating slightly distorted octahedral [Zn(phen)$_2$(sac)(H$_2$O)]$^+$ and noncoordinated saccharinate. The zinc bound aqua is hydrogen bonded to an oxygen of carbonyl in the saccharinate ligand and the SO$_2$ group in the saccharinate counter-ion from an adjacent molecule. Intermolecular and intramolecular hydrogen bonds and C–H $\cdots$ O and C–H $\cdots$ N short contacts lead to a 3-D network.

Keywords: Zn(II) complexes; 1,10-Phenanthroline; 2,9-Dimethyl-1,10-phenanthroline; Saccharinate; Crystal structure

1. Introduction

Non-caloric artificial sweetener saccharin (also known as 1,2-benzisothiazol-3(2H)-one 1,1-dioxide or *o*-benzosulfimide) is commercially available as water-soluble alkali salts. Its deprotonated form, saccharinate (sac), is a versatile polyfunctional ligand in coordination chemistry, coordinating to metal ions through the negatively charged imino nitrogen and through the carbonyl and sulfonyl oxygens as a mono- or bidentate ligand, as well as a bridging ligand between two metal ions. This multifuctionality can be used to study the structural preferences of small heterocycles containing conjugated CO/NH or NH/SO$_2$ groups. The saccharinate exists as a counter ion, coordinated ligand, or simultaneously as ionic and coordinated species in coordination compounds.

Some compounds of saccharinate with various metal ions were suspected to be potentially carcinogenic [1–3], protease inhibitors [4, 5], mimicking superoxide

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958970903380786

dismutase (SOD) [6, 7], and antidote for metal poisoning [8, 9]. Because of the biological importance of these complexes, there have been several studies on the coordination complexes of saccharinate with a range of metal ions, especially first-row transition metal centers. Interest has been directed to the structural properties of zinc-saccharinate systems. For the synthesis of mixed-ligand saccharinate complexes, it is common to use $[Zn(sac)_2(H_2O)_4] \cdot 2H_2O$ as a synthetic precursor since the aqua ligands are labile and can be readily displaced by neutral ligands. X-ray structural characterization of the $[Zn(sac)_2(H_2O)_4] \cdot 2H_2O$ has shown this complex to be isostructural with other first-row transition metals V(II) to Cu(II)) with *trans* N-bonded saccharinate in octahedral geometry around the metal [10–14]. This zinc precursor showed an inhibitory effect over carbonic anhydrase [15] and also is a candidate for a therapeutic additive for dentifrices [16]. Because of potential pathological effects, research has expanded to include mono- (imidazole, pyridine) or polycyclic N-donor ligand (2,2′-bipyridine, 1,10-phenanthroline) adducts. Several reports about mixed ligand complexes containing saccharinate and these N-donor ligands of various first-row transition metals such as V(II) [17, 18], Cr(II) [19], Mn(II) [20–22], Fe(II) [23, 24], Co(II) [20, 25, 26], Ni(II) [26–28], and Cu(II) [29–36] were reported. A good review about metal complexes of saccharinate was published by Baran and Yilmaz [37]. So far, crystal structures of $[Zn(sac)_2(im)_2]$ [38], $[Zn(sac)_2(py)_2]$ [39], $[Zn(sac)_2(bipy)_2](H_2O)$ [29], and $[Zn(sac)(bipy)_2(H_2O)]sac$ [40] were determined by single crystal X-ray. Zinc(II)-saccharinate can form a coordination polymer in the presence of a bridging ligand such as pyrazine, as it has been found in $[Zn(sac)_2(\mu\text{-pyz})(H_2O)]_n$ [41]. Although thermal behavior of the 1,10-phenanthroline saccharinato complex of Zn(II) has been reported [42], its crystal structure has not been determined by X-ray crystallography.

In this work, we report the structure of $[Zn(phen)_2(sac)(H_2O)]sac$ (**1**) by single crystal X-ray. We also synthesized $[Zn(sac)(dmp)(H_2O)](sac)$ (**2**) by the same method. Both complexes are characterized by IR and ^1H NMR spectra and conductivity.

2. Experimental

2.1. *Materials and measurements*

All chemicals and solvents are of reagent grade, obtained from either Merck or Aldrich, and used without purification. Elemental analyses (C, H, and N) were carried out with a Heraeus Elemental Analyser CHN–O-rapid elemental analysis system, GmbH. A FTIR spectrometer (Unicam Matsum1000) was used for obtaining IR spectra in KBr pellets ($4000–400\,cm^{-1}$). ^1H NMR spectra were recorded on a Bruker FT-NMR 500 (500 MHz) spectrophotometer (DMSO-d_6 solvent). A Jenway-4010 conductivity meter was used for conductivity measurements.

2.2. *Preparation of metal complexes*

$[Zn(sac)_2(H_2O)_4] \cdot 2H_2O$ was prepared according to a method reported earlier [10]. An ethanolic solution (40 mL) of phenanthroline monohydrate (0.198 g, 1 mmol) was added dropwise to a stirred warm clear solution of $[Zn(sac)_2(H_2O)_4] \cdot 2H_2O$ (0.266 g, 0.5 mmol) in distilled water (25 mL, 80°C) and the mixture was heated on a hot plate with stirring for an hour to reduce the volume to *ca* 30 mL. The colorless solution was left undisturbed at room temperature until slow evaporation of solvent resulted in the formation of white crystals of $[Zn(sac)(phen)_2(H_2O)](sac)$. The crystals were collected by suction filtration, washed with three 5 mL portions of cold water and ethanol, and dried over silica gel. Crystals suitable for single crystal X-ray were obtained by the recrystallization of white crystals in water/ethanol 3 : 1 solution (yield *ca* 72%). Anal. Calcd for $C_{38}H_{26}ZnN_6O_7S_2$ (%): C, 56.4; H, 3.2; N, 10.4. Found (%): C, 56.2; H, 3.3; N, 10.6. IR (cm^{-1}) selected bonds: 3362 (m) ν(O–H), 1643 (vs) ν(C=O), 1301 (s) $\nu_{as}(SO_2)$, 1140 (s) $\nu_{sym}(SO_2)$, 1341 (m) ν_{sym}(CNS), 951 (s) ν_{as}(CNS). ^{1}H NMR (DMSO-d_6, 350 K) [δ (ppm)]: 2.5 (m, $2H_{H_2O}$), 7.5 (m, $4H_{sac}$), 7.6 (m, $4H_{sac}$), 8.0 (q, $4H_{phen}$), 8.3 (s, $4H_{phen}$), 8.7 (br, $4H_{phen}$), 8.9 (d, $4H_{phen}$). Electrical conductivity: (Λ_M at 10^{-3} M, 22°C, DMSO): 52 Ω^{-1} cm^2 $mole^{-1}$.

Compound **2** was prepared by following the same procedure described for **1**. The white crystals of **2** were collected (yield *ca* 69%). Anal. Calcd for $C_{28}H_{22}ZnN_4O_7S_2$ (%): C, 52.7; H, 3.1; N, 8.7. Found (%): C, 53.2; H, 3.2; N, 8.9. IR (cm^{-1}) selected bonds: 3447 (m) ν(O–H), 1651 (vs) ν(C=O), 1281 (s) $\nu_{as}(SO_2)$, 1156 (s) $\nu_{sym}(SO_2)$, 1341 (m) ν_{sym}(CNS), 963 (s) ν_{as}(CNS). ^{1}H NMR (DMSO-d_6, 350 K) [δ (ppm)]: 2.5 (m, $2H_{H_2O}$), 3.0 (m, $6H_{CH_3dmp}$) 7.6 (m, $4H_{sac}$), 7.7 (m, $4H_{sac}$), 7.9 (br, $2H_{dmp}$), 8.1 (br, $2H_{dmp}$), 8.8 (br, $2H_{dmp}$). Electrical conductivity (Λ_M at 10^{-3} M, 22°C, DMSO): 55 Ω^{-1} cm^2 $mole^{-1}$.

2.3. *X-ray crystallography*

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. A colorless plate of $C_{38}H_{26}ZnN_6O_7S_2$ having approximate dimensions of $0.30 \times 0.10 \times 0.06$ mm^3 was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 8233 unique reflections ($R_{int} = 0.0413$). Data were collected at a temperature of 293(2) K to a maximum 2θ value of 55.92° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [43] software package. The numerical absorption coefficient, μ, for Mo-Kα radiation is 0.895 mm^{-1}. A numerical absorption correction was applied using X-RED [44] and X-SHAPE [45] software. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and subsequent difference Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [46]. All hydrogen atoms were located in a difference Fourier map and then refined isotropically. Subsequent refinement converged with R factors and parameter errors were significantly better than for all attempts to model the solvent disorder. Atomic factors are from the International Tables for X-ray Crystallography [47]. All refinements were performed using the X-STEP32 crystallographic software package [48]. A summary of the crystal data, experimental details, and refinement results is given in table 1.

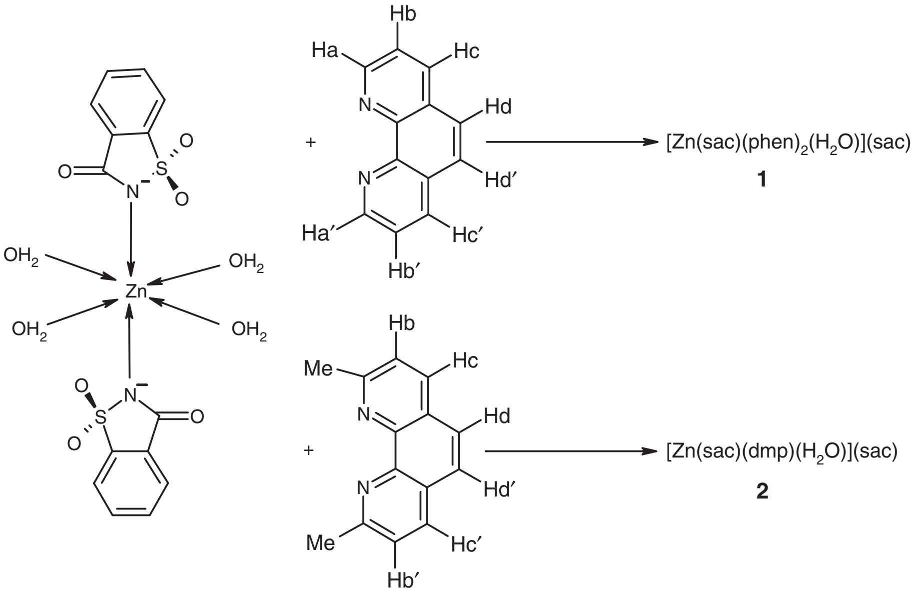
3. Results and discussion

3.1. *Synthesis*

Aqua ligands in $[Zn(sac)_2(H_2O)_4] \cdot 2H_2O$ were replaced with phenanthroline and 2,9-dimethyl-1,10-phenanthroline by direct reaction in ethanol in good yield according to the reactions shown in scheme 1.

Table 1. Crystal data and structure refinement for [Zn(sac)(phen)$_2$(H$_2$O)](sac).

Empirical formula	$C_{38}H_{26}N_6O_7S_2Zn$
Molecular weight	808.14 g
Temperature (K)	293(2)
Wavelength (Å)	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Color and description	White and plate
Unit cell dimensions (Å, °)	
a	7.9019(14)
b	14.455(3)
c	15.366(3)
α	98.202(15)
β	96.126(14)
γ	90.952(15)
Volume (Å^3), Z	1726.4(5), 2
Calculated density (mg m^{-3})	1.555
Absorption coefficient (mm^{-1})	0.895
F(000)	828
Crystal size (mm^3)	$0.3 \times 0.1 \times 0.06$
θ range for data collection (°)	1.81–27.96
Limiting indices	$-10 \le h \le 10$; $-19 \le k \le 16$; $-20 \le l \le 20$
Reflections collected	18,019
Independent reflection	8233 [$R_{\text{int}} = 0.0413$]
Completeness to $\theta = 27.96$ (%)	98.9
Absorption correction	Numerical
Max. and min. transmission	0.955 and 0.890
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8233/0/591
Goodness-of-fit on F^2	1.160
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0576$, $wR_2 = 0.0873$
R indices (all data)	$R_1 = 0.0858$, $wR_2 = 0.0946$
Largest difference peak and hole (e Å^{-3})	0.309 and −0.359



Scheme 1. Reaction pathway for the synthesis of **1** and **2**.

Addition of phen or dmp resulted in the removal of one sac and three aqua ligands from the coordination sphere. Compound **1** contains a six-coordinate metal ion in a distorted octahedral geometry; coordination environment in **2** is consistent with those previously proposed to be four-coordinate. Both complexes are soluble in water, ethanol, and DMSO and are air-stable in the solid state. Conductivity of both complexes (Λ_M at 10^{-3} M, 22°C, DMSO) was almost equal, $52\,\Omega^{-1}\,cm^2\,mol^{-1}$ for **1** and $55\,\Omega^{-1}\,cm^2\,mol^{-1}$ for **2**, in the range for 1.1 electrolytes in DMSO [49]. Thus, the number of ions in solution is almost identical for both compounds, suggesting a saccharinate counterion in each of these ionic complexes. This, together with the spectroscopic and C, H, and N analysis is in agreement with the proposed four-coordinate zinc in **2** and presence of saccharinate as a counter ion in both complexes. These results are also consistent with previous studies on zinc-related complexes, such as six-coordinate zinc complexes of $[Zn(ea)_2(sac)_2]$ [50], $[Zn(sac)_2(ampy)_2]$ [50], $[Zn(sac)(bipy)_2(H_2O)]sac$ [40] and four-coordinate zinc of $[Zn(sac)_2(py)_2]$ [39], $[Zn(sac)_2(im)_2]$ [38], $[Zn(sac)_2(aepy)]$ [51], $ApyH[Zn(sac)_3(H_2O)]$ [52], and $[Zn(sac)_2(bzim)_2]_2 \cdot 2EtOH \cdot H_2O$ [38]. The coordination number of these complexes is influenced by the ligand geometry, and especially in the case of Zn mixed-ligand complexes containing dmp, the steric hindrance of methyl groups may prevent the ligands binding the metal center in **2** strongly.

3.2. *Spectral properties*

Compound **1** shows six ^1H NMR resonances. H_2O protons appear as multiplets at 2.5 ppm and two other multiplets at 7.5 and 7.6 ppm correspond to the hydrogens of saccharinates (bonded and counter ion). Protons of phenanthroline appear as four signals at 8.0–8.9 ppm. For **2**, a multiplet at 2.5 ppm arises from methyl protons, H_2O protons appear as multiplets at 2.5 ppm, and two multiplets at 7.6 and 7.7 ppm correspond to the saccharinates. Protons of the aromatic rings of 2,9-dimethyl-1,10-phenanthroline appear as three broad signals at 7.9–8.8 ppm. These hydrogen atoms are labeled as shown in scheme 1 and the data are collected and assigned in Supplementary material. The relative intensities of these signals are in accord with the proposed structures. Hydrogen signals are slightly shifted in comparison with the same signals in the free ligand, demonstration of coordination of the ligands to zinc.

The IR spectra for both complexes exhibit a strong broad absorption in the range $3500–3200\,cm^{-1}$ due to $\nu(OH)$ from water. This very broad band can also indicate the presence of strong hydrogen bonds. Bands centered at 3100–3000 can be assigned to C–H vibrations. A sharp absorption at $1643\,cm^{-1}$ for **1** and $1651\,cm^{-1}$ for **2** is characteristic of C=O. The non-existence of two clearly resolved bands in the CO stretching region may be explained by the similarity of the two C–O distances, as these distances are (1.229(4) and 1.239(3) Å) in the crystallography nonequivalent saccharinates in **1** (table 2). $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, arising from the stretching vibrations of SO_2 groups, appear at $1300–1100\,cm^{-1}$. Prominent bands at 1301 and $1281\,cm^{-1}$ are assigned to asymmetric $\nu(SO_2)$ modes for **1** and **2**, respectively, and prominent bands at $1140\,cm^{-1}$ for **1** and $1156\,cm^{-1}$ for **2** are from symmetric $\nu(SO_2)$. Sharp absorptions around $1430\,cm^{-1}$ due to the $\nu(C–N)$ vibrations are present for both complexes. Additional medium peaks at $1600–1400\,cm^{-1}$ correspond to phenyl ring $\nu(C–C)$. $\nu(C=N)$ of phenanthroline should be at $1650\,cm^{-1}$, but overlap with $\nu(C=O)$ of sac.

Table 2. Bond lengths (Å) around zinc in [Zn(sac)(phen)$_2$(H$_2$O)](sac).

Zn(1)–O(1)	2.136(2)	S(1)–O(3)	1.433(3)
Zn(1)–N(1)	2.144(2)	S(1)–O(4)	1.434(3)
Zn(1)–N(5)	2.154(2)	C(32)–N(6)	1.356(4)
Zn(1)–N(2)	2.167(2)	C(32)–O(5)	1.229(4)
Zn(1)–N(4)	2.177(2)	S(2)–N(6)	1.593(3)
Zn(1)–N(3)	2.184(3)	S(2)–O(6)	1.437(3)
C(25)–N(5)	1.353(4)	S(2)–O(7)	1.452(3)
C(25)–O(2)	1.239(3)	O(1)–H(1B)	0.76(4)
S(1)–N(5)	1.643(2)	O(1)–H(1C)	1.01(6)

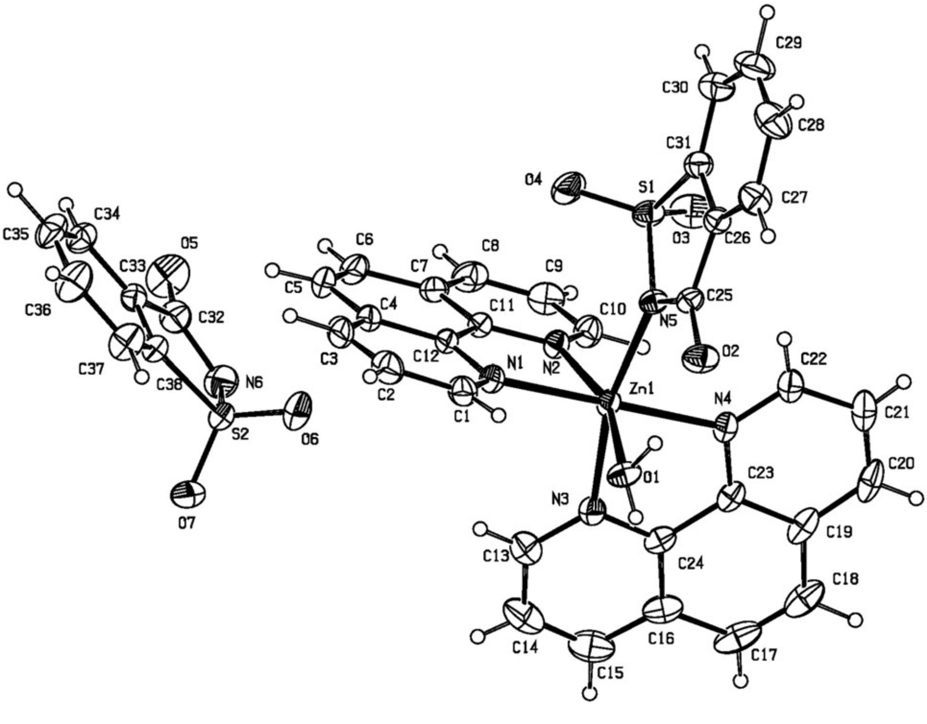


Figure 1. Molecular structure and labeling scheme for [Zn(sac)(phen)$_2$(H$_2$O)](sac).

A band around 1230 cm^{-1} is probably due to ring vibrations. Additional peaks at 1340 and 950 cm^{-1} are assigned to the symmetric and asymmetric stretching of the CNS of sac ligands. Low-intensity bands below 500 cm^{-1} may be attributed to Zn–N vibrations. All these findings are in good agreement with *ab initio* calculations on saccharinato ion [53, 54].

3.3. *Description of the crystal structure of [Zn(phen)$_2$(sac)(H$_2$O)]sac*

The molecular structure of [Zn(phen)$_2$(sac)(H$_2$O)]sac (**1**) (figure 1) consists of polymeric cation chains composed of Zn(phen)$_2$(sac)(H$_2$O)$^+$ cations and sac$^-$ anions (1 : 1) held together by hydrogen bonds and van der Waals' interactions. In the cation, Zn(II)

Table 3. Bond angles (°) around zinc in [Zn(sac)(phen)$_2$(H$_2$O)](sac).

O(1)–Zn(1)–N(1)	87.91(10)	N(1)–Zn(1)–N(5)	91.17(10)
O(1)–Zn(1)–N(5)	90.75(10)	N(1)–Zn(1)–N(2)	77.49(9)
O(1)–Zn(1)–N(2)	162.13(10)	N(1)–Zn(1)–N(4)	177.65(10)
O(1)–Zn(1)–N(4)	93.98(9)	N(1)–Zn(1)–N(3)	102.01(10)
O(1)–Zn(1)–N(3)	87.61(10)	N(2)–Zn(1)–N(4)	100.40(9)
N(5)–Zn(1)–N(4)	90.22(10)	N(2)–Zn(1)–N(3)	85.47(9)
N(5)–Zn(1)–N(2)	99.68(9)	N(4)–Zn(1)–N(3)	76.68(10)
N(5)–Zn(1)–N(3)	166.64(9)		

Table 4. Hydrogen-bonding and short contact interaction geometry for [Zn(sac)(phen)$_2$(H$_2$O)](sac).

D–H···A	d(D–H)	d(D···A)	d(H···A)	∠(DHA)	Eq. positions
O1–H1B···O7	0.757(0.038)	2.759(0.004)	2.004(0.038)	175.45(3.83)	x, y, z
O1–H1C···O2	1.006(0.053)	2.668(0.004)	1.731(0.051)	153.36(4.66)	x, y, z
C3–H3···O5	0.929(0.040)	3.460(0.005)	2.565(0.039)	162.14(3.07)	$-x+1, -y+1, -z+1$
C2–H2···N6	0.941(0.036)	3.333(0.005)	2.679(0.039)	127.15(2.87)	$-x+1, -y+1, -z+1$

is bound to five nitrogens from saccharinate [N5], two crystallographically independent bidentate 1,10-phenanthroline molecules [N1/N2] and [N3/N4], and one oxygen of water in a distorted octahedron. This structure is similar to the structure of [Mn(sac)(phen)$_2$(H$_2$O)](sac) [20]. Selected bond lengths and angles are presented in tables 2 and 3.

The two phenanthroline units are mutually *cis*, as are the coordinated saccharinate and H$_2$O, which is seen in Zn(bipy)$_2$(sac)(H$_2$O)]sac and [Mn(phen)$_2$(sac)(H$_2$O)]sac. Both phen ligands are essentially planar and almost perpendicular to each other. The angle between the corresponding planes is 88.88(4) Å. The Zn–N$_{phen}$ distances range from 2.144(2) to 2.184(3) Å with one of the phen ligands (N1/N2) bound more asymmetrically than the other, as was also found in the structure of [Zn(bipy)$_2$(sac)(H$_2$O)]sac. The Zn–N$_{sac}$ bond length of 2.154(2) Å is close to the bond length of 2.159(3) Å in the bipyridine complex and shorter than the corresponding distance of 2.196(3) Å in [Zn(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O [11]. The Zn(1)–O(1) separation of 2.136(2) Å in this complex is longer than the similar bond in the bipyridine complex (2.064(3) Å), possibly reflecting greater steric requirements of the phenanthroline ligands, and is intermediate between the two independent Zn–O$_w$ distances of 2.058(2) and 2.159(2) Å in [Zn(sac)$_2$(H$_2$O)$_4$] · 2H$_2$O.

Bond angles and distances are similar to previously observed values for the metal complexes containing phenanthroline [20, 21, 55]. In comparison with bond angles in [Zn(bipy)$_2$(sac)(H$_2$O)]sac, bond angles about zinc in [Zn(sac)(phen)$_2$(H$_2$O)](sac) show greater distortion from idealized octahedral geometry with O(1)–Zn(1)–N(2) = 162.13(10)°, N(1)–Zn(1)–N(4) = 177.65(10)°, and N(5)–Zn(1)–N(3) = 166.64(9)°. This is expected for the more sterically demanding phenanthroline ligands, and the steric hindrances created by phenanthroline chelate rings are similar to those found in the isomorphous manganese analogue reported previously [20]. The hydrogen-bonding geometry of **1** is shown in table 4.

Comparing zinc complexes with phenanthroline and bipyridine shows very similar hydrogen bonds between bound water and carbonyl oxygen of saccharinate with bond

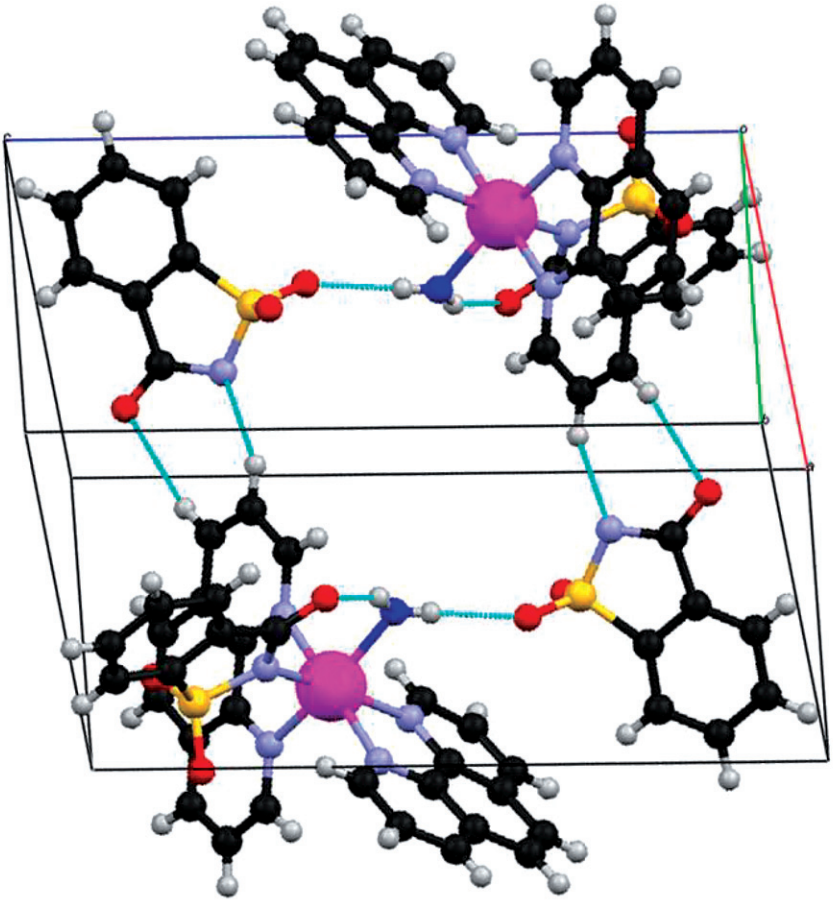


Figure 2. Unit cell and hydrogen bonds for [Zn(sac)(phen)$_2$(H$_2$O)](sac).

distances of 2.664(4) and 2.668(0.004) Å, respectively. The second saccharinate, which is present as a counter ion, is also involved in a hydrogen bond with water. A difference between phenanthroline containing structure and the structure of the bipyridine complex is that water attached to zinc is hydrogen bonded to SO$_2$ in the free saccharinate anion (figure 2), with O1–H1B $\cdots$ O7 distance of 2.004(.038) Å; in the latter, the water is hydrogen bonded to nitrogen of sac counter-ion. While both hydrogens of water participate in hydrogen bonding, the Zn–O$_w$ distance is shorter than the corresponding distance in [Zn(sac)$_2$(H$_2$O)$_4$] $\cdot$ 2H$_2$O. The relevant angles for O1–H1B $\cdots$ O7 and O1–H1C $\cdots$ O2 are 175.45(3.83)°. Short donor–acceptor distances and nearly linear donor–H-acceptor angles indicate that these interactions are very strong.

This complex is an example of "cation–anion pair" through hydrogen bonds that is highly directional and specific. The packing and hydrogen bonds are shown in figure 2. Ionic structural units are linked with each other by O–H $\cdots$ O$_{SO_2}$ hydrogen bonds and intermolecular short contacts. The structure demonstrates two significant intermolecular contacts, C2–H2 $\cdots$ N6 (2.67(8) Å) and C3–H3 $\cdots$ O5 (2.56(6) Å) with angles of 127.15((2.87)° and 162.14(3.07)°, respectively, in addition to the hydrogen bonds

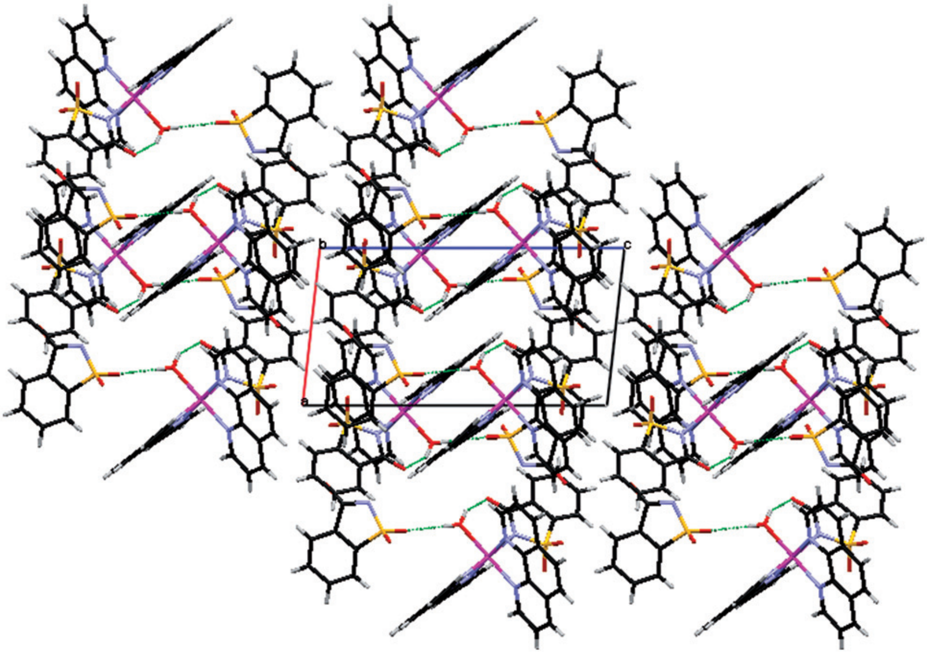


Figure 3. The packing diagram for [Zn(sac)(phen)$_2$(H$_2$O)](sac) showing the 3-D network formed via hydrogen bonding and short interactions.

between O7 in SO$_2$ of saccharinate counter ion and O2 in saccharinate ligand with the bound water. The overall hydrogen-bond scheme can be described as a 3-D network formed by the saccharinate anions, the free saccharinate, and water (figure 3) with the formation of channels supported by hydrogen bonds and short interaction.

4. Conclusion

We have presented herein the characterizations of compounds **1** and **2**. Using [Zn(sac)$_2$(H$_2$O)$_4$]$\cdot$2H$_2$O and the same synthesis method with two different ligands resulted in two complexes with different coordination numbers. Compound **1** is six coordinate, but the methyl hindrance in dmp resulted in a four-coordinate complex of **2**.

Complex **1** is characterized by X-ray as a slightly distorted octahedral arrangement and is also hydrogen bonded to an oxygen of SO$_2$ in the saccharinate counter-ion from an adjacent molecule and a carbonyl of ligated saccharinate. The intermolecular and intramolecular hydrogen bonding and short interactions stabilize the system and make a 3-D network. This complex is an example for the formation of "cation–anion pair" through hydrogen bonds that have little dependence on the properties of metal ions.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication No. CCDC 628928. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgment

We are grateful to the Research Council of Sharif University of Technology for their financial support.

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