

POLYMERS OF UNIDIRECTIONAL COORDINATION $[M(\text{sac})_2(\text{H}_2\text{O})(\text{pyz})]_n$, ($M = \text{Ni}^{2+}$, Cu^{2+} AND Zn^{2+} , sac =saccharinate, pyz= pyrazine), SPECTROSCOPY AND MAGNETIC PROPERTIES.

Grettel Valle-Bourrouet¹ and Thomas Weyhermüller²

¹ Escuela de Química, Universidad de Costa Rica, 11501-2060 San José, Costa Rica

²Max-Planck-Institut für Bioanorganische Chemie, 34-36 Stiftstrasse, D-45470 Muelheim an der Ruhr, Stiftstr. 34-36, Germany.

Abstract

Coordination polymers have been prepared by the hydrothermal reaction of M^{2+} saccharinates ($M = \text{Ni}$, Cu and Zn) and pyrazine, pyz, in a ratio 1:1. The complexes of formula $[M(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}]_n$, $M = \text{Ni}^{2+}$ and Zn^{2+} and $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})\text{pyz}]_n$ were characterized by spectroscopic methods and elemental analysis, magnetic measurements, single and powder x-ray diffraction. The compounds crystallize in the triclinic space group $P\bar{1}$. The zinc ion is octahedrally coordinated by two sac ions, two water and two pyrazine molecules. The copper ion is penta-coordinated in a distorted square pyramidal geometry with the pyrazine molecules in the axial position. The metal atoms are connected via pyrazine μ -N,N'-coordination and form linear chains, containing a network of hydrogen bonds between the chains, that build a 2D sheet structure.

Keywords: complexes, hydrogen bonds, pyrazine, transition metals, cobalt, nickel, copper, zinc.

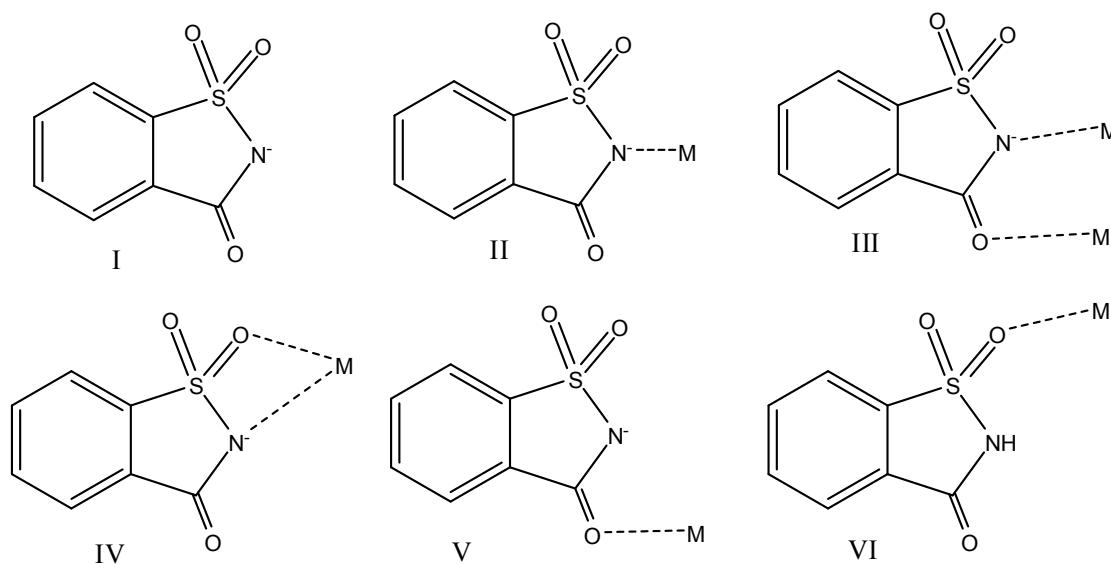
I. Introduction

Crystal engineering of new solid-state coordination architectures with bidentate ligands and various transition metal ions, offers an exciting approach to the discovery of novel multi-dimensional arrays, which may possess functional properties. Self-assembly is the most efficient approach towards the design of 1-, 2-, and 3-D organic/inorganic hybrid materials [1, 2]. These polymeric arrangements

Author to whom correspondence should be addressed, grettel.valle@ucr.ac.cr, Tel.: 00506-2511-4232

attracted much attention because of the possible applications as new materials for solvent inclusion [3] or gas adsorption [4] characteristics or materials with electronic [5] or nonlinear optical properties [6].

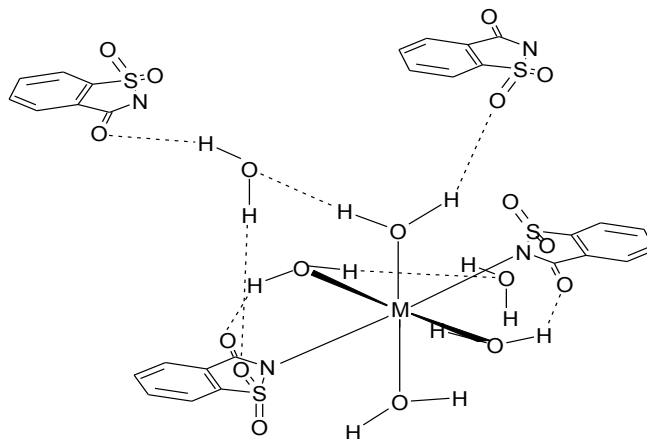
Several years ago, we became interested in the possibility of preparing compounds of Cr(II) [7] using the saccharine anion, (*sac*), (**I**). The presence of several potential donor sites such as the imino nitrogen, the carbonyl group and two sulfonyl oxygen atoms, make the *sac* anion a versatile polyfunctional ligand (Scheme I).



Scheme I

The *sac* ion is flat enough to permit the building of one- and bidimensional polymeric structures using pyrazine, (pyz), or 4,4'-bipyridine, (4,4'-bipy), as rigid spacing blocks.

The saccharinate complexes $[M(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, with M^{2+} = first row transition metal ions [7-10], are good starting points to prepare mixed-ligand *sac* complexes with N- and O-donor ligands. These saccharinate, (*sac*), complexes $[M(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ have an extensive hydrogen bonding network, as shown in scheme II, and form an isostructural series. Substitution of two or more coordinated water molecules by non-hydrogen bonding ligands disrupts this network. The resulting molecular geometry is due primarily to intrinsic metal ion stereochemistry and electronic demands, as shown in our previous papers [7, 11- 13]. This feature makes even attractive the study of new complexes with saccharine, especially a series of compounds with hydrogen-bonds that would allow to compare the strength of the hydrogen bonding net against the intrinsic metal ion stereochemistry.



Scheme II

We report herein the synthesis and characterization of the catena complexes $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})(\text{pyz})]_n$ and $[\text{Zn}(\text{sac})_2(\text{H}_2\text{O})_2(\text{pyz})]_n$ that form 1-D linear-chains and through inter-chain hydrogen bond build a 2D supramolecular structure.

II. Experimental

Methods and Materials: Solvents, methanol, ethanol, pyrazine (pyz), nickel(II) nitrate, copper(II) nitrate, zinc(II) nitrate, sodium saccharinate were used as commercially available products. The complexes $[M(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, where $M = \text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$, were prepared as described in the literature[7, 10] and isolated as crystalline materials.

Physical-chemical measurements: FT-IR spectra were recorded using KBr pellets with a Perkin Elmer Spectrum 1000. Temperature-dependent (2-298 K) magnetization data was recorded on a SQUID magnetometer (MPMS Quantum Design) with an external magnetic field of 1.0 T. The experimental susceptibility data was corrected for underlying diamagnetism by using tabulated Pascal's constants.

Synthesis of the complexes

$[\text{Ni}(\text{sac})_2(\text{H}_2\text{O})_2(\text{pyz})]_n$, **1**

Pyrazine, 80 mg (4.0 mmol) was added to a solution of 0.50 g (1.0 mmol) of nickel saccharinate in 20.0 mL of water. The reaction mixture was refluxed for 1 h. A light-blue microcrystalline solid was obtained. It was filtered and washed with cold water. Yield: 0.40g (74%). Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}_8\text{S}_2\text{Ni}$: C, 40.06; H, 2.96; N, 10.38. Found: C, 39.80; H, 3.05; N, 10.30. IR(KBr pellet, cm^{-1}): 3512(m), 3130(s), 2841(br), 1618(vs), 1587(vs), 1418(s), 1344(m), 1275(vs), 1170(vs), 1158(vs), 1118(m), 962(m), 747(m), 680(m), 528(m). $\mu_{\text{eff}}(299\text{K})$: 3.2 B.M.

[Cu(sac)₂(H₂O)(pyz)]_n, 2

Pyrazine, 0.48 g (4.0 mmol) was added to a solution of copper saccharinate 1.10 g (2.0 mmol) in 60 mL water. The reaction mixture was refluxed for 1h while stirring. A sky blue microcrystalline precipitate was obtained. Yield 0.50 g (46%). Crystals suitable for X-ray measurements were obtained by slow evaporation of the mother liquid over a few days. Anal. Calcd for C₁₈H₁₆N₄O₈S₂Cu: C, 39.70; H, 2.94; N, 10.29 Found: C, 39.73; H, 2.98; N, 10.19. IR(KBr pellet, cm⁻¹): 3622(s), 3547(m), 3489(m), 3394(m), 3490(s), 3109(m), 3057(m), 1683(s), 1663(vs), 1636(vs), 1592(vs), 1423(vs), 1326(m), 1285(vs), 1251(s), 1170(s), 1159(m), 1118(m), 1069(m), 976(s), 967(s), 823(m), 749(m), 678(s), 600(s). μ_{eff} : 1.67 B.M.

[Zn(sac)₂(H₂O)₂(pyz)]_n, 3

Pyrazine, 0.27 g (4.0 mmol) was added to a solution of zinc saccharinate 0.53 g (1.0 mmol) in 50.0 mL water. The reaction mixture was refluxed for 45 min. The resulting solution was cooled and allowed to evaporate slowly over a few days at room temperature, and a crop of crystals was obtained. Colorless crystals suitable for X-ray analysis were collected by suction, filtrated and dried in air. Yield 0.22 g (40%). Anal. Calcd. for C₁₈H₁₆N₆O₆S₂Zn: N, 15.4; Zn, 11.9. Found: N, 15.3; Zn, 11.7. IR(KBr pellet, cm⁻¹): 3500(s), 3123(s), 2853(br), 1623(vs), 1587(vs), 1459(m), 1418(m), 1343(m), 1275(s), 1257(s), 1169(vs), 1157(vs), 1117(vs), 1058(s), 960(s), 820(m), 746(m), 528(m).

X-Ray Crystallographic Data Collection and Refinement of the Structure.

Single blue crystal of **2** was coated with perfluoropolyether, picked up with a nylon loop and mounted in the nitrogen cold stream of a Bruker-Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source. Graphite monochromated Mo-K α radiation ($\lambda=0.71073\text{\AA}$) was used. Final cell constants were obtained from least squares fits of all measured reflections. Intensity data were corrected for absorption using intensities of redundant reflections. The structures were readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens ShelXTL [14] software package was used for solution and artwork of the structures, ShelXL97[15] was used for the refinement. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters, except for hydrogen atoms of coordinated and non-coordinated water molecules, which were located from the difference map and refined. Crystallographic data are listed in Table 1.

TABLE 1: Crystal data and structure refinement for $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})(\text{pyz})]_n$ $[\text{Zn}(\text{sac})_2(\text{H}_2\text{O})_2(\text{pyz})]_n$

Empirical formula	C ₁₈ H ₁₆ CuN ₄ O ₈ S ₂	C ₁₈ H ₁₆ N ₄ O ₈ S ₂ Zn
Formula weight	544.01	545.84
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 6.8908 (3) Å α = 92.188 (3)° b = 7.0438 (4) Å β = 93.132 (3)° c = 21.3389 (8) Å γ = 99.964(3) °	a = 7.1912 (8) Å α = 106.32 (1)° b = 7.6615 (8) Å β = 95.54 (1)° c = 10.5620 (12) Å γ = 108.86 °
Volume	1017.39(8) Å ³	517.12 (10) Å ³
Z	2	1
Density (calculated)	1.772 Mg/m ³	1.7353 Mg/m ³
Absorption coefficient	1.337 mm ⁻¹	1.446 mm ⁻¹
F(000)	554	278
Crystal size	0.21 x 0.11 x 0.04	0.24 X 0.08 x 0.08 mm
Theta range for data collection	2.94 to 33.16 °	4.11 a 33.21 °
Reflections collected	31892	5915
Independent reflections	7732 [R(int) = 0.0380]	3897 [R(int) = 0.0690]
Absorption correction	Semi-empirical from equivalents	Gaussian, face-indexed
Max. and min. transmission	0.9485 and 0.7666	0.9052 and 0.7186
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7732/ 0/ 310	3894 / 8 / 175
Goodness-of-fit-on F ²	1.041	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0831	R1 = 0.0390, wR2 = 0.0989
R indices (all data)	R1 = 0.0431, wR2 = 0.0875	R1 = 0.0463, wR2 = 0.1038
Largest dic. peak and hole	0.525 and -0.841 e. Å ⁻³	0.668 -0.949 e. Å ⁻³

Single colorless crystal of **3** was coated with perfluoropolyether, picked up with a nylon loop and was mounted in the nitrogen cold stream of the diffractometer. A Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo-Kα, λ=0.71073Å) was used. Final cell constants were obtained from a least squares fit of all integrated reflections. Intensity data were corrected for absorption using the Gaussian method embedded in the XPREP program of ShelXTL [16].

The structure was readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens ShelXTL software package was used for solution and artwork of the structure, ShelXL97 [15] was used for the refinement. All non-hydrogen atoms were refined

anisotropically. Hydrogen atoms were located from the difference map and were refined with isotropic displacement parameters which were set to 1.3 times U_{eq} of the atom they are attached to in the case of aromatic protons and 1.5 times this value for water protons. C-H and O-H distances were refined with similar distances using the SADI instruction of ShelXL97. Crystallographic data of the compounds are listed in Table 1.

III. Results and Discussion

Synthesis

The aim of the work was to study the substitution of water molecules in the saccharinate complexes by pyrazine, to build coordination polymers. They were prepared by adding pyrazine to aqueous solutions of the saccharinate complexes. The elemental analyses resulted in good agreement with the empirical formulas $[M(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}]_n$ for $M^{2+} = \text{Ni}$ and Zn , and $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})\text{pyz}]_n$, and as well as the X-ray structure analysis.

Crystal structure

Compounds **2** and **3** have a one dimensional linear chain structure along the crystallographic a-axis, which is formed by bridging pyrazine ligands connecting the $M(\text{sac})_2(\text{H}_2\text{O})_x$ units, $X = 1$ for **2** and 2 for **3**. A thermal ellipsoid plot of the one-dimensional polymer is depicted in Figures 1 and 2.

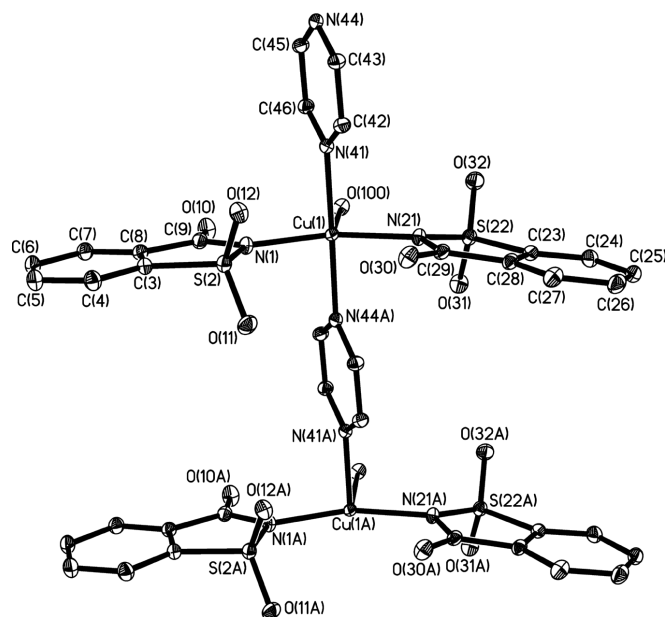


FIGURE 1. Structural representation of the local coordination of Cu atoms and the linear chain in $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})(\text{pyz})]_n$

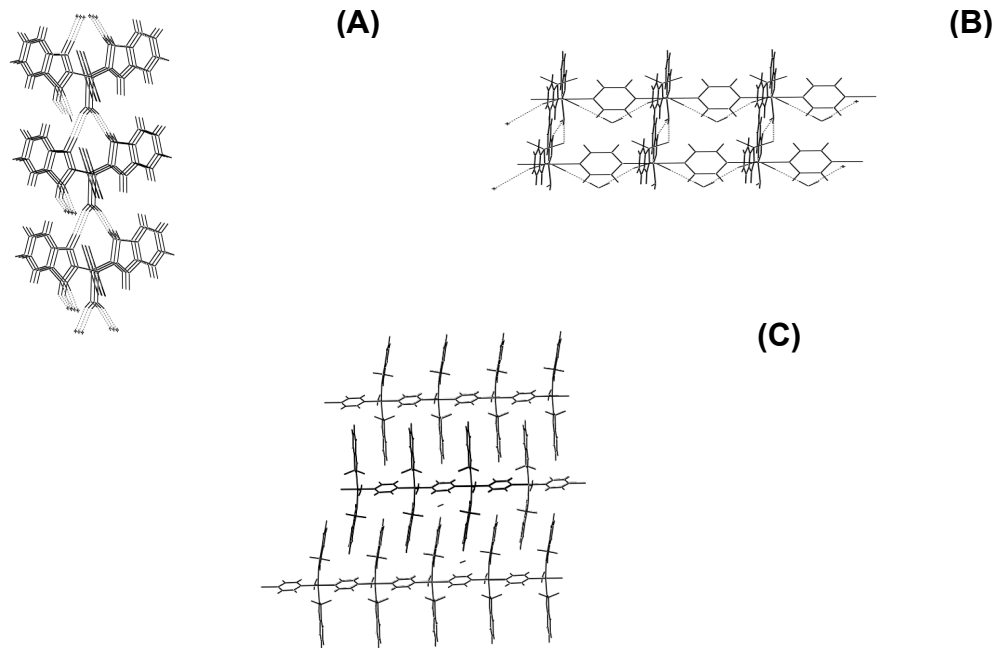


FIGURE 2. Packing diagram of $[\text{Cu}(\text{sac})_2(\text{H}_2\text{O})(\text{pyz})]_n$, showing the crystal structures linked via hydrogen bonding, $\text{O-H} \cdots \text{O}$. **A.** Cross-sectional view in the plane bc . Inter-chain H-bonds between H coordinated water molecule and the carbonyl and sulfonyl oxygen atoms from saccharinate molecules in the neighbors chain. **B.** Cross-sectional view in the plane ac showing H-bonds between crystal water molecules and sulfonyl oxygen atoms. **C.** Packing 2D layers into 3D network along the c -axis, showing aromatic $\pi \cdots \pi$ stacking interactions between sac ligands.

Compound **2** and **3** crystallize in the triclinic space group $P-1$. Relevant bond lengths and angles are given in table 2. The Cu atom in complex **2** is coordinated by four nitrogen atoms from two saccharinate ions and two pyrazine molecules and one water molecule, forming a distorted square pyramidal coordination sphere. The pyrazine and saccharinate ion nitrogen atoms form the equatorial plane with separation angles of $\text{N}(44)\text{-Cu-N}(41)$ $179.05(5)^\circ$ and $\text{N}(1)\text{-Cu-N}(21)$ $151.26(5)^\circ$, respectively. The saccharinate molecule has the same orientation as in the former saccharinate complex. The corresponding bond lengths are $\text{Cu}(1)\text{-N}(1)$ $1.9931(12)$ Å, $\text{Cu}(1)\text{-N}(21)$ $2.0091(12)$ Å, $\text{Cu}(1)\text{-N}(44\text{A})$ 2.0482 Å, $\text{Cu}(1)\text{-N}(41)$ $2.0552(12)$ Å and $\text{Cu}(1)\text{-O}(100)$ $2.1918(12)$ Å. The bond lengths are in agreement with those observed in Cu-pyz and also in Cu-sac compounds [8, 17]. The Cu atoms are bridged by pyrazine ligands with the nearest $\text{Cu} \cdots \text{Cu}$ separation of 6.891 Å, a little longer than reported lengths of Cu-pyz-Cu, as 6.8519 Å, in the chain compounds $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$. [17] The coordinated water molecule is hydrogen bonded a saccharinato carbonyl (2.835 Å) and one sulfonyl oxygen (2.782 Å) of the neighbor polymer, thus creating a 2D supramolecular structure along the b -axis (Figure 2a).

TABLE 2: Selected interatomic distances (Å) and angles (°) for [Cu(sac)₂(H₂O)(pyz)]_n (2) [Zn(sac)₂(H₂O)₂(pyz)]_n (3)

[Cu(sac)₂(H₂O)(pyz)]_n

Bond lengths		Bond angles	
Cu(1)-O(100)	2.1918(12)	N(1)-Cu(1)-N(21)	151.26(5)
Cu(1)-N(1)	1.9931(12)	N(1)-Cu(1)-N(44) #1	89.25(5)
Cu(1)-N(21)	2.0091(12)	N(21)-Cu(1)-N(44) #1	89.68(5)
Cu(1)-N(44) #1	2.0482(12)	N(1)-Cu(1)-N(41)	89.91(5)
Cu(1)-N(41)	2.0552(12)	N(21)-Cu(1)-N(41)	90.84(5)
C(9)-O(10)	1.2209(19)	N(44) #1-Cu(1)-N(41)	179.05(5)
C(29)-O(30)	1.2298 (18)	N(1)-Cu(1)-O(100)	111.07(5)
S(2)-O(11)	1.4470(12)	N(21)-Cu(1)-O(100)	97.67(5)
S(2)-O(12)	1.4525(12)	N(44) #1-Cu(1)-O(100)	90.93(5)
S(22)-O(31)	1.4502(12)	N(41)-Cu(1)-O(100)	89.79(5)
S(22)-O(32)	1.4477(12)		

Symmetry transformations used to generate equivalent atoms: #1 x-1,y, z #2 x+1, y, z

[Zn(sac)₂(H₂O)₂(pyz)]_n (3)

Zn(1)-O(30)	2.0895(13)	O(30)-Zn(1)-O(30)#1	180.0
Zn(1)-N(21)	2.1966(14)	O(30)-Zn(1)-N(21)	87.51(5)
Zn(1)-N(2)	2.2115(15)	O(30)#1-Zn(1)-N(21)	92.49(5)
Zn(1)-N(2)#1	2.2115(15)	O(30)-Zn(1)-N(2)	86.03(5)
C(3)-O(12)	1.237(2)	O(30)#1-Zn(1)-N(2)	93.97(5)
S(1)-O(10)	1.4494(14)	N(21)-Zn(1)-N(2)	92.25(5)
S(1)-O(11)	1.4451(14)	N(21)#1-Zn(1)-N(2)	87.75(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1

There is also a lattice water molecule per copper atom, that binds the adjacent sulfonyl oxygen atoms along the polymer chain (Figure 2b).

The packing of the sheets in lattices produces an alternating sheet motif as shown in Figure 2c. The phenyl rings of the *sac* ligands within a hydrogen bonded assembly form almost a parallel array with the other *sac* in the neighboring hydrogen-bonded sheets, and consequently, this result in weak aromatic face-to-face $\pi(\text{sac})-\pi(\text{sac})$ stacking interactions. The C=O bond distances from **2**, are 1.2209(19) Å and 1.2298(18) for C(9)-O(10) and C(29)-O(30), respectively. Both lengths are shorter than 1.238(4) Å, from the starting saccharinate complex, and in both cases, the bond distance is in agreement with the weak-moderate hydrogen bond in **2**. The S=O distances in S(2)-O(11) 1.4470(12) Å, S(2)-O(12) 1.4525(12) Å, S(22)-O(31) 1.4502 (12) Å and S(22)-O(32) 1.4477(12) Å, revealed a small difference probably due to the hydrogen-bond with water molecules. The zinc ion in complex **3** lies on a center of inversion and is pseudo-octahedrally coordinated by two saccharinate ions and two water molecules in a *trans* configuration, occupying the vertices perpendicular to the chain direction, as shown in Figure 1. The Zn-N(sac) bond distance, 2.2115(15) Å is longer than the Zn-N(py_z), 2.1966(14) Å. The Zn-O(30) bond 2.0895 Å is longer than in the former complex, Zn(sac)₂(H₂O)₄, 2.058(2) Å [3]. The water molecule is moderately hydrogen bonded with the carbonyl oxygen atom by a short distance, O-H...O O(30)...O(12), 2.597(2) Å. In the former complex the distance is 2.712(2) Å, and is also intermolecular with the sulfonyl oxygen atom, O(30)...O(10), 2.776(2) Å, from the adjacent chain saccharinate molecule. The C=O bond distance from **3**, 1.237(2) Å is shorter than 1.240(2) Å, from the starting saccharinate, and in both cases the bond distance is longer than that of the carbonyl group without hydrogen-bond interactions, about 1.21 Å, that is in agreement with the moderate hydrogen bond in **3**. The S=O distances S(1)-O(10) 1.4494(14) Å and S(1)-O(11) 1.4451(14) Å, comprise a small difference probably due to the hydrogen-bond build by O(10).

The $[\text{Zn}(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}]_n$ chain-structures are linked into a two-dimensional structure through hydrogen bonding O(30)...O(10), which are formed between adjacent chains (Figure 4). As in compound **2** one saccharinate phenyl ring intercalate with one of the neighbor chains, forming an alternating motive, with weak aromatic face-to-face $\pi(\text{sac})-\pi(\text{sac})$ stacking interactions (Figure 4).

There are a few examples of 1-D straight chains with pyrazine [18-20]. Recently, the structure of the $[\text{M}(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}]_n$ $M = \text{Mn}$, Fe and Co was published elsewhere, revealing that they are isomorph with the zinc complex [21].

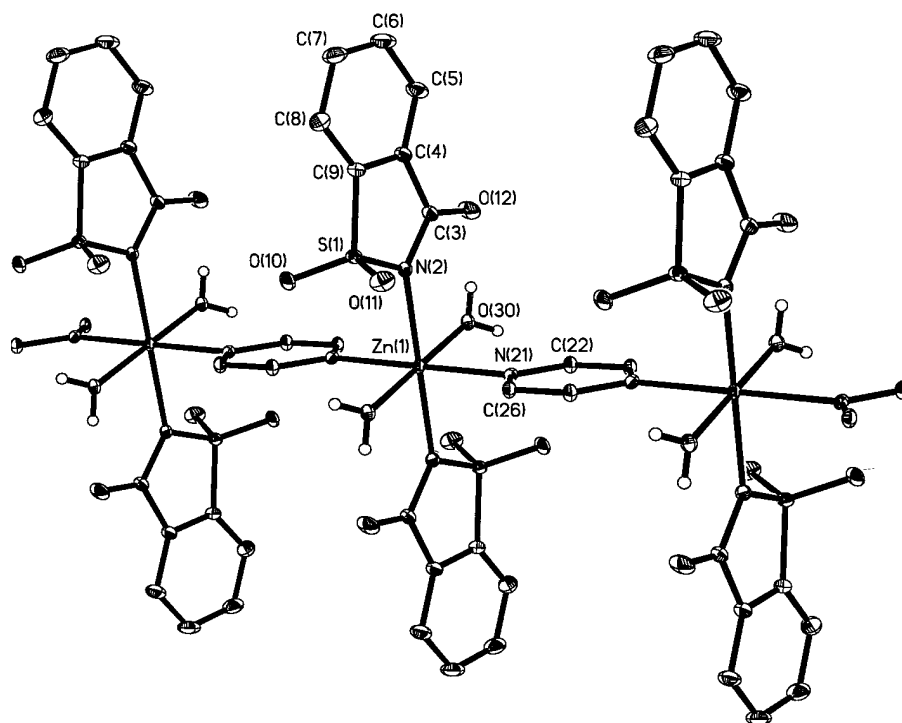


FIGURE 3: Structural representation of the local coordination of Zn atoms and the linear chain in $[\text{Zn}(\text{sac})_2(\text{H}_2\text{O})_2(\text{pyz})]_n$

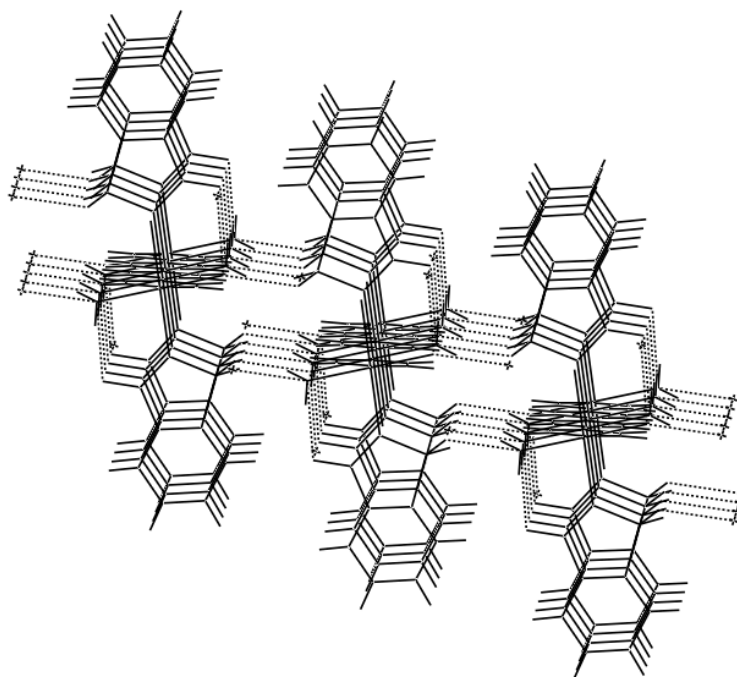


FIGURE 4. Packing diagram of $[\text{Zn}(\text{sac})_2(\text{H}_2\text{O})_2(\text{pyz})]_n$, showing the crystal structures linked via hydrogen bonding, $\text{O}-\text{H} \cdots \text{O}$.

Spectroscopic Properties

The FT-IR spectra were used for identification of the prepared compounds and are shown in Figure 5. The characteristic absorption bands originating from the OH, CO and SO₂ stretching vibrations are summarized in Table 3. It can be noticed that the spectra of the Ni(II) and Zn(II) complexes have a very similar spectrum and appreciably different from the spectrum of the Cu complex. The OH region in the spectra of the Ni(II) and Zn(II) compounds extends from 3500 cm⁻¹ to about 2800 cm⁻¹. This νOH frequency range implies that some water molecules participate in moderate strong hydrogen bonds. As commented above, the coordinated water molecule builds two hydrogen bonds, one intramolecular with the carbonyl oxygen atom and one intermolecular with the adjacent chain sulphonyl oxygen. Steine (2002) showed a correlation between the νOH frequency and hydrogen bond distance [22], where the frequencies shown by the zinc compound, 3500 cm⁻¹ and 2853 cm⁻¹ can be correlated with the hydrogen bond distances 2.77 Å and 2.59 Å respectively, with a good agreement. Compounds $[M(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}]_n$ $M = \text{Mn}$, Fe and Co were prepared and they IR investigated. All showed the same broad band and the hydrogen bond lengths correlated with the νOH frequency (Table 3). Similar behavior had been observed in other chain complexes, like $[\text{Mn}(4\text{-methylpyrazole})_3(\text{H}_2\text{O})(\text{tp})]$ and $[\text{Mn}(4\text{-methylpyrazole})_4(\text{tp})_n]$, with hydrogen bond distance around 2, 6 Å and a νOH frequency between 3000 and 2600 cm⁻¹. [23] The copper compound has one-coordinated and one-lattice water molecules; both build intermolecular hydrogen bonds, that according to bond lengths, lie in a region of weak hydrogen bond [22, 24-26]. The more frequently employed infrared bands for structural studies of various saccharinates are those corresponding to the stretching modes of the carbonyl and sulfonyl groups [27, 28]. The ν(CO) bands in the spectra of saccharinates are frequently obscured by some modes localized in the six-membered ring of the saccharinate ligand and by the water bending bands in the case of solid hydrates. In addition, pyrazine ring stretching vibrations are expected to occur in the same region. However, similarly to the ring modes of coordinate pyridine [24, 26], the benzenoid stretches are expected to appear below 1610 cm⁻¹. On the other hand, it is known that the bands from the modes localized in the heterocyclic basic ligands, do not undergo drastic changes upon complexation [26]. As it is expected from the electron redistribution within the five-membered ring of the saccharinate ligand upon deprotonation of the N-H, the saccharinate ν(CO) frequencies in the spectra of the complexes are lower than the corresponding frequency in the spectrum of saccharin itself (1725 cm⁻¹). The hydrogen bonding interactions OH...O (carbonyl) can also contribute to the lowering of the ν(CO) frequency. The Ni and Zn complexes show the ν(CO) band around 1620 cm⁻¹, the copper compound shows three bands (1682, 1663 and 1634 cm⁻¹) in the carbonyl stretching region. The appearance of three carbonyl stretching bands in the spectra of the copper compound can be the result of structural inequivalence among the CO groups in the structure, vibrational interaction of the ν(CO) imposed by symmetry factors, and hydrogen bonding interactions OH...O (carbonyl). [27-30]. The IR absorptions due to the sulfonyl groups are also important in the study of metal saccharin complexes. The symmetric and antisymmetric SO₂ stretches in the present complexes appear around 1158 cm⁻¹ and 1275 cm⁻¹, and seems to be comparable with the corresponding vibration in the metal saccharin compounds without any secondary ligands (1150 and 1280 cm⁻¹) [31]. The SO₂ stretching vibrations are less sensitive to hydrogen bonding interactions.

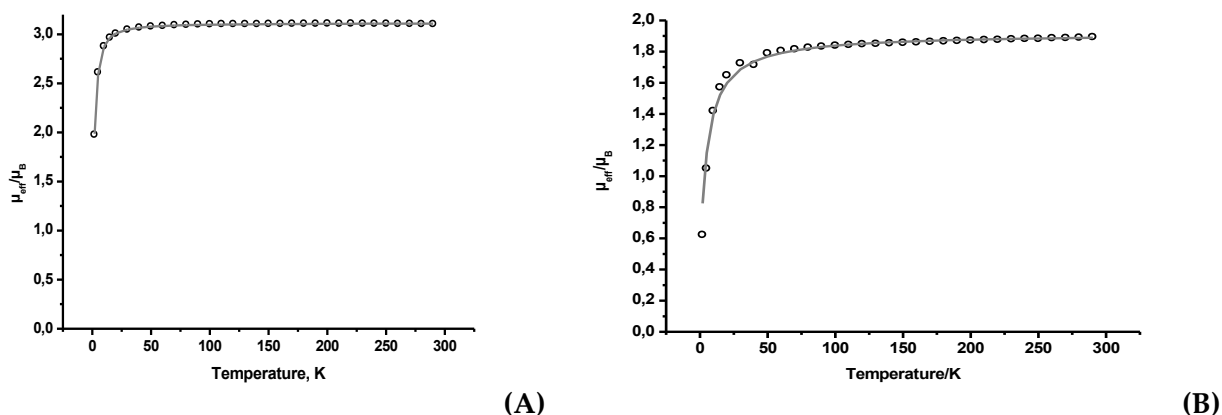


FIGURE 5: Plots of the magnetic moment as a function of temperature., **A.** The solid line represent the best fit obtained for **1** with $g = 2.20$, $D = 1.093 \text{ cm}^{-1}$ and $\theta = -1.057 \text{ K}$ for **1**. **B.** Best fit parameter for **2**: $g = 2.21$ and $\theta = -8.79 \text{ K}$.

TABLE 3. The $\nu(\text{OH})$, $\nu(\text{CO})$ and $\nu(\text{SO}_2)$ regions of the FT-IR spectra of the complexes **1**, **2**, **3** and **4**.

Assignment	Mn	Fe	Co	1 (Ni)	2 (Cu)	3 (Zn)
$\nu(\text{O-H})$, intermolecular		2489	3491	3522 s	3623 / 3546 3490 / 3394	3500 s
O...O length, Å	2.771	2.772	2.775		3,038 / 2,969 2,835 / 2,782,	2.776
$\nu(\text{O-H})$, intramolecular		2873	2798	2841 m, br		2853 m, br
O...O length, Å	2.610	2.591	2.580			2.597
$\nu(\text{C=O})$		1623	1620	1620	1682/1663/ 1634	1623
vas (SO_2)		1274	1274	1275	1285	1273
vs (SO_2)		1157	1158	1158	1159	1157
Ref.	21	21	21	This work	This work	This work

Magnetic properties

The expected $S = 1$ ground state of octahedral Ni(II) compound in **1** was confirmed by magnetic susceptibility measurements on a solid sample of **1** (1.0 T, 4-300K). The magnetic moment, μ_{eff} , is temperature-independent in range of 70-300K at $3.10 \mu_{\text{B}}$. The best fit parameter of the spin

Hamiltonian simulation lead to $g = 2.20$, $D = 1.09 \text{ cm}^{-1}$, and $\theta = -1.06 \text{ K}$ and TIP of $24,0 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$, (Figure 5a). These values are in agreement with the expected magnetic behavior of an octahedral nickel complex. It should show moments about 10% above the spin only value for $S=1$ ($2.83 \mu_B$), due to the spin-orbit coupling, $\lambda = -315 \text{ cm}^{-1}$. $[\text{32}] \mu_{\text{Ni}}$ decrease very slowly from 70K to 30 K, where they decrease rapid until $1.9 \mu_B$. This decrease arise from zero field splitting, $D = 1.09 \text{ cm}^{-1}$ and weak antiferromagnetic coupling effects fitted as a Curie Weiss correction $\theta = -1.06 \text{ K}$, which indicate a weak coupling effect.

The copper compound **2**, shows a similar magnetic behavior (Figure 5b). For copper it is not expected a zero field splitting, and the decreasing values at low temperature ~~is~~ are due to a weak antiferromagnetic coupling, as confirmed with the best fit parameter $g = 2.2$ and a Curie Weiss temperature of -8.79 K and TIP of $80 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. It has been pointed out that the stereochemistry, whether octahedral or tetrahedral or square pyramid, is expected to have little effect on the moment of the cupric ion, with a spin-orbit coupling constant, $\lambda = -850, \text{ cm}^{-1}$ about $1.9 \mu_B$. at room temperature, that matches with the experimental value of $1.98 \mu_B$. Similar chain compounds $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ [17] and $\text{Cu}(\text{OTf})_2(\text{R-pyz})$ [33] show also a weak antiferromagnetic coupling with theta values of -8.1 K and -2.5 K , respectively.

IV. Conclusions

The results of this work show an isomorphic series of complexes $M(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}$, where $M = \text{Mn}$, Fe , Co , Ni and Zn , possibly favored by intra- and inter-molecular hydrogen bond interactions. The copper compound, $\text{Cu}(\text{sac})_2(\text{H}_2\text{O}) \text{pyz}$, does not match in this series probably due to Jahn-Teller distortions. In both cases, a 2D supramolecular arrangement was assembled through inter-molecular hydrogen-bond interactions. The structural similarity and possible isomorphism of the Ni(II) and Zn(II) complexes were revealed by the similarities of the IR spectra of the $M(\text{sac})_2(\text{H}_2\text{O})_2\text{pyz}$, and corroborated by powder X-ray diffraction.

Acknowledgements

We are grateful to the Vicerrectoría de Investigación, Universidad de Costa Rica; (Grant No. 115-98 375). GVB thanks DAAD for a research fellowship and to Prof. Karl Wieghardt for allowing use of the research facilities at the Max-Planck-Institute for Bioinorganic Chemistry.

Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge crystallographic Data Center as supplementary publication No 635314. Copies of the data

can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: int. code +(1223)336-033. E-mail for inquiry: fileserv@ccdc.cam.ac.uk.

VI. References

1. Archer, R. D. *Inorganic and Organometallic Polymers*. Wiley-VCH New York, 2001, p 2-25
2. Lehn-Jahn-Marie. *Supramolecular Chemistry, Concepts and Perspectives*. VCH: Weinheim, 1995, p 1-9
3. Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A.J.; O'Keeffe, M.; Yaghi, O. M. *Nature*, **2004**, *427*, 523.
4. Fletcher, A.J.; Cussen, E. J.; Prior, T.J.; Rosseninky, M. J.; Kepert, C. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 10001.
5. Zhao, H.; Heinz, R. A. Ouyang, X.; Dunbar, K. R.; Campana, C. F.; Rogers, R. D. *Chem, Mater.* **1999**, *11*, 736.
6. Lin, W.; Evans, O. R. *Acc. Chem. Res.* **2002**, *35*, 511.
7. Cotton, F. A.; Lewis, G.E.; Murillo, C. A.; Schwotzer, Valle, G. *Inorg.Chem.* **1984**, *23*, 4038.
8. Haider, S. Z.; Malik, K. M. A.; Ahmed, K. J.; Hess, H.; Riffel, H.; Hursthouse, M.G. *Inorg. Chim. Acta* **1983**, *72*, 21.
9. Kamenar, B.; Javanovski, G. *Cryst. Struct. Commun.* **1982**, *11*, 257.
10. Haider, S. Z.; Malik, K. M. A.; Ahmed, K. J. *Inorg. Synth.* **1985**, *23*, 47.
11. Cotton, F.A.; Falvello, L.R.; Murillo, C. A.; Valle, G.; *Z. anorg. allg. Chem.* **1986**, *540/541*, 67.
12. Cotton, F.A.; Falvello, L.R.; Murillo, C. A. Valle-Bourrouet, G.; *Inorg. Chim. Acta* **1991**, *190*, 89.
13. Pineda, L. W.; Valle-Bourrouet, G.; Falvello, L.; Lusar, R.; Weyhermueller, T. *Polyhedron*, **2007**, *26*, 4470.
14. ShelXTL 6.14 Bruker AXS Inc., Madison, WI, USA 2003.
15. ShelXL97, G. M. Sheldrick, University of Göttingen, Germany, 1997.
16. ShelXTL V.5, Siemens Analytical X-Ray Inst. Inc., Madison, WI, USA 1994.
17. Manson, J. L.; Conner, M. M.; Schuleter, J. A.; Lancaster, T.; Blundel, S. L.; Brooks, M. L.; Pratt, F. L.; Ppageorgiou, T.; Bianchi, A. D.; Wosnitza, J.; Whangbo, M. -H. *Chem. Commun.* **2006**, 4894.
18. Maekawa, M; Sugimoto, K.; Kuroda-Sowa, T.; Suenaga, Y.; Munakata, M. *J. Chem. Soc., Dalton Trans.* **1999**, 4357.
19. Yu, K. B.; Gou, S.H.; You, X. Z. *Z. Naturforsch., Teil C* **1991**, *47*, 2653.
20. Näther C., Greve, J. Jess I. *Z. Naturforsch., teil B*, **2003**, *58*, 1.

21. Yimals, V. T.; Senel, E.; Kazac, C. *Polyhedron*, **2007**, *26*, 3199.
22. Steine, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
23. Hong, C.S.; Yoo, J.H.; You, Y. S. *Inorg. Chim. Acta.* **2005**, *358*, 3341.
24. Hesse, M.; Meir, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*. Georg Thieme: Stuttgart, 2005, p 49, 56.
25. Conley T. R. *Infrared Spectroscopy*, 2ed. Allyn and Bacon Inc.:Boston, 1972, pp 131,132.
26. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed. Wiley, New York, 1986, pp 206, 228.
27. Jovanovski, G.; Šoptrajnov, B. *J. Mol. Struct.* **1988**, *174*, 467.
28. Naumov, P.; Jovanovski, G. *J. Mol. Struct.* **2001**, *563-564*, 335.
29. Naumov, P.; Jovanovski, G. Grupče, J. *J. Mol. Struct.* **1999**, *121*, 482.
30. Çakir, S.; Bulut, İ.; Naumov, Biçer, E.; Çakir, O. *J. Mol. Struct.* **2001**, *560*, 1.
31. Naumov, P.; Jovanovski, G.; Todorovska, A. *J. Mol. Struct.* **2001**, *563-564*, 341.
32. Figgis, B.N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37.
33. Manson, J.L.; Donovan, J.; Twamley, B. *Polyhedron*, **2008**, *27*, 2650.