

Crystal Structure and Vibrational Behaviour of Tetraaqua-di(nicotinamide)M(II)-Saccharinates, with M(II) = Co, Ni, Zn

Eduardo E. Castellano^a, Oscar E. Piro^b, Beatriz S. Parajón-Costa^c, and Enrique J. Baran^c

^a Instituto de Física de São Carlos, Universidade de São Paulo, 13560 São Carlos (SP), Brazil

^b Departamento de Física and Instituto IFLP (CONICET), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, 1900 La Plata, Argentina

^c Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Facultad de Ciencias
Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, Argentina

Reprint requests to Prof. Dr. E. J. Baran. E-mail: baran@quimica.unlp.edu.ar

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Cobalt(II), Nickel(II), Zinc(II), Aqua(nicotinamide)metal(II)-Saccharinates

The crystal structures of $[M(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ (nic = nicotinamide; sac = saccharinate anion) with $M = \text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$, have been determined at 116 K by single-crystal X-ray diffractometry. The compounds crystallize in the triclinic space group $P\bar{1}$ with $Z = 1$, and the $M(\text{II})$ cations present a slightly distorted MN_2O_4 octahedral environment, with equatorially coordinated water molecules and axially pyridine N-bound nicotinamide ligands. The saccharinate anions act as counteranions, and are not part of the first coordination sphere. Some comparisons with related structures have been made and the most important features of their IR spectra discussed.

Introduction

A series of mixed-ligand saccharinato complexes of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ with nicotinamide were recently reported [1]. Although no structural information could be obtained, the spectroscopic characterization suggested that the $\text{Cu}(\text{II})$ complex was different from those of the other metal cations.

As a part of our own studies on mixed-ligand saccharinato complexes [2 - 6], we have recently solved the structure of the pertinent $\text{Cu}(\text{II})$ complex, of stoichiometry $[\text{Cu}(\text{sac})_2(\text{nic})_2(\text{H}_2\text{O})]$, in which the metal cation has a CuN_4O square pyramidal environment, equatorially coordinated to the N-atoms of two saccharinato moieties and the pyridine N-atom of two nicotinamide ligands and the O-atom of the water molecule located at the pyramid apex [7]. As a continuation of this investigation we have now determined the crystal structures of the three remaining complexes, which have the general composition $[M(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$, consisting of a slightly distorted MN_2O_4 octahedral cationic complex with the saccharinate anions acting only as counteranions, out of the coordination sphere of the divalent cations.

Experimental Section

Synthesis of the complexes

The three complexes were obtained by addition of nicotinamide to 40 ml of warm stirred aqueous solutions of saccharin and the corresponding metal(II) acetates in stoichiometric amounts [1]. By slow concentration of the solutions pale pink crystals of the $\text{Co}(\text{II})$ complex, pale green crystals of the $\text{Ni}(\text{II})$ complex and colourless crystals of the $\text{Zn}(\text{II})$ complex were obtained. The products were separated by filtration and dried in air between sheets of filter paper.

Spectroscopic measurements

The IR spectra of the complexes and those of pure nicotinamide and sodium saccharinate monohydrate were recorded in the range between 4000 and 300 cm^{-1} on a Perkin Elmer 580B spectrophotometer, using the KBr pellet technique.

Crystal structure determination

Measurements were performed at 116 K, with a Kappa CCD diffractometer (graphite monochromated Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) and employing an Oxford Cryosystems low-temperature device. Crystal data, collection procedures and refinement results for the three

Table 1. Crystal data and structure refinement for the $[M(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ complexes ($M = \text{Co}, \text{Ni}, \text{Zn}$).

	Co-complex	Ni-complex	Zn-complex
Empirical formula	$C_{26}H_{28}O_{12}N_6S_2Co$	$C_{26}H_{28}O_{12}N_6S_2Ni$	$C_{26}H_{28}O_{12}N_6S_2Zn$
Formula weight	739.60	739.37	746.05
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.6687(2)	8.5798(2)	8.6483(2)
b (Å)	8.8855(2)	8.9435(2)	8.9000(2)
c (Å)	10.2515(2)	10.2574(3)	10.2671(2)
α (°)	82.788(1)	83.586(1)	83.031(1)
β (°)	78.562(1)	78.467(1)	78.578(1)
γ (°)	87.328(1)	86.979(2)	87.355(1)
Volume (Å ³)	767.63(3)	765.99(3)	768.69(3)
D_c (g·cm ⁻³)	1.600	1.603	1.612
Z	1	1	1
Reflections collected	9085	9362	10279
Independent refls	3001 [$R(\text{int}) = 0.038$]	2995 [$R(\text{int}) = 0.057$]	3014 [$R(\text{int}) = 0.048$]
Observ.refl [$I > 2\sigma(I)$]	2850	2858	2816
Data/restr/params	3001/0/231	2995/0/231	3014/0/231
Goodn.-of-fit on F^2	1.102	1.175	1.067
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.027, wR2 = 0.072$	$R1 = 0.038, wR2 = 0.105$	$R1 = 0.027, wR2 = 0.071$
Final R indices (all data)	$R1 = 0.029, wR2 = 0.074$	$R1 = 0.043, wR2 = 0.121$	$R1 = 0.033, wR2 = 0.073$

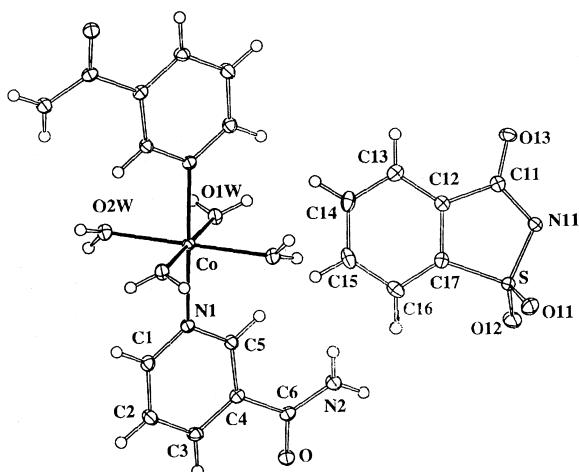


Fig. 1. ORTEP plot of the $[Co(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ complex showing the labeling scheme of the non-H atoms and their displacement ellipsoids at 50% probability level. Full lines indicate cobalt-ligand bonds. Only one of the two saccharinate counteranions is shown.

isomorphous complexes are summarized in Table 1. The structures were solved by direct and Fourier methods and the final molecular models obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms. All H-atoms were positioned stereochemically and refined with the riding model except those of the water molecules, which were located from a difference Fourier map and refined isotropically. Intensity data were cor-

rected for Lorentz, polarization, extinction and experimental absorption [8]. The unit cell dimensions were obtained by least-squares refinement of the angular settings for 9085 (Co), 9362 (Ni) and 10279 (Zn) reflections in the $2.04 < \theta < 26.00^\circ$ range. Programs used were DENZO and SCALEPACK [10] for data reduction and correction and SHELXS-97 [11] and SHELXL-97 [12] for structure solution and refinement, respectively.

As the three complexes are isomorphous, only the molecular structure of $[Co(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ is described in detail, as a typical example for the full series.

Tables containing complete information on atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters and hydrogen coordinates are available from the authors upon request and have been deposited at the Cambridge Crystallographic Data Centre, reference numbers CCDC-182692 (Co-complex), CCDC-182693 (Ni-complex) and CCDC-182694 (Zn-complex).

Results and Discussion

Crystal structure

An ORTEP [12] drawing of the structure of $[Co(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ is presented in Fig. 1. Intramolecular bond distances and angles around Co(II) are given in Table 2.

The metal cation is located on a crystallographic inversion center in a slightly distorted octahedral

Table 2. Interatomic bond distances (\AA) and angles ($^\circ$) around Co(II) in $[\text{Co}(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2^a$.

Co-O(1w)	2.065(1)	Co-O(2w)	2.130(1)
Co-N(1)	2.153(1)		
O(1w)-Co-O(2w)	88.93(5)	O(1w)-Co-O(2w)	91.07(5)
O(1w')-Co-N(1)	93.03(5)	O(1w)-Co-N(1)	86.97(5)
O(2w')-Co-N(1)	89.05(5)	O(2w)-Co-N(1)	90.95(5)

^a Primed atoms are obtained from unprimed ones by the inversion symmetry operation $-x, -y, -z$.

environment, equatorially coordinated to four water molecules [Co-Ow distances of 2.065(1) and 2.130(1) \AA] and axially to two symmetry related pyridine N-atoms of the nicotinamide ligands [$d(\text{Co}-\text{N}) = 2.153(1) \text{\AA}$]. The ring plane of the nicotinamide nearly bisects adjacent coordination planes containing the octahedron axis. The NC=O plane subtends an angle of 17.4(2) $^\circ$ with the ring plane.

As expected, the molecular skeleton of the saccharinate anions is nearly planar (rms deviation of atoms from the mean plane of 0.034 \AA) and the N-C and N-S bond distances (1.351(2) and 1.615(1) \AA , respectively) are close to those found in sodium saccharinate [13] and in the recently reported $[\text{Fe}(\text{o-phen})_3](\text{sac})_2 \cdot \text{Hsac}$ complex [6].

The structure is further stabilized by a net of interionic N-H \cdots O bonds involving the nicotinamide and saccharinate carbonyl oxygen atom [the strongest with $d(\text{H}_2\text{A}\cdots\text{O}) = 2.038 \text{\AA}$, $\angle(\text{N}_2\text{H}_2\text{A}\text{O}) = 173.0^\circ$], Ow-H \cdots O bonds with saccharinate sulfoxide and nicotinamide carbonyl oxygen atoms [the strongest with $d(\text{H}_1\text{wA}\cdots\text{O}11) = 1.891 \text{\AA}$, $\angle(\text{O}1\text{w}-\text{H}1\text{w}\cdots\text{O}11) = 174.8^\circ$], and a Ow-H \cdots N bond with a saccharinate nitrogen atom [$d(\text{H}_1\text{wB}\cdots\text{N}11) = 1.878 \text{\AA}$, $\angle(\text{O}1\text{w}-\text{H}1\text{wB}\cdots\text{N}11) = 168.8^\circ$].

The small differences in the unit cell volumes of the three isomorphous complexes can be clearly correlated with the differences in the ionic radii of the cations ($r_i \text{Zn(II)} = 0.75 \text{\AA} > r_i \text{Co(II)} = 0.74 \text{\AA} > r_i \text{Ni(II)} = 0.70 \text{\AA}$ [14]). These differences are also reflected in the metal-to-ligand bond distances as shown in Table 3. In the case of the Ni(II) and Co(II) complex, these bond distances are comparable to those reported in the respective pyridine (py) complexes of composition $[\text{M}(\text{py})_2(\text{H}_2\text{O})_4](\text{sac})_2 \cdot 4\text{H}_2\text{O}$ in which the metal centers have a similar distorted octahedral arrangement [15].

Finally, it is interesting to mention that the title compounds constitute new examples of a class of

Table 3. Comparison of bond distances in the three isomorphous $[\text{M}(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ complexes.

	M-O(1w)	M-O(2w)	M-N(1)
M = Ni(II)	2.047(1)	2.093(1)	2.106(2)
M = Co(II)	2.065(1)	2.130(1)	2.153(1)
M = Zn(II)	2.076(1)	2.143(1)	2.153(1)

Table 4. Assignment of the most characteristic IR bands of the three $[\text{M}(\text{nic})_2(\text{H}_2\text{O})_4](\text{sac})_2$ complexes (band positions in cm^{-1}).

M = Co(II)	M = Ni(II)	M = Zn(II)	Assignment
3385 vs	3382 vs	3381 vs	$\nu_{as}(\text{NH}_2)$
3190 vs	3195 vs	3186 vs	$\nu_s(\text{NH}_2)$
1685 m	1684 m	1688 m	$\nu(\text{C}=\text{O})\text{amide}$
1663 vs	1666 vs	1662 vs	$\delta(\text{HOH})$
1627 sh	1625 sh	1625 sh	$\delta(\text{NH}_2)$
1618 vs	1616 vs	1615 vs	$\nu(\text{C}=\text{O})\text{sac}$
1578 vs	1580 vs	1578 vs	$\nu(\text{CN}) + \nu(\text{CC})\text{ nic}$
1426 s	1427 s	1427 s	$\nu(\text{CN})\text{ amide}$
1279 vs	1279 vs	1278 vs	$\nu_{as}(\text{SO}_2)$
1163 vs	1162 vs	1162 vs	$\nu_s(\text{SO}_2)$
1119 m	1119 m	1117 m	$\rho(\text{NH}_2)$
964 vs	963 s	965 s	$\nu(\text{CNS})$
646 m	649 m	645 m	$\delta(\text{ring})\text{nic}$
437 w	438 w	430 w	$\delta(\text{ring})\text{nic}$
541w/	542w/	539sh/	$\rho(\text{H}_2\text{O})$ (?)
531m	530m	530m	

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder.

complexes containing the saccharinate anion out of the coordination sphere, acting simply as a counterion. Only a very limited number of systems of this type have so far been reported (*cf.* for example refers [15 - 19]).

Infrared spectra

The assignment of some of the most characteristic IR bands of the three complexes is shown in Table 4. The analysis of the spectra was performed in comparison with those of sodium saccharinate monohydrate, nicotinamide and the previously investigated $[\text{Cu}(\text{sac})_2(\text{nic})_2(\text{H}_2\text{O})]$ complex [7]. Some aspects of these assignments are commented as follows:

- The region of the NH₂ stretching vibrations is relatively broadened by partial superposition with the O-H vibrations of the coordinated water molecules. Notwithstanding, the two characteristic $\nu(\text{NH}_2)$ -bands could be clearly identified.

• The region involving the carbonyl stretching vibrations is relatively complex, as both the C=O vibrations of saccharin and of the amide group lie closely together, and also the bending modes of the coordinated water molecules and of the NH₂-moiety are expected in the same region [7]. The $\nu(\text{C}=\text{O})$ mode of the saccharinate anion lies slightly lower than in sodium saccharinate (1642 cm^{-1}) in agreement with its participation in hydrogen bonding. The respective vibration of nicotinamide is, apparently, less affected by such interactions, as in the free ligand the $\nu(\text{C}=\text{O})$ mode is observed at 1682 cm^{-1} [7].

• The ν_{as} (CNS) mode of saccharinate lies at a lower frequency than in $[\text{Cu}(\text{Sac})_2(\text{nic})_2(\text{H}_2\text{O})]$ [7]. The corresponding symmetric mode, located at 1336 cm^{-1} in sodium saccharinate [2], appears as a part of a medium intensity doublet band at $1337/1350 \text{ cm}^{-1}$, which involves a characteristic nicotinamide vibrational mode found at 1341 cm^{-1} in the free ligand.

• The two SO₂-stretching vibrations appear at similar frequencies as in sodium saccharinate (1258

and 1150 cm^{-1} [2, 7]), showing also for this moiety that its involvement in hydrogen bonding has negligible spectral consequences.

• The ligand bands located at 624 and 411 cm^{-1} and related to deformational modes of the nicotinamide ring [7] are slightly displaced to higher frequencies after coordination, showing a behaviour similar to that observed for simple pyridine complexes [2, 20]. Some other of the typical nicotinamide bands are only slightly displaced after coordination, remaining in their characteristic absorption regions.

• Vibrations related to the Cu-N and Cu-O vibrations could not be identified with certainty.

To conclude, this brief spectroscopic analysis is clearly compatible and consistent with the reported structural characteristics of the complexes.

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