

**VIBRATIONAL STUDIES OF THE IMIDAZOLE AND PYRIDINE  
ADDUCTS OF METAL(II) SACCHARINATES. I. THE OH/OD AND  
NH/ND STRETCHING REGIONS OF THE COBALT(II) AND  
NICKEL(II) COMPLEXES**

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**Abstract:** The  $\nu(XY)$  ( $X = O, N; Y = H, D$ ) regions of the FT IR spectra of both protiated and deuterated analogues of Co(II) and Ni(II) *pyridine* saccharinato complexes with the general formula  $[M(H_2O)_4(py)_2](sac)_2 \cdot 4H_2O$  and *imidazole* saccharinato complexes of type  $[M(HIm)_4(H_2O)_2](sac)_2$  are recorded.

The bands that are mainly due to the OH, OD, NH and ND stretchings are assigned and correlated with the crystallographic data. The appearance of the NH stretching region in the spectra of the studied imidazole adducts can be explained as a result of Evans type Fermi resonance of the NH stretchings with non-fundamental modes. In spite of the existence of a single type of asymmetrically bonded water molecules in the structures of the studied imidazole complexes, an unexpected ratio 1:2 of the integral intensities of the two isotopically isolated  $\nu(OD)$  stretchings in their spectra is found.

**Key words:** FT IR spectra, imidazole adducts, pyridine adducts, saccharinates, OH/OD stretchings, NH/ND stretchings.

## 1. Introduction

The structural properties of the saccharinato salts and complexes, as a basis for understanding the potential mechanisms for the action of saccharin on biological systems, are of scientific interest. Bearing in mind the well-known importance of the hydrogen bonding in the life processes, we have focused our attention on its spectroscopic manifestation in various saccharinato adducts.

Recently, we determined the crystal structures of the isomorphous *pyridine* saccharinato complexes of Co and Ni with general formula  $[M(H_2O)_4(py)_2](sac)_2 \cdot 4H_2O$  [1]<sup>1</sup>. The crystal structures of the isomorphous *imidazole* adducts of Co [2] and Ni [3] saccharinates of type  $[M(HIm)_4(H_2O)_2](sac)_2$  were published previously. Due to the structural similarities between these two pairs of compounds, such as the existence of purely ionic saccharinato species, the octahedral coordination around the metal atom and the isomorphism between the members of each pair of compounds, we decided to study their vibrational spectra simultaneously. In this paper, we report on the water and imino stretching regions in the FT IR spectra of protiated and deuterated analogues of the title compounds recorded at various temperatures.

<sup>1</sup> The acronyms "HIm", "py" and "sac" denote imidazole, pyridine and saccharinato ion or a ligand, respectively. When used in a formula, henceforward "M" stands for Co or Ni.

## 2. Experimental

The compounds were synthesized according to the procedures described in the papers reporting their structures [1-3]. Deuterated analogues of the complexes were prepared either by action of D<sub>2</sub>O vapors on the protiated samples in an evacuated dessicator or by recrystallization of the protonated samples from the corresponding D<sub>2</sub>O/H<sub>2</sub>O mixtures.

The FT infrared spectra in the 4000-1800 cm<sup>-1</sup> frequency range were recorded with a System 2000 interferometer (Perkin-Elmer). 32 background and 64 sample spectra were typically averaged; resolution was 1 to 4 cm<sup>-1</sup>. Since no differences were found with the sample spectra recorded in paraffin oil, the spectra of the imidazole complexes were recorded from KBr pellets. Due to partial dehydration, however, spectral changes occurred during the pellet preparation in case of the studied pyridine complexes and therefore their spectra were recorded from Nujol or Fluorolube suspensions placed between KBr discs. A P/N 21525 (Graseby Specac) variable-temperature cell equipped with KBr windows was used for the low-temperature measurements.

## 3. Results and Discussion

### 3.1. Water Stretching Modes

#### 3.1.1. Imidazole Saccharinates

Along with the presence of a *single* type of asymmetrically bonded water molecules in the structure [2], *two*  $\nu(\text{OD})$  bands are present in the difference<sup>2</sup> spectrum of the partially deuterated Co imidazole saccharinate with low deuterium content (Fig. 1). The frequency difference between the two  $\nu(\text{OD})$  modes (74 cm<sup>-1</sup>) implies that the water molecules are not very distorted.

As was found in numerous solid hydrates [4-6], the two isotopically isolated  $\nu(\text{OD})$  fundamentals have different intensities (Fig. 1). The difference between the integral intensities of the two  $\nu(\text{OD})$  modes (their ratio is 1:1.98, and thus very close to 1:2) in the present case, however, especially taking into account their rather "normal" frequency split, is unexpectedly large. The possibility of eventual disorder as a reason for such observation at LNT should not be excluded, although this was not observed by the structure determination at RT [2, 3].

#### 3.1.2. Pyridine Saccharinates

*Four* overlapped and apparently complex  $\nu(\text{OD})$  bands featuring different halfwidths exist in the difference spectrum of slightly deuterated Co pyridine saccharinate (Fig. 2). Since there are four structural types of water molecules placed on general positions (one of which is disordered), *nine* types of OH oscillators exist in the structure. *Nine* bands of similar integral intensities could be successfully resolved with the curve-fitting procedure. Having in mind the structural complexity of the system in the present case, however, no other analyses of the IR data but these general considerations will be attempted here.

If the positions of the isolated  $\nu(\text{OD})$  modes are taken as measure, then the similar frequency *ranges* (Figs. 1 and 2) are implying similar ranges of the hydrogen bonding strength in the studied pyridine and imidazole saccharinates.

<sup>2</sup> The spectrum of the protiated sample was subtracted from the spectrum of the slightly deuterated one.

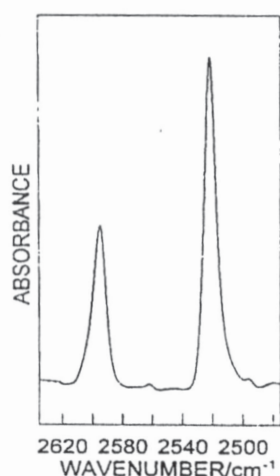


Fig. 1

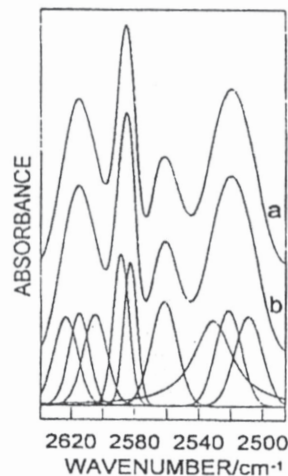


Fig. 2

Fig. 1. The  $\nu(\text{OD})$  Region in the Difference Spectrum of  $[\text{Co}(\text{HIm})_4(\text{H}_2\text{O})_2](\text{sac})_2$  with Low Deuterium Content

Fig. 2. The Difference (a) and the Reconstructed (b) Spectrum of Isotopically Isolated HDO Molecules in  $[\text{Co}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$  in the  $\nu(\text{OD})$  Region (the unlabeled bands are the component bands)

### 3.2. Stretching Modes of the Imino Groups

Six prominent  $\nu(\text{NH})$  bands can be seen in the  $3200\text{--}2800\text{ cm}^{-1}$  region of the spectra of the studied imidazole complexes (Fig. 3), but only *four*  $\nu(\text{ND})$  bands appear in the difference spectrum of the deuterated ( $\sim 30\%$  mole ratio of deuterium to hydrogen) analogues (Fig. 4).

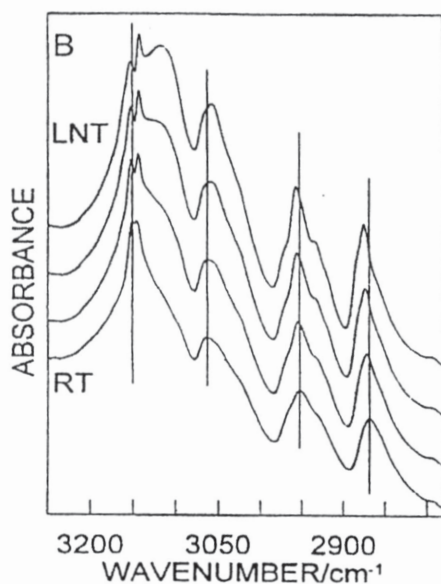


Fig. 3

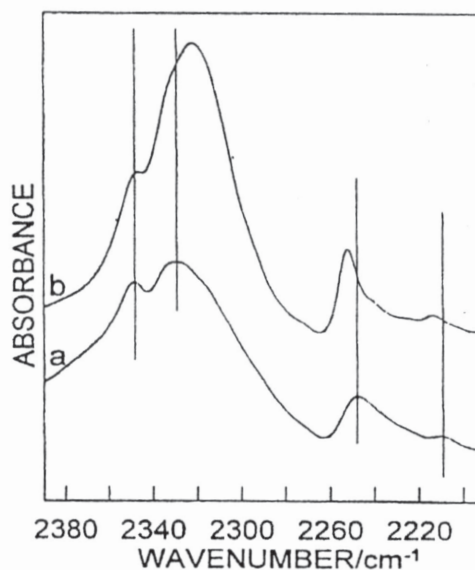


Fig. 4

Fig. 3. Temperature Effects on the  $\nu(\text{NH})$  Bands in the Spectrum of  $[\text{Ni}(\text{HIm})_4(\text{H}_2\text{O})_2](\text{sac})_2$  (the temperature lowers from the lowest to the uppermost curve)

Fig. 4. The Difference Spectrum of Deuterated ( $\sim 30\%$ D)  $[\text{Ni}(\text{HIm})_4(\text{H}_2\text{O})_2](\text{sac})_2$  at RT (a) and LNT (b) in the  $\nu(\text{ND})$  Region

Having in mind the presence of only *two* non-equivalent types of imino groups in the structure [2, 3], it can be inferred that vibrational interactions contribute largely to the appearance of the regions of deuterioimino and, therefore, of the imino stretchings, resulting in the appearance of *four*  $\nu(\text{ND})$  bands in the *deuterated* samples. The presence of *two* additional bands, and thus of overall of *six* bands in the  $\nu(\text{NH})$  region ( $3200\text{-}2800\text{ cm}^{-1}$ ) of the protiated samples (Fig. 3) can be explained by Evans type Fermi resonance of the two highest-frequency  $\nu(\text{NH})$  modes with non-fundamental modes. Indeed, more detailed inspection of the temperature behavior and the overall spectral appearance between the imino stretchings in the deuterated (Fig. 4) and protiated (Fig. 3) samples implies that the minima between the  $\nu(\text{NH})$  band pairs around  $3145$  and  $3075\text{ cm}^{-1}$  are, in fact, transmission windows (Evans holes) on the broad  $\nu(\text{NH})$  absorptions.

#### 4. Conclusions

In general, the spectral appearance in the  $\nu(\text{XY})$  ( $\text{X} = \text{O}, \text{N}; \text{Y} = \text{H}, \text{D}$ ) regions of the studied isomorphous couples of imidazole and pyridine saccharinates are consistent with the data obtained from the X-ray diffraction experiments [1-3]. However, the appearance of the LNT spectrum of isotopically isolated  $\nu(\text{OD})$  modes in the compounds of type  $[\text{M}(\text{HIm})_4(\text{H}_2\text{O})_2](\text{sac})_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) does not conform exactly the structural data for these compounds at RT. More detailed low-temperature structural studies are needed, therefore, to explain the observed discrepancy.

#### 5. References

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## ВИБРАЦИОНО ИЗУЧУВАЊЕ НА АДУКТИТЕ НА МЕТАЛ(II) САХАРИНАТИ СО ИМИДАЗОЛ И ПИРИДИН. I. ВАЛЕНТНИ ОН/ОД И NH/ND ОБЛАСТИ КАЈ КОМПЛЕКСИТЕ НА КОБАЛТ(II) И НИКЕЛ(II)

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**Апстракт:** Снимени се областите на XY ( $\text{X} = \text{O}, \text{N}; \text{Y} = \text{H}, \text{D}$ ) валентните вибрации во Фурие-трансформните инфрацрвени спектри на протирани и деутерирани аналози на Co(II) и Ni(II) пиридин сахаринатите  $[\text{M}(\text{H}_2\text{O})_4(\text{py})_2](\text{sac})_2 \cdot 4\text{H}_2\text{O}$  и на имидазол сахаринатите со формула  $[\text{M}(\text{HIm})_4(\text{H}_2\text{O})_2](\text{sac})_2$ .

Лентите што главно се должат на ОН, ОД, NH и ND валентните вибрации се асигнирани и корелирани со кристалографските податоци. Изгледот на NH валентната област кај изучуваните имидазолни адукти може да се објасни со Фермиевска резонанца од Евансовски тип на NH валентната вибрација со модови од повисок ред. Спротивно на постоењето на единствен тип на асиметрично сврзани молекули вода во структурата на изучуваните имидазолни комплекси, најден е неочекуван однос 1:2 за интегралните интензитети на двата изотопски изолирани  $\nu(\text{OD})$  мода.