Experimental and theoretical studies on complex of Ni(II) ion with oximic derivative of L-alanine

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INTRODUCTION
The 2-hydroxyiminopropanoic acid [H₂-C-C(OOH)=NOH, hpa] ligand is a structural derivative of L-alanine. This modification of amino acid group can lead to considerable variation in coordination features. In our previous work [1] we presented structural and spectroscopic properties of the copper(II) complex of hpa. As the extension of these studies, we now present a new solid complex of Ni(II) ion with hpa. Its structure was studied by IR and Raman spectroscopy and DFT calculations (optimized geometry, harmonic frequencies and IR and Raman intensities). Additionally, we performed potential energy distribution calculations to show a detailed description of vibrational modes.

EXPERIMENTAL
The nickel (II) complex of hpa was synthesized using 1:2 molar ratio of nickel(II) ion to hpa at pH 8 by the similar procedure to those reported in [1,2]. The Raman spectrum was measured on a Bio-Rad step-scan spectrometer model FTS 6000 equipped with an Nd:YAG laser (excitation at 1064 nm) and a Bio-Rad Raman accessory (FTS 40). However, the IR spectra were run on Bruker (IFS 48) and Bio-Rad (FTS 60V) spectrometers in the mid and far IR regions, respectively.

COMPUTATIONAL
B3LYP [3,4] calculations with LanL2DZ basis set [5,6] (for model structures of nickel complex) were carried out using Gaussian 98 set of programs [7]. The computational details for hpa were presented in [1]. Raman intensities were determined by RA INT program [8], while the potential energy distributions (PED) were obtained from the Veda program [9].

RESULTS
Potentiometric and UV-VIS studies have suggested that the nickel complex exists as NiH(hpa)₂ species at pH 8, where two hpa molecules are bound in cis configuration [10]. However, crystallographic data of this complex synthesized in methanol solution showed the octahedral trans structure [11] (c.f. Fig.1).

In order to identify the molecular structure of Ni-hpa complex we analyzed experimental vibrational spectra and made theoretical simulation for trans and cis model structures (c.f. Fig. 1). The comparison of IR and Raman Ni-hpa spectra with those for well-defined cis Cu-hpa complex [1] indicates clearly a different configuration of ligand molecules around the metal ion. Furthermore, the comparison of vibrational spectra of Ni-hpa shows C₂v symmetry of the studied complex that is typical for the trans isomer (see Fig. 2). Additionally, the theoretical simulation of the vibrational spectra of trans and cis models confirmed trans coordination mode of Ni-hpa. Thus,
geometrical parameters and vibrational spectra are discussed below for trans bis-chelate square planar model of the hpa complex with Ni(II).

Figure 1. Suggested structures of the nickel complex of hpa.

Computed bond lengths obtained for the tetrameric structure [1] of hpa and its nickel complex present here are shown in Table 1 and show good agreement with other oximic ligands and their complexes studied so far [12-14].

<table>
<thead>
<tr>
<th>Bond</th>
<th>hpa HF/6-31G(d)</th>
<th>Ni-hpa B3LYP/Lanl2DZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=N</td>
<td>1.256</td>
<td>1.301</td>
</tr>
<tr>
<td>N-O</td>
<td>1.343</td>
<td>1.403</td>
</tr>
<tr>
<td>C=O</td>
<td>1.198</td>
<td>1.240</td>
</tr>
<tr>
<td>C-O</td>
<td>1.306</td>
<td>1.354</td>
</tr>
<tr>
<td>Coximic-Cmethyl</td>
<td>1.501</td>
<td>1.492</td>
</tr>
<tr>
<td>Ni-N</td>
<td>-</td>
<td>1.861</td>
</tr>
<tr>
<td>Ni-O</td>
<td>-</td>
<td>1.878</td>
</tr>
</tbody>
</table>

All bonds involved in metal ion binding lengthen considerably by 0.04-0.06 Å. This trend is typical for coordination by the oximic and carboxylic groups found so far. The comparison of metal-ligand bond lengths of the hpa complexes shows a significant lengthening of these bonds when Cu(II) ion is replaced by Ni(II) (~ 0.06 Å and ~ 0.04 Å for M-O and M-N, respectively). That indicates stronger chelation of Cu(II) ion by the hpa molecule. The same behavior has been observed for the alanine complexes [15].

The computed and experimental vibrational frequencies and assignments of the selected modes for Ni-hpa are summarized in Table 2. Several vibrations are interesting to consider since they change positions upon coordination. They are discussed below. According to symmetry constrains of the trans model, the in-counter-phase modes are observed in IR, whereas the in-phase counterparts are present in the Raman spectrum. One of the characteristic feature of the vibrational spectra of the studied class of complexes is the lowering frequencies of the asymmetric carboxylate stretching [\nu_{as}(COO)]. This mode is assigned to bands at 1600 and 1618 cm\(^{-1}\), in IR and Raman
spectra, respectively. DFT predicted similar separation of this vibration (16 \text{ cm}^{-1}). For the trans nickel complex of L-alanine, this mode has been found in IR spectrum at 1580 \text{ cm}^{-1} [16]. Chelation of Ni(II) ion by hpa causes lowering of v_{as}(COO) by 95 cm^{-1} in comparison to the neat hpa. According to our calculations, the COO symmetric stretching is observed at 1129 cm^{-1} in IR, whereas the Raman counterpart contributes to a band at 1103 cm^{-1}. The DFT-predicted frequencies are in very good agreement with the experimental results: 1143 (IR) and 1153 cm^{-1} (RA).

From our normal coordinate analysis, the C=N stretching mode shows a large contribution (over 60\%) to the medium bands at 1667 and 1655 cm^{-1} in IR and Raman spectra, respectively. DFT predicted separation of these bands very accurate and confirmed again trans configuration of Ni-hpa.

![Figure 2. Experimental spectra of complex of Ni(II) with hpa.](image)

A strong, sharp IR band at 1059 cm^{-1} can be ascribed to the Ni-hpa v(N-O) mode. It is worth to note that this vibration is slightly shifted to higher frequency comparing to hpa (1040 cm^{-1} in IR). Otherwise it was found in the cis copper complex of hpa [1] were v(N-O) is observed at 1142 cm^{-1}. Certainly, it results from the large change of the N-O bond length in cis complex comparing to the trans.

Table 3. Computed [with potential energy distribution (PED, \%) ] and experimental IR and Raman frequencies (in \text{cm}^{-1} ) and intensities (in relative units) of the selected stretching modes for the hpa complex with Ni(II).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Ni-hpa (exptal)</th>
<th>Ni-hpa (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
<td>Raman</td>
</tr>
<tr>
<td>v_{as}COO</td>
<td>1600</td>
<td>vs,br</td>
</tr>
<tr>
<td>v_{s}COO</td>
<td>1129</td>
<td>m</td>
</tr>
<tr>
<td>vC=N</td>
<td>1667</td>
<td>m,sh</td>
</tr>
</tbody>
</table>
According to the DFT calculations and the PED, the weak intensity IR bands at 556 and 486 cm\(^{-1}\) are assigned to the in-counter-phase stretches of Ni-N and Ni-O bonds, respectively. However, their equivalent in-phase modes are observed at 210 and 295 cm\(^{-1}\) in the Raman spectrum. It should be mentioned that the corresponding stretching vibrations of the Ni-alanine complex [16] were observed at 466 [\(\nu\)(Ni-N)] and 378 cm\(^{-1}\) [\(\nu\)(Ni-O)] in IR. This indicates that the metal-ligand bond in the complex studied here is stronger than that in the L-alanine complex.

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REFERENCES: