RAMAN, INFRARED, FAR-INFRARED AND THEORETICAL STUDIES OF OCTAHEDRAL ACETONITRILE COMPLEXES OF Mn(II) AND Cu(II)

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Abstract: Vibrational spectra of [M(NCCH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} complexes (where M=Mn\textsuperscript{2+} and Cu\textsuperscript{2+}) have been recorded involving [Mn(NCCD\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} species. Complete assignments and force constant calculations have been performed.

An interesting and useful phenomenon in coordination chemistry is the alteration of ligand vibrations upon coordination to different metal ions. In many cases the magnitudes of the wavenumber shifts give information about the bonding forces between the ligand and the metal ion. Generally the shifts of stretching frequencies of the donating groups (\textsuperscript{>}C=O, \textsuperscript{>}S=O, \equiv P=O etc.) are negative upon coordination.

However, methyl cyanide shows a positive shift in the \textsuperscript{C≡N} stretching frequency when coordinated to metal ions, due to the rehybridization at the nitrogen atom. In spite of the practical and theoretical interest of acetonitrile complexes, there have been relatively few reports on the vibrational spectra [1]. Previous spectroscopic investigations have been mainly concerned with the infrared spectra, very few Raman or far-infrared studies have been reported. We now report the complete vibrational spectroscopic and force field studies of [Mn(NCCH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+}, [Mn(NCCD\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} and [Cu(NCCH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} complexes, combined with various anions ([BF\textsubscript{4}]\textsuperscript{-}, [B(C\textsubscript{5}F\textsubscript{5})\textsubscript{4}]\textsuperscript{-}).

Both the Mn\textsuperscript{2+} [2] and Cu\textsuperscript{2+} [3] complexes have an octahedral symmetry due to the X-ray studies. Considering the CH\textsubscript{3} and CD\textsubscript{3} groups of the acetonitrile as point masses, the distribution of the so called “skeletal” vibrations among symmetry species are(O\textsubscript{h}-point group):

\[ \Gamma(\text{complex}) = 3A\textsubscript{1g} + 3E\textsubscript{g} + 2F\textsubscript{1g} + 3F\textsubscript{2g} + 6F\textsubscript{1u} + 3F\textsubscript{2u}. \]

Where \( A\textsubscript{1g}, E\textsubscript{g} \) and \( F\textsubscript{2g} \) are Raman and \( F\textsubscript{1u} \) species are infrared active modes.

Five infrared and four Raman features were observed in the CN stretching region (Table 1). Overtones and Fermi resonances made very complicated this spectral range. Overtones and combination bands of CH\textsubscript{3} deformation and C-C stretching vibrations were completely removed from the CN stretching region due course of deuteration of acetonitrile ligand, and only a single band at 2296 cm\textsuperscript{-1} has been recorded for [Mn(NCCD\textsubscript{3})\textsubscript{6}]\textsuperscript{2+} complex.

Fundamental infrared and Raman modes of skeletal vibrations of the complexes are summarized in Table 2.

Force filed calculations have been performed for complexes, considering methyl groups as point masses. Coordination (bonding) properties, \textit{trans}- influence and special vibrational behavior will be discussed in this paper.
TABLE 1. Assignment of the CN stretching region.

<table>
<thead>
<tr>
<th></th>
<th>[Mn(NCCH₃)₆]²⁺</th>
<th>[Mn(NCCD₃)₆]²⁺</th>
<th>ASSIGNMENT</th>
</tr>
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<tbody>
<tr>
<td>IR</td>
<td>Raman</td>
<td>Infrared</td>
<td></td>
</tr>
<tr>
<td>2404 vw</td>
<td></td>
<td></td>
<td>1374 + 1031 a</td>
</tr>
<tr>
<td>2313 vs 2285 vs</td>
<td>2314 s</td>
<td></td>
<td>A₁g CN stretches</td>
</tr>
<tr>
<td></td>
<td>2296 vs</td>
<td></td>
<td>F₁u</td>
</tr>
<tr>
<td></td>
<td>2290 vs 2279 s</td>
<td></td>
<td>E₉</td>
</tr>
<tr>
<td>2246 w, sh</td>
<td></td>
<td>2271 m,s</td>
<td>CD₃ asym str</td>
</tr>
<tr>
<td>2119 w, m</td>
<td></td>
<td>2248 vw</td>
<td>¹³CN stretch (F₁u)</td>
</tr>
<tr>
<td>2065 m</td>
<td></td>
<td>2x1031 a</td>
<td></td>
</tr>
</tbody>
</table>

a The bands at 1374, 1031 and 940 cm⁻¹ are the fundamental vibrations of coordinated acetonitrile, namely CH₃ umbrella, CH₃ rocking and C – C stretching modes, respectively.

b Spilling of the bands due to Fermi resonance with 1374+940 cm⁻¹ combination.

c Solid state splitting.

TABLE 2. Infrared and Raman active skeletal vibrations of [Mn(NCCH₃)₆]²⁺ complexes (M= Mn²⁺, Cu²⁺)

<table>
<thead>
<tr>
<th></th>
<th>[Mn(NCCH₃)₆]²⁺</th>
<th>[Mn(NCCD₃)₆]²⁺</th>
<th>[Cu(NCCH₃)₆]²⁺</th>
<th>Assignment</th>
</tr>
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<tr>
<td>IR</td>
<td>Raman</td>
<td>IR</td>
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<tr>
<td>2299 s a</td>
<td>2314 s</td>
<td>2296 vs</td>
<td>2297 s</td>
<td>2306 m</td>
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<td></td>
<td>2284.5 a</td>
<td>2297 s</td>
<td>2271 s</td>
<td>A₁g CN stretches</td>
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<td>940 m</td>
<td>2306 m</td>
<td>849 m</td>
<td>928 w</td>
<td>F₁u</td>
</tr>
<tr>
<td></td>
<td>940 m</td>
<td>928 w</td>
<td>940 m</td>
<td>E₉</td>
</tr>
<tr>
<td></td>
<td>934 w</td>
<td>928 w</td>
<td>934 w</td>
<td></td>
</tr>
<tr>
<td>384 s</td>
<td>362 s</td>
<td>388 m</td>
<td>395 s</td>
<td>F₁u M-N stretches</td>
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<td>395 s</td>
<td>388 m</td>
<td>395 s</td>
<td>A₁g</td>
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<td></td>
<td>294 m</td>
<td>388 m</td>
<td>270 m</td>
<td>E₉</td>
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<tr>
<td>378 s</td>
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<td>360 w</td>
<td>406 m,sh</td>
<td>F₁u</td>
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<tr>
<td></td>
<td>370 w, sh</td>
<td>360 w</td>
<td>406 m,sh</td>
<td>F₂g</td>
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<td>230 w</td>
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<td>236 w</td>
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<td></td>
<td>230 w</td>
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<td>F₂g</td>
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<td>94 s</td>
<td>126 m</td>
<td>90 m</td>
<td>127 w</td>
<td>F₁u</td>
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a Averaged values of frequencies listed in Table 1.

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References: