Research Paper

Preparation and Properties of Dinuclear Schiff Base Complexes of Co(II) and Ni (II) Via Inter-Complex Reaction

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Abstract: Homo and hetero dinuclear Schiff base complexes were prepared by inter – complex reaction between Co (II) and Ni (II) complexes of o-vanillin and o-aminophenol. Elemental composition and thermal properties of the complexes were established. Structures of the complexes were elucidated by spectroscopic methods like infrared spectroscopy, UV-visible spectroscopy and mass spectrometry. The powder X-ray diffractogram indicated crystalline nature with tetragonal symmetry of the complexes. Magnetic properties of these complexes were extensively studied using Gouy balance and VSM at variable temperatures. Low temperature ferromagnetism was exhibited by homodinuclear complexes while the heterodinuclear complex displayed antiferromagnetic coupling at low temperatures. The structure with minimum energy was identified using molecular mechanical method.

Keywords: Dinuclear Complex, Schiff Base, Magnetic Property, inter-complex reaction.

Introduction
Extensive research work has been done on transition metal complexes [11,2]. These studies include ordinary complexes, chelates and mixed ligand complexes. Inclusion of a variety of ligands in complexes has enabled their applications as biocides, catalysts, NMR shift reagents and DNA binders [3]. The properties of complexes originating due to metal ions may get enhanced in polynuclear complexes. Moreover, the interaction between the metal ions in such complexes may give rise to new properties [4-6]. Homopolymeric complexes are generally obtained using polydentate ligands in which all the donor groups are unable to coordinate with the same metal ion [7]. The preparation of heteropolynuclear complexes has always remained a challenge for synthetic chemists. Such complexes have been prepared successfully using an approach ‘Complexes as Ligands’ [8-10]. Here, a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL) [11, 12]. This MOL is capable of further coordination with a different metal ion resulting in formation of mixed metal complexes [13].

We report here, a novel approach of synthesizing mixed metal complexes. It has been hypothesized that the coordinated ligands of two metal chelates can be reacted to obtain a new metal chelate. In the present work, we have allowed to react, two such complexes under the conditions that permit coordinated NH₂ to react with the coordinated CHO group. Here, as ionic bonds of the precursor do not dissociate, metal-ligand bonding in both the complexes remained intact [9]. Due to a reaction between coordinated amino and aldehyde groups, Schiff bases were formed. The imine nitrogen of the Schiff base was allowed to coordinate with the metal nearby while the deficiency created at the metal ion on aldehyde end was sufficed by aquo ligands liberated during imine formation. The resultant dinuclear complex thus has one of the metal ions in diaquo form. When the metal ions in the reacting complexes were different, the resultant complex was mixed metal complex.

Material and Methods
Reagents: o-aminophenol and o-vanillin (≥ 99.0%) were purchased from Sigma-Aldrich. Cobalt acetate, nickel acetate, sodium hydroxide and solvents (≥ 99.0%) were purchased from E-Merck Ltd, Mumbai (India). The purification was done according to the needs through known procedures [14].

Measurements: Elemental analysis (C, H, and N) was carried out on PERKIN ELMER, Series II, 2400 CHNS/O Analyzer. The metal composition of the
complexes was determined by EDTA titration subsequent to the decomposition of metal complexes with an acid mixture of HClO₄, H₂SO₄ and HNO₃ (1:1:2.5). The metal composition of the complexes was carried out by following method. In case of Co Ni (SB)₂ (H₂O)₂ after decomposition of the complex, Ni (II) was precipitated as dimethylglyoxime complex and the filtrate containing Co (II) ion was titrated against standard EDTA solution.

For the complexes Ni₂ (SB)₂ (H₂O)₂ and Co₂ (SB)₂ (H₂O)₂ the nickel content and cobalt content were calculated by precipitation method and titration method respectively. Infrared spectra were recorded on a Fourier transform infrared (FTIR), GX FT-IR PERKIN ELMER, in the range 4000-400 cm⁻¹ by making a KBr pellet of the compound. The electronic spectra of samples were recorded on UV Lambda 19 PERKIN ELMER spectrophotometer. Thermogravimetric analysis was carried out on NETZSCH. The mass spectra are obtained using API QSTAR Pulsar LC-MS quadruple and TOF based single mass spectrometer.

The X-ray diffraction studies were carried out on XRD diffractometer (powder) Philips model Xpert MPD. The magnetic moments were measured on Gouy balance. The Gouy tube was calibrated using mercury (II) tetrathiocyanatocobaltate (II). Magnetic study of the complex at variable temperature and mercury Gouy balance. The Gouy tube was calibrated using absolute alcohol (~20 ml), were carried out on XRD diffractometer (powder) Philips model Xpert MPD. The melting point of all the complexes was found to be higher than 350 °C.

Results and Discussion
IR spectral studies: The IR spectra of reactant complexes and dinuclear complexes displayed some similarities and dissimilarities. Significant IR bands are shown in Table 1. The spectra of reactant complex M (O-VAN)₂ showed a broad and strong band at 1635 cm⁻¹ attributed to C = O stretching. The C - O (H) phenolic stretching frequencies were observed in the region of 1290 cm⁻¹. A broadband appearing at 1033 cm⁻¹ was assigned to the presence of -OCH₃ group. A weak band at 450 cm⁻¹ observed in the spectra was due to M - O stretching frequency.

IR spectra of the reactant complex M’ (2-AP)₂ showed a strong absorption at 1598 cm⁻¹ which was assigned to coupled vibrations of NH₂ bending and C - N stretching [15]. Absorptions at 3234 cm⁻¹ and 3260 cm⁻¹ were attributed to NH₃ asymmetric and symmetric stretching frequency respectively. A weak band at 547 cm⁻¹ was observed in the complex which was assigned to the M - N stretching frequency.

Table 1
FT - IR spectral frequencies of complexes

<table>
<thead>
<tr>
<th>System</th>
<th>ν_C=O cm⁻¹</th>
<th>ν_O-H cm⁻¹</th>
<th>ν_M-O cm⁻¹</th>
<th>ν_M-N cm⁻¹</th>
<th>δ_H₂O (coord.) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>M (O-VAN)₂</td>
<td>-</td>
<td>-</td>
<td>450</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M (2-AP)₂</td>
<td>-</td>
<td>-</td>
<td>445</td>
<td>547</td>
<td>-</td>
</tr>
<tr>
<td>Co Ni (SB)₂ (H₂O)₂</td>
<td>1610</td>
<td>3405</td>
<td>450</td>
<td>557</td>
<td>1588</td>
</tr>
<tr>
<td>Ni₂(SB)₂ (H₂O)₂</td>
<td>1605</td>
<td>3400</td>
<td>455</td>
<td>555</td>
<td>1585</td>
</tr>
<tr>
<td>Co₂(SB)₂ (H₂O)₂</td>
<td>1608</td>
<td>3400</td>
<td>458</td>
<td>560</td>
<td>1587</td>
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</table>
Table 2
Electronic transitions and their assignments in complexes

<table>
<thead>
<tr>
<th>System</th>
<th>ν1 cm⁻¹</th>
<th>ν2 cm⁻¹</th>
<th>N3 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoNi(SB)₂(H₂O)₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A₂ (F) → 4T₁ (F)</td>
<td></td>
<td>18900</td>
<td>23000</td>
</tr>
<tr>
<td>3T₁g (F) → 3T₂g (F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₂(SB)₂(H₂O)₂</td>
<td>10000</td>
<td>12000</td>
<td>22100</td>
</tr>
<tr>
<td>3T₁g (F) → 3T₂g (F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₂(SB)₂(H₂O)₂</td>
<td>9600</td>
<td>20900</td>
<td>23300</td>
</tr>
<tr>
<td>4A₂ (F) → 4T₁ (F)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*= Absent

Figure 1: Reaction scheme for the synthesis of dinuclear complexes

A band seen around 3050 cm⁻¹ was attributed to the aromatic ring vibrations in both reactant complexes. An absence of a broad band in the region of 3400 cm⁻¹ in the reactant complexes indicated the absence of any coordinated water molecule.
The bands due to transitions for a Co (SB) attached to C = O stretching (1629 cm\(^{-1}\)) were found to be absent. However, emergence of a new sharp and strong peak in the region of 1610 cm\(^{-1}\) was the evidence of imine formation. The stronger bands appearing at 540 - 560 cm\(^{-1}\) and 450 - 460 cm\(^{-1}\) were assigned to M - N and M - O stretching frequencies. A band seen at 1280 cm\(^{-1}\) was assigned to C - O stretching. The peak due to \(\text{OCH}_3\) group reactant complex retained its position without any shifting which indicated the refrainment of the –OCH\(_3\) group from coordination. A new band appearing in the range 740 – 750 cm\(^{-1}\) was assigned to the wagging mode of the coordinated water\(^{[16]}\).

**Electronic Spectra:** Electronic absorption spectra of all three complexes were carried out in DMSO. Absorption spectra are shown in Figure 2. Band position and their assignments are summarized in Table 2. The spectrum of complex Co (SB)\(_2\) (H\(_2\)O)\(_2\) showed broad peaks at 23000 cm\(^{-1}\) and 18900 cm\(^{-1}\). These bands were assigned to \(3T_{1g} (F) \rightarrow 3T_{1g} (P)\) and \(3T_{1g} (F) \rightarrow 3A_{2g} (F)\) transitions suggesting a tetrahedral environment for Ni (II) ion. The same two bands were also assigned to \(4A_{2} (F) \rightarrow 4T_{1} (F)\) and \(4A_{2} (F) \rightarrow 4T_{1} (P)\) transitions for a Co (II) ion in tetrahedral geometry. The bands due to transitions \(3T_{1g} (F) \rightarrow 3T_{2g} (F)\) in Ni (II) and \(4A_{2} (F) \rightarrow 4T_{2} (F)\) in Co (II) were not observed. Ni\(_2\) (SB)\(_2\) (H\(_2\)O)\(_2\) exhibited three bands at 221000 cm\(^{-1}\) and 12000 cm\(^{-1}\) and 10000 cm\(^{-1}\) and were assigned to \(3T_{1g} (F) \rightarrow 3T_{1g} (P)\), \(3T_{1g} (F) \rightarrow 3A_{2g} (F)\) and \(3T_{1g} (F) \rightarrow 3T_{2g} (F)\) transitions suggesting tetrahedral symmetry of Ni (II). The spectrum of Co\(_2\) (SB)\(_2\) (H\(_2\)O)\(_2\) displayed three bands at 23300 cm\(^{-1}\), 20900 cm\(^{-1}\) and 9600 cm\(^{-1}\) which were assigned to \(4A_{2} (F) \rightarrow 4T_{1} (F)\), \(4A_{2} (F) \rightarrow 4T_{1} (P)\) and \(4A_{2} (F) \rightarrow 4T_{2} (F)\) transition respectively for a Co (II) in a tetrahedral geometry\(^{[17]}\).

**Elemental and thermal analysis:** The elemental analysis along with metal estimation data is shown in Table 3. The experimental data strongly supported the theoretical values\(^{[18]}\). Thermal degradation of the complexes was seen in the TGA thermograms as shown in Figure 3. A negligible weight loss was observed below 150°C, this was attributed to the presence of small amounts of adsorbed water. In the first step, a loss of two coordinated water molecules (H\(_2\)O\(_2\)) with mass losses of (obs. = 5.56%, Calc. = 5.65%) was observed. The complexes exhibited thermal stability up to 350°C after which an accelerated weight loss of the organic fraction, with mass loss (obs. = 70.9%, Calc. = 70%) in the region of 400°C to 550°C was observed. The residual weight was not considered.

### Table 3
Analytical data of the complexes

<table>
<thead>
<tr>
<th>System</th>
<th>Mol. Wt. g/mole</th>
<th>Color</th>
<th>% Yield (g)</th>
<th>(\mu_{\text{eff}}) per ion B.M.</th>
<th>Elemental Analysis % Found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Co Ni (SB)(_2) (H(_2)O)(_2)</td>
<td>636.14</td>
<td>Yellowish Brown</td>
<td>80 (1.017)</td>
<td>*</td>
<td>52.87 (52.84)</td>
</tr>
<tr>
<td>Ni(_2) (SB)(_2) (H(_2)O)(_2)</td>
<td>635.90</td>
<td>Yellow</td>
<td>85 (1.081)</td>
<td>3.3</td>
<td>52.89 (52.85)</td>
</tr>
<tr>
<td>Co(_2) (SB)(_2) (H(_2)O)(_2)</td>
<td>636.38</td>
<td>Brown</td>
<td>78 (0.992)</td>
<td>4.4</td>
<td>52.85 (52.83)</td>
</tr>
</tbody>
</table>

* Could not be calculated

### Table 4
Powder X-ray diffraction data for Co\(_2\) (SB)\(_2\) (H\(_2\)O)\(_2\)

<table>
<thead>
<tr>
<th>h k l</th>
<th>(\Delta d)</th>
<th>d (Obs.)</th>
<th>d (Cal.)</th>
<th>(\Delta d)</th>
<th>Intensity (Obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>0.004</td>
<td>3.5333</td>
<td>3.5291</td>
<td>0.0042</td>
<td>100</td>
</tr>
<tr>
<td>1 1 0</td>
<td>0.151</td>
<td>2.2588</td>
<td>2.2659</td>
<td>0.0071</td>
<td>45</td>
</tr>
<tr>
<td>2 0 1</td>
<td>0.082</td>
<td>2.0921</td>
<td>2.0632</td>
<td>0.0289</td>
<td>34</td>
</tr>
<tr>
<td>2 2 0</td>
<td>0.435</td>
<td>1.7809</td>
<td>1.7645</td>
<td>0.0164</td>
<td>16</td>
</tr>
<tr>
<td>1 1 3</td>
<td>-0.105</td>
<td>1.6132</td>
<td>1.6055</td>
<td>0.0077</td>
<td>10</td>
</tr>
</tbody>
</table>

80
Figure 3: TGA thermograms of complexes

Figure 4: Mass spectra of Co$_2$(SB)$_2$(H$_2$O)$_2$ complex
Figure 5: Fragmentation pattern for Co$_2$(SB)$_2$(H$_2$O)$_2$ complex

Figure 6: X-ray diffraction pattern of Co$_2$(SB)$_2$(H$_2$O)$_2$ complex

**Mass spectra:** Mass spectra of the complexes was carried out in a polar aprotic solvent, acetonitrile as ESI-MS. The spectra of Co$_2$(SB)$_2$(H$_2$O)$_2$ showed peaks attributed to the molecular ion at m/z of 636.
(M') and m/z of 638 (M+2) (Figure 4). The spectra of Ni₂(SB)₂(H₂O)₂ and Co Ni (SB)₂(H₂O)₂ showed peaks at m/z 636 (M') and 638 (M+2). These molecular ion peaks were in line with the proposed structures of the complexes. Several peaks for fragments with m/z = 605, 509, 413, 380, 360 and 244 were also noticed in the spectrum, which corresponded to the fragments associated with a different number of H⁺ ions shown in Figure 5.

**Powder X-ray diffraction:** Powder X-ray diffraction pattern showed sharp intense peaks suggesting the crystalline nature of all the complexes. All the reflections were indexed for h, k and l values (Table 4) using methods reported in the literature. The observed inter planer spacing values i.e. d-spacing with 20 angles were measured from experimental diffractogram (Figure 6) and compared with standard reference pattern. The complex was found to be tetragonal crystal having unit cell parameters such as a =4.9910, b=4.9910 and c=5.4089 with maximum deviation of θ = 0.025 and α = 90, β = 90, γ = 90 at the wavelength of 1.540598.

**Magnetic studies:** The magnetic properties of the complexes were studied by Gouy balance (Table 3). The effective magnetic moments at room temperature were slightly higher than expected. Temperature dependent magnetic properties were studied using well ground samples in the temperature range 2-300 K using a vibrating sample magnetometer. The graph of magnetic susceptibility (emu/g) vs. temperature indicated a paramagnetic behavior of the complexes in the given temperature range. The plot of inverse of magnetic moment vs. temperature followed the Curie - Weiss law (χ = C / T-θ) where, θ is Curie - Weiss temperature and C is Curie's constant. The positive and negative values of Curie - Weiss temperature designate ferromagnetic and antiferromagnetic interactions respectively [20-22]. Figures 7, 8 and 9 represents the plots of χ vs. T and 1/χ vs. T for the complex Co Ni (SB)₂(H₂O)₂, Ni₂(SB)₂(H₂O)₂ and Co₂(SB)₂(H₂O)₂ respectively. For Co Ni (SB)₂(H₂O)₂ Curie -Weiss temperature was found to be negative (T_N = -7 K) which suggested antiferromagnetic interaction at lower temperature in the complex. For homodinuclear complexes Ni₂(SB)₂(H₂O)₂ and Co₂(SB)₂(H₂O)₂ Curie Weiss temperature was found to be positive (T_N = 25 K and T_N =10 K) which indicated a ferromagnetic interaction in both compounds [23, 24].

**Structure and Bonding:** IR spectra of the samples clearly indicated the presence of imine group, M - O and M - N bonds as well as coordinated water. The electronic spectra and elemental analysis coupled with thermogravimetric analysis suggested the formation of dinuclear complexes with metal ions in tetrahedral symmetry and two coordinated water molecules. Formation of dinuclear complexes was also evident from the mass spectra. The results from the magnetic studies could also help in narrowing the numbers of possible structures for the complexes under present investigation. The powder X-ray diffraction studies supported the above observations and suggested a tetragonal symmetry for the complexes. The proposed structure (Figure 1) was obtained by minimization of energy using the molecular mechanical method.

**Conclusion**

The preparation of dinuclear complexes by a new synthetic route is strongly supported by analytical data.
The infrared spectra, electronic spectra, elemental analysis and thermal data unanimously favored the success of the proposed reaction. The molecular ion peaks in the mass spectra also supported the formation of dinuclear complexes. Powder X-ray data suggested a tetragonal symmetry for the complexes. The ferromagnetic and antiferromagnetic behavior revealed from the magnetic studies offer interesting potential applications of these materials. Many new complexes can be prepared using this novel synthetic route.

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