

Synthesis and Characterization of Homo and Heterodinuclear Complexes of Co(II) and Ni(II)

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Abstract: Homo and heterodinuclear complexes of Co(II) and Ni(II) were obtained by reaction between the corresponding complexes of salicylaldehyde and *o*-aminophenol. Elemental and metal compositions of these mixed metal complexes were obtained using analytical methods. Thermal characterization of the complexes was done using TGA. Spectral methods like infrared spectroscopy, UV-Visible spectroscopy, spectrofluorimetry and mass spectrometry were employed for structural elucidation. Magnetic properties of these complexes were extensively studied using Guoy Balance and VSM at variable fields and temperatures. Low temperature ferromagnetism was exhibited by homodinuclear complexes while the heterodinuclear complex showed antiferromagnetic coupling at low temperature. The most stable structure was identified using molecular mechanical method.

Keywords: Dinuclear complex, Schiff base, Magnetic property

Introduction

Plenty of research work has been done on transition metal complexes¹⁻³. These studies include ordinary complexes, chelates and mixed ligand complexes. Inclusion of varieties of ligands in complexes has enabled the tailor making of the properties of the complexes originating due to ligands. In order to fiddle with the properties of the complexes originating due to metal ions, polynuclear complexes with inclusion of different metals is imperative. Mixed-metal complexes are a class of compounds which can have properties that are not present in ordinary complexes⁴⁻¹¹. However, the preparation of mixed metal complexes has always remained a challenge for synthetic chemists. Mixed metal complexes have been prepared^{3-5,12} successfully using an approach 'Complexes as Ligands'. Here, a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL). This MOL is capable of further coordination with a different metal ion resulting in formation of mixed metal complexes.

For the first time, 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.

Polydentate ligands bind the metal ion in complexes using coordinate covalent as well as ionic bonds¹³⁻¹⁴. Ligands like aminophenols and hydroxyaldehydes to form the metal chelates with different transition metals are well known. In the present work, we made two such complexes to react with each other under the conditions that permit coordinated NH_2 to react with the coordinated CHO group. Due to a reaction between amino and aldehyde the Schiff base complex was formed.

Experimental

2-Aminophenol and salicylaldehyde ($\geq 99.0\%$) were purchased from Sigma-Aldrich. Cobalt acetate, nickel acetate, sodium hydroxide and solvents ($\geq 99.0\%$) were purchased from E-Merck Ltd, Mumbai (India). The purification was done according to the needs through known procedures¹⁵.

Measurements

Elemental analysis (C, H and N) was done using Perkin Elmer, Series II, 2400 CHNS/O Analyzer. The metal content of the complexes was determined by EDTA titration subsequent to the decomposition of metal complexes with an acid mixture of HClO_4 , H_2SO_4 and HNO_3 (1:1.5:2.5). In case of $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ after decomposition of the complex, Ni(II) was precipitated as dimethylglyoxime complex and the filtrate containing Co(II) ion was titrated against the standard EDTA solution. For the complexes $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ and $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ the nickel content and cobalt content were estimated 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 $4000\text{--}400\text{ cm}^{-1}$ by making a KBr pellet of the compound. The electronic spectra of samples were obtained using UV Lambda 19 Perkin Elmer spectrophotometer. The fluorescence spectra of the complexes dissolved in dimethyl formamide was obtained on Perkin Elmer, LS-50B spectrofluorimeter. Thermogravimetric analysis was recorded on Mettler Toledo. The mass spectra are obtained using API QSTAR Pulsar LC-MS quadrupole and TOF based single mass spectrometer. The magnetic moments were measured on Gouy balance. The Gouy tube was calibrated using mercury(II) tetrathio-cyanatocobaltate(II). Magnetic study of the complex at variable temperature and magnetic field was carried out on Lakeshore VSM7410 vibrating sample magnetometer.

Synthesis

The synthesis consisted of three steps as shown below. In the first step, 20 mL of 0.488 g (0.2 M) salicylaldehyde (SAL) dissolved in absolute alcohol and 20 mL of 0.5 g ($\sim 0.1\text{ M}$) cobalt/nickel acetate dissolved in rectified spirit were mixed and stirred for an hour to obtain a four coordinated complex *viz.* $\text{M}(\text{SAL})_2$ in solution. In the second step, 20 mL of 0.436 g (0.2 M) 2-aminophenol (2-AP) dissolved in absolute alcohol and 0.5 g ($\sim 0.1\text{ M}$) cobalt / nickel acetate dissolved in absolute alcohol were mixed and stirred for 1 h separately to obtain a four coordinated complex *viz.* $\text{M}'(2\text{-AP})_2$ in solution.

Finally, the solution of $\text{M}(\text{SAL})_2$ was slowly added to the refluxing solution of $\text{M}'(2\text{-AP})_2$. After six hours, new colored products separated under slightly alkaline conditions created by sodium hydroxide. These precipitates were filtered, washed with cold water and rectified spirit and finally dried under vacuum for 72 hours

Results and Discussion

Infrared studies

In order to derive the structures of the dinuclear complexes, similarities and dissimilarities in the IR spectra of the reactant complexes and the resulting complexes were brought out.

Significant IR bands are shown in Table 1. The spectra of reactant complex $M(\text{SAL})_2$ exhibited a broad and strong peak at 1635 cm^{-1} which was assigned to the $\text{C}=\text{O}$ stretching in the complex. A weak band at 457 cm^{-1} observed in the spectra was due to $\text{M}-\text{O}$ stretching frequency.

Table 1. FT - IR spectral frequencies of complexes

| System | $\nu_{\text{C}=\text{N}}\text{ cm}^{-1}$ | $\nu_{\text{O}-\text{H}}\text{ cm}^{-1}$ | $\nu_{\text{M}-\text{O}}\text{ cm}^{-1}$ | $\nu_{\text{M}-\text{N}}\text{ cm}^{-1}$ | $\delta_{\text{H}_2\text{O (coord.)}}\text{ cm}^{-1}$ |
|--|--|--|--|--|---|
| $M(\text{SAL})_2$ | - | - | 457 | - | - |
| $M(2\text{-AP})_2$ | - | - | 450 | 567 | - |
| $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ | 1605 | 3400 | 450 | 565 | 1585 |
| $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | 1613 | 3405 | 450 | 565 | 1587 |
| $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | 1607 | 3400 | 445 | 560 | 1585 |

IR spectra of the reactant complex $M'(2\text{-AP})_2$ showed a strong absorption at 1598 cm^{-1} which was assigned to coupled vibrations of NH_2 bending and $\text{C}-\text{N}$ stretching¹⁶⁻¹⁸. Absorptions at 3324 cm^{-1} and 3260 cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequency respectively. A weak band at 567 cm^{-1} was observed in the complex which was assigned to the $\text{M}-\text{N}$ stretching frequency.

Both the complexes showed a band in the region of 3050 cm^{-1} arising due to aromatic ring vibrations. The spectra of both the reactant complexes did not show a broad band in the region of 3400 cm^{-1} which indicated the absence of any coordinated water molecule.

In the spectra of resulting dinuclear complexes *viz.* $\text{MM}'(\text{SB})_2(\text{H}_2\text{O})_2$, peaks due to $\text{C}=\text{O}$ stretching (1629 cm^{-1}), NH_2 bending and NH_2 stretching (3324 cm^{-1} and 3260 cm^{-1}) were found to be absent. New stronger bands appearing at $560\text{-}570\text{ cm}^{-1}$ and $450\text{-}460\text{ cm}^{-1}$ were assigned to $\text{M}-\text{N}$ and $\text{M}-\text{O}$ stretching frequencies. A band seen at 1249 cm^{-1} was assigned to $\text{C}-\text{O}$ stretching. A sharp and strong peak at 1605 cm^{-1} which may be attributed to $\text{C}=\text{N}$ stretching was in accordance with the proposed structure of the dinuclear complex.

Electronic spectra

All the complexes showed absorption peaks in the near ultra - violet region and these high intensity bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand. The electronic absorption spectra of the complexes are shown in Figure 1. Band positions and their assignments are summarized in Table 2. The complex $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ in dimethylformamide showed a broad peak at 23200 cm^{-1} and 18800 cm^{-1} . These bands are assigned to ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ and ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{A}_{2\text{g}}(\text{F})$ transitions suggesting¹⁹ tetrahedral symmetry of $\text{Ni}(\text{II})$. The same bands are assigned to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition of $\text{Co}(\text{II})$ in tetrahedral geometry. The bands due to transitions ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$ in $\text{Ni}(\text{II})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ in $\text{Co}(\text{II})$ were not observed in the mixed metal complex.

Table 2. Electronic transitions and their assignments in complexes

| System | $\nu_1\text{ cm}^{-1}$ | $\nu_2\text{ cm}^{-1}$ | $\nu_3\text{ cm}^{-1}$ |
|--|---|---|---|
| $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ | - | 18800 | 23200 |
| | ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ | ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ | ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ |
| | ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$ | ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{A}_{2\text{g}}(\text{F})$ | ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ |
| $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | 10000 | 12000 | 22000 |
| | ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$ | ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{A}_{2\text{g}}(\text{F})$ | ${}^3\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ |
| $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | 9500 | 20800 | 23200 |
| | ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ | ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ | ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ |

* = Absent

In case of $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$, peaks were observed at 23200 cm^{-1} and 20800 cm^{-1} and 9500 cm^{-1} respectively. These bands were assigned to $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$, $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ and $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_2(\text{F})$ transition as expected for Co(II) in tetrahedral geometry.

$\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ exhibited peaks at 22000 cm^{-1} and 12000 cm^{-1} and 10000 cm^{-1} respectively. These bands were assigned to $^3\text{T}_{1g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$, $^3\text{T}_{1g}(\text{F}) \rightarrow ^3\text{A}_{2g}(\text{F})$ and $^3\text{T}_{1g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ transitions suggesting tetrahedral symmetry of Ni(II)²⁰.

Fluorescence spectra

The Fluorescence spectra of complexes shown in Figure 1 were conducted in dimethyl-formamide. All the complexes exhibited a broad band around 18800 cm^{-1} and another strong band in the vicinity of 11600 cm^{-1} . The former broad band was attributed to the coupling of $\pi \rightarrow \pi^*$ transition in the ligand with one or two of the d-d transitions observed in absorption spectra^{10,12,21}. A Stoke's shift of about 1200 cm^{-1} was observed here. The emission at 11600 cm^{-1} was probably the mirror image of the absorption band observed in the nickel containing complexes around 12000 cm^{-1} .

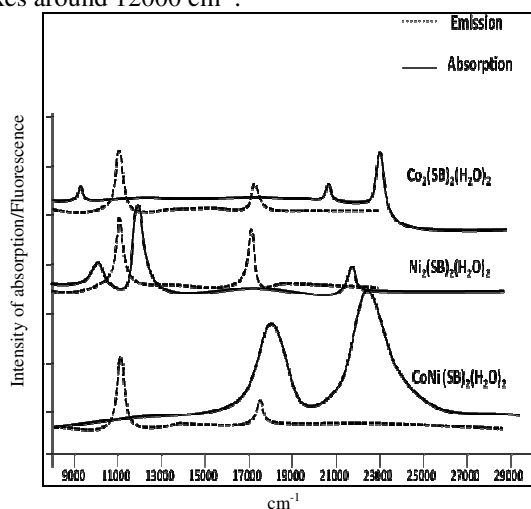


Figure 1. Absorptions and emissions in complexes

Elemental and thermal analysis

The C, H, N analysis along with metal estimation data shown in Table 3 supported the coordination number four for the metals¹⁹. Moreover, it suggested the presence of two water molecules in the complex.

Table 3. Analytical data of the complexes

| System | Mol. Wt. g/mole | %Yield, g | μ_{eff} per ion B.M. | Elemental analysis % Found (Calculated) | | | | |
|--|-----------------|-----------|---------------------------------|---|----------------------------|--------|---------|------|
| | | | | C | H | N | Co | Ni |
| $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ | 575.62 | 75 | * | 54.28 | $\text{CoNi}(\text{SB})_2$ | 575.62 | 75 | * |
| | | (0.862) | | (54.21) | $(\text{H}_2\text{O})_2$ | | (0.862) | |
| $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | 575.39 | 80 | 3.60 | 54.19 | $\text{Ni}_2(\text{SB})_2$ | 575.39 | 80 | 3.60 |
| | | (0.920) | | (54.23) | $(\text{H}_2\text{O})_2$ | | (0.920) | |
| $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | 575.86 | 70 | 4.59 | 54.21 | 3.84 | 4.88 | 20.34 | - |
| | | (0.805) | | (54.18) | (3.85) | | (20.45) | |

* Could not be calculated

The TGA thermograms of the complexes shown in Figure 2 exhibited weight loss during all the phases. A negligible weight loss was observed below 150 °C, this was attributed to the presence of small amounts of adsorbed water. The weight loss in the first step above 150 °C was found to be around 6-7% which accounts for two coordinated water molecules in the calculated molecular weight. The complexes exhibited thermal stability up to 350 °C after which an accelerated weight loss was observed in the region of 400 °C to 550 °C which was attributed to ligand decomposition.

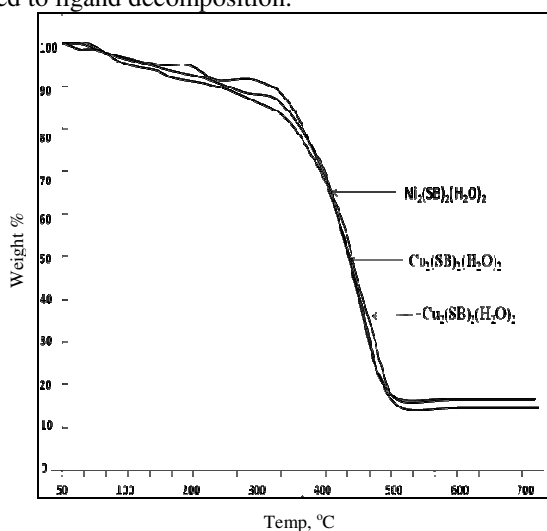


Figure 2. TGA thermograms of complexes

Mass spectra

Mass spectra of the complexes were carried out by dissolving it in acetonitrile as the ESI-MS method. The spectra of the complex $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ showed peaks attributed to the molecular ion at $m/z=576$ (M^+) and $m/z=578$ for ($\text{M}+2$). The spectra of the complexes also exhibited peaks at $m/z= 542, 452, 348, 331, 213$ and 182 for the stable fragments of the complexes.

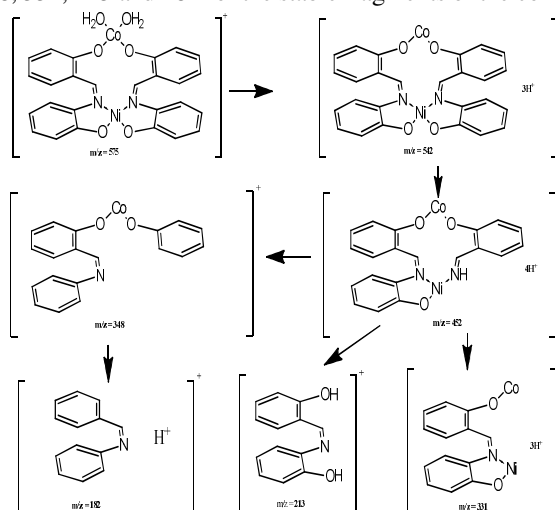


Figure 3. Fragmentation pattern of the dinuclear complex

Powder XRD

We have tried to isolate single crystal of the complexes for accurate x-ray crystal study but could not succeed to develop single crystal. The powder diffraction of the compound was carried out to presume the lattice dynamics and structure of complexes. The observed inter planer spacing values *i.e.* *d*-spacing were measured from the diffractogram of the compounds. Moreover, the Miller indices *h*, *k* & *l* assign to each *d*-value along with 2θ angles for $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$ is given in the Table 4. The results show that the complexes belong to the tetrahedral crystal system having unit cell parameter such as $a = 4.9910$, $b = 4.9910$ and $c = 5.4089$ with maximum deviation of $\theta = 0.025$ and $\alpha = 90$, $\beta = 90$, $\gamma = 90$ at the wavelength of 1.540598. The sharp peaks suggests the all complexes are crystalline in nature with tetragonal symmetry.

Table 4. The powder diffraction data of the $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$

| <i>h k l</i> | 2θ (Obs.) | 2θ (Cal.) | $\Delta 2\theta$ | <i>d</i> (Obs.) | <i>D</i> (Cal.) | Δd | Intensity (Obs.) |
|--------------|---------------------|---------------------|------------------|--------------------|--------------------|------------|---------------------|
| 1 0 0 | 17.421 | 17.757 | - 0.336 | 5.0905 | 4.9910 | 0.0995 | 19 |
| 1 1 0 | 25.211 | 25.214 | - 0.003 | 3.5320 | 3.5291 | 0.0029 | 100 |
| 2 0 1 | 39.910 | 39.747 | 0.163 | 2.2588 | 2.2659 | -0.0071 | 46 |
| 2 1 1 | 43.345 | 43.843 | - 0.498 | 2.0915 | 2.0632 | 0.0283 | 39 |
| 2 2 0 | 51.325 | 51.766 | - 0.441 | 1.7802 | 1.7645 | 0.0157 | 21 |
| 1 1 3 | 57.214 | 57.340 | - 0.124 | 1.6128 | 1.6055 | 0.0073 | 13 |

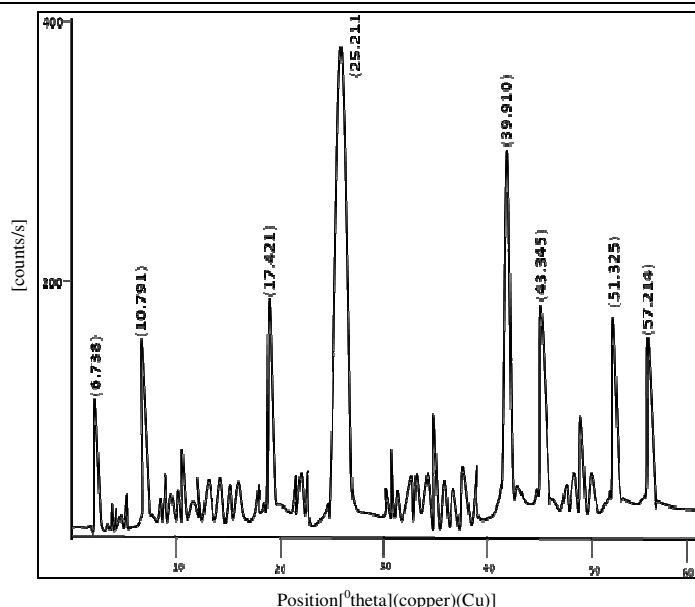


Figure 4. Powder diffraction pattern of $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$

Magnetic studies

The magnetic properties of the complexes were studied by Gouy balance (Table 3) and then by vibrating sample magnetometer with a temperature variation. The effective magnetic moment at room temperature for $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was found to be 3.60 BM for each Ni(II) ion which was slightly higher than spin only value of tetrahedral nickel (~ 2.82 BM). The

effective magnetic moment at room temperature for $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was found to be 4.59 BM for each Co atom which was also slightly lower than spin only value for cobalt(II) ion in the tetrahedral environment (~ 3.87 BM). For the heterodinuclear complex $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$, it was difficult to find the effective magnetic moment per each ion. These higher values of the effective magnetic moment suggested the presence of some ferromagnetic interactions at room temperature^{22,23}.

The temperature dependent magnetic properties were studied using well ground samples in the temperature range 2-300 K using a vibrating sample magnetometer. The magnetism values were measured in (emu/g).

The results were then represented in form of $\chi_m T$ vs. T plots as shown in Figure 5a, 5b and 5c. For a paramagnet the molar susceptibility χ_m is given by Curie's law in SI units as shown in equation (4). The $\chi_m T$ values at 298 K obtained from Figures 3a, 3b and 3c were substituted in equation (5) which is another form of the equation (4) to obtain the effective magnetic moment (μ_{eff}) values at 298 K in Bohr magnetons per formula unit.

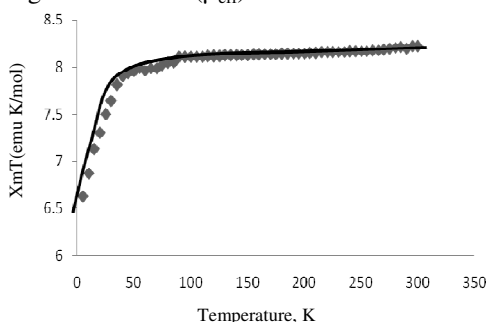


Figure 5a. A plot of $\chi_m T$ vs. T for $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$

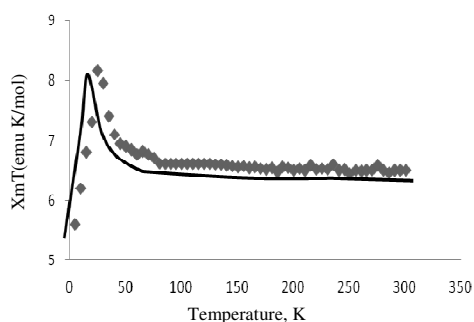


Figure 5b. A plot of $\chi_m T$ vs. T for $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$

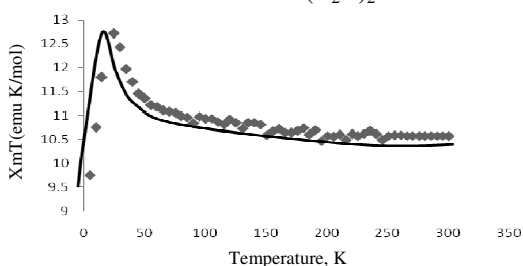


Figure 5c. A plot of $\chi_m T$ vs. T for $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$

$$\chi_m = \frac{\mu_o N_A \mu_{\text{eff}}^2 \mu_B^2}{3k_B T} \quad (4)$$

$$\mu_{\text{eff}} = 2.827 \sqrt{\chi_m^{\text{cgs}} T} \approx \sqrt{8 \chi_m^{\text{cgs}} T} \quad (5)$$

For the heterodinuclear complex $\text{CoNi}(\text{SB})_2(\text{H}_2\text{O})_2$, $\chi_m T$ value at 300 K was found to be $8.22 \text{ emu K mol}^{-1}$ ($\mu_{\text{eff}} = 8.11$ BM) which decreased gradually with the decrease in temperature. The distribution of effective magnetic moment per each ion could not be done. At 40 K the $\chi_m T$ and μ_{eff} values became $7.90 \text{ emu K mol}^{-1}$ and 7.94 BM respectively. Below 40 K, these values decreased drastically and reached a minima at 5 K ($6.62 \text{ emu K mole}^{-1}$ and 7.27 BM) suggesting an antiferromagnetism at low temperature.

For $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$, magnetization at variable temperature was carried out. In the $\chi_m T$ vs. T plot for this complex, the $\chi_m T$ value increased gradually with a decrease in temperature. At 300 K, $\chi_m T$ and μ_{eff} values were $6.5 \text{ emu K mol}^{-1}$ and 7.2 BM. This value of the effective magnetic moment was distributed as 3.6 BM per each Ni(II) ion. Upon cooling further, $\chi_m T$ value increased gradually up to 50 K. Below 50 K, a sharp increase in $\chi_m T$ and μ_{eff} values was observed to exhibit a maxima at 25 K ($8.1 \text{ emu K mol}^{-1}$ and 8.04 BM), which suggested a ferromagnetic coupling at very low temperatures.

The $\chi_m T$ vs. T plot for $\text{Co}_2(\text{SB})_2(\text{H}_2\text{O})_2$, also exhibited a steady increase in the $\chi_m T$ value with a decrease in temperature. At 300 K, $\chi_m T$ and μ_{eff} values were $10.56 \text{ emu K mol}^{-1}$ and 9.19 BM. This value of the effective magnetic moment was distributed as 4.59 BM per each Co(II) ion. Upon cooling further, $\chi_m T$ value increased gradually up to 50 K. Below 50 K, a sharp increase in $\chi_m T$ and μ_{eff} values was observed to exhibit a maxima at 20 K ($13.44 \text{ emu K mol}^{-1}$ and 10.36 BM), which suggested a ferromagnetic coupling at very low temperatures.

Conclusion

The synthesis of dinuclear complexes via novel synthetic route is strongly supported by analytical, spectral and thermal data. The formation of the imine group was clearly indicated from infrared spectra. The effective magnetic moment and electronic spectral data coupled with emission spectra supported the tetrahedral environment in the metal ions. The presence of two coordinated water molecules was detected both from elemental analysis and thermogravimetric analysis. The molecular ion peaks in the mass spectra also supported the formation of dinuclear complexes. The magnetic studies of the complexes revealed ferromagnetic and antiferromagnetic coupling in the complexes under present investigation. Finally, the molecular mechanical method used for energy minimization corroborated the proposed structure of the complexes. This first report on the synthesis of bimetallic magnetic material capable of opening a new era in the preparation of magnetic materials with lot more variations.

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