RESEARCH ARTICLE

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Preparation and Properties of Dinuclear Schiff Base Complexes from Salicylaldehyde and 2-Aminophenol Complexes of Cu (II), Co (II) and Ni (II)

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Abstract

Dinuclear complexes from salicylaldehyde and 2-aminophenol with Cu (II), Ni (II) & Co (II) were obtained by new synthetic route and characterized. Elemental and metal compositions of these complexes were obtained. Infrared, UV – visible (absorption & emission) spectroscopy and mass spectrometry data were utilized for structure elucidation. The TGA thermograms of the complexes supported proposed structure. Magnetic properties of these complexes were extensively studied using Guoy balance at room temperature and vibrating sample magnetometer at variable temperatures. Low temperature intramolecular ferromagnetism was exhibited by homodinuclear complex while the heterodinuclear complexes showed antiferromagnetic coupling. A probable mechanism for the formation of the complexes was proposed. The most stable structure was identified using molecular mechanical method.

Keywords: Dinuclear complex; Schiff base; Magnetic property.

1. Introduction

The chemistry of metal complexes including ordinary complexes, chelates and mixed ligand complexes has been extensively studied till date for their bioinorganic relevance as well as a wide range of physicochemical properties [1, 2]. 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 [3, 4]. Mixed metal complexes are a class of compounds which can have properties that are not present in ordinary complexes [5-8]. However, synthetic route leading to heteropolynuclear complexes with pre-established structures and properties has always remained a challenge for synthetic chemists. Numerous homopolynuclear complexes have been characterized so far [9, 10]. These complexes are generally obtained using polydentate ligands in which some of the donor atoms are unable to coordinate with the same metal ions due to steric factors. This unutilized functionality is drawn on another metal ion forming polynuclear complex [11-13]. A one-pot procedure for template synthesis of hetero metallic complexes has not been well established yet. This difficulty has been overcome to some extent using an approach 'Complexes as Ligands' [5, 6, 14]. Here, a complex with some unutilized functionality on ligand is considered as a ligand and named as metal organic ligand (MOL). This MOL when allowed to react with metal ions results in formation of mixed metal complexes.

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 NH_2 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 [11]. 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 binuclear 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.

2. Methods

2.1. Reagents

2-aminophenol and salicylaldehyde (≥ 99.0%) were purchased from Sigma-Aldrich. Copper acetate, 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[15].

2.2. Measurements

Elemental analysis (C, H and N) was done using PERKIN ELMER, Series II, 2400 CHNS/O Analyzer. The cobalt and copper 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 order to separate the copper from nickel and cobalt in mixed metal complexes, the solution containing a mixture of metal ions was first treated with H_2S gas under mild acidic condition at a temperature of 60°C. The precipitated coppersulphide was dissolved in a minimum quantity of concentrated hydrochloric acid and an aqueous solution of Cu (II) was prepared. The Cu (II) was then determined by EDTA titration technique. Ni (II) was estimated as dimethylglyoxime complex. 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 obtained using UV Lambda 19 PERKIN ELMER spectrophotometer. Thermogravimetric analysis was recorded on METTLER TOLEDO. The fluorescence spectra of the complexes dissolved in dimethyl formamide was obtained on PERKIN ELMER, LS-50B spectrofluorimeter. The mass spectra are obtained using API QSTAR Pulsar LC-MS quadruple and TOF based single mass spectrometer. 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 was carried out on LAKESHORE VSM7410 vibrating sample magnetometer.

2.3. Synthesis

In the first step, 0.488 g of salicylaldehyde (SAL) was dissolved in 20 ml of absolute alcohol to make (0.2 M) solution. Similarly, 0.400 g of copper acetate was dissolved in 20 ml rectified spirit to make (0.1 M) solution. Both these solutions were mixed and stirred for an hour to obtain a four coordinated complex viz. M $(SAL)_2$ in solution. The reaction is shown in equation 1.

$$M + 2SAL \rightarrow M\,(SAL)_2 \quad (1)$$

In the second step, 0.436 g of 2-aminophenol (2-AP) and 0.500 g Co (II) / Ni (II) acetate or 0.400 g Cu (II) acetate were dissolved in 20 ml of absolute alcohol and rectified spirit respectively were mixed and stirred for an hour to obtain a four coordinated complex viz. M $(2\text{-}AP)_2$ in solution. The reaction is shown in equation 2.

$$M' + 2(2\text{-}AP) \rightarrow M'\,(2\text{-}AP)_2 \quad (2)$$

Finally, the solution of M $(SAL)_2$ was slowly added to the refluxing solution of M' $(2\text{-}AP)_2$. The new colored products separated under slightly alkaline conditions created by sodium hydroxide after six hours of reflux. Precipitates obtained were filtered, washed with cold water and rectified spirit and finally dried under vacuum for 72 hours. The reaction of the third step is depicted in equation (3).

$$M\,(SAL)_2 + M'\,(2\text{-}AP)_2 \rightarrow MM'\,(SB)_2(H_2O)_2 \quad (3)$$

The heterodinuclear complexes Cu Ni $(SB)_2$ $(H_2O)_2$ and Cu Co $(SB)_2$ $(H_2O)_2$ were obtained in the case of M = Cu (II) and M' = Ni (II) and Co (II) respectively. Whereas, the homodinuclear complex $Cu_2(SB)_2(H_2O)_2$ was obtained when both M and M' = Cu (II) and Cu (II).

3. Results and Discussion

3.1. Infrared studies

In order to derive the structures of the dinuclear complexes, similarities and dissimilarities in the IR spectra of the precursor (reactant complex) and the resulting complexes were brought out. Significant IR bands are shown in Table 1. The spectra of reactant complex M $(SAL)_2$ exhibited a broad and strong peak at 1632 cm^{-1} which was assigned to the C=O stretching in the complex. The band in the vicinity of 1298 cm^{-1} was assigned to the C-O (H) bending frequency. A weak band at 443 cm^{-1} was also observed because of M-O stretching frequency. On the other hand, reactant complex M' $(2\text{-AP})_2$ showed IR spectra with a strong absorption at 1593 cm^{-1} which was assigned to coupled vibrations of NH_2 bending and C-N stretching [16-18]. Absorptions at 3320 cm^{-1} and 3250 cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequency respectively. A weak band appearing at 557 cm^{-1} was assigned to the M-N stretching frequency. Both the complexes showed a band in the region of 3050 cm^{-1} arising due to aromatic ring vibrations. In the region of 3400 cm^{-1}, the spectra of reactant complexes did not show any broadband indicating the absence of coordinated water.

Table 1: FT - IR spectral frequencies of complexes.

System	$\nu_{C=N}$ cm^{-1}	ν_{O-H} cm^{-1}	ν_{M-O} cm^{-1}	ν_{M-N} cm^{-1}	$\delta_{C-O\ (H)}$ cm^{-1}	$\delta_{H2O\ (coord.)}$ cm^{-1}
M $(SAL)_2$	-	-	443	-	1298	-
M $(2\text{-AP})_2$	-	-	445	557	1298	-
$Cu_2\ (SB)_2\ (H_2O)_2$	1609	3400	450	560	1249	1585
Cu Ni $(SB)_2\ (H_2O)_2$	1605	3400	445	555	1250	1587
Cu Co $(SB)_2\ (H_2O)_2$	1612	3405	450	560	1252	1585

In the spectra of MM' $(SB)_2$ $(H_2O)_2$, peaks due to C=O stretching (1629 cm^{-1}), NH_2 bending and NH_2 stretching (3324 cm^{-1} and 3260 cm^{-1}) were found to be absent. The appearance of a new stronger band at 550-560 cm^{-1} and 440-450 cm^{-1} was attributed to M-N and M-O stretching frequencies respectively while a band corresponding to the C-O stretching was observed at 1245-1250 cm^{-1}. A sharp and strong peak originating due to C=N stretching was observed at 1605 - 1615 cm^{-1} which was an important evidence of the Schiff base formation in accordance with the proposed structure of the dinuclear complex.

3.2. Electronic spectra

Table 2: Electronic transitions and their assignments in complexes.

System	ν_1 cm^{-1}	ν_2 cm^{-1}	ν_3 cm^{-1}
$Cu_2\ (SB)_2\ (H_2O)_2$	8800 $^2T_{2g} \rightarrow {}^2E_g$	-	-
Cu Ni $(SB)_2\ (H_2O)_2$	8900 $^2T_{2g} \rightarrow {}^2E_g$ 10200 $^3T_{1g}$ (F) $\rightarrow$ $^3T_{2g}$ (F)	- - 12300 $^3T_{1g}$ (F) $\rightarrow$ $^3A_{2g}$ (F)	- - 22000 $^3T_{1g}$ (F) $\rightarrow$ $^3T_{1g}$ (P)
Cu Co $(SB)_2\ (H_2O)_2$	8900 $^2T_{2g} \rightarrow {}^2E_g$ 9700 $^4A_2$ (F) $\rightarrow$ $^4T_2$ (F)	- - 20500 $^4A_2$ (F) $\rightarrow$ $^4T_1$ (P)	- - 23200 $^4A_2$ (F) $\rightarrow$ $^4T_1$ (F)

All the complexes showed absorption peaks in the near UV region around 33000 cm^{-1} 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 $Cu_2\ (SB)_2\ (H_2O)_2$ in dimethylformamide showed only one broad peak at 8800 cm^{-1} which is assigned to $^2T_{2g} \rightarrow {}^2E_g$ transition occurring for a Cu(II) ion in tetrahedral environment.

Cu Ni $(SB)_2\ (H_2O)_2$ exhibited peaks at 22000 cm^{-1} and 12300 cm^{-1} and 10200 cm^{-1} respectively. These bands 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 band at 8900 cm^{-1} observed in this complex is again assigned to $^2T_{2g} \rightarrow {}^2E_g$ transition corresponding to tetrahedral geometry of Cu (II) ion.

The spectra of Cu Co $(SB)_2\ (H_2O)_2$ showed bands at 23200 cm^{-1}, 20500 cm^{-1} and 9700 cm^{-1} corresponding to $^4A_2$ (F) $\rightarrow$ $^4T_1$ (F), $^4A_2$ (F) $\rightarrow$ $^4T_1$ (P) and $^4A_2$ (F) $\rightarrow$ $^4T_2$ (F) transitions of Co (II) ion in a tetrahedral geometry. A band corresponding to $^2T_{2g} \rightarrow {}^2E_g$ transition for a tetrahedral Cu (II) ion was observed in this complex at 8900 cm^{-1} [19].

3.3. Fluorescence spectra

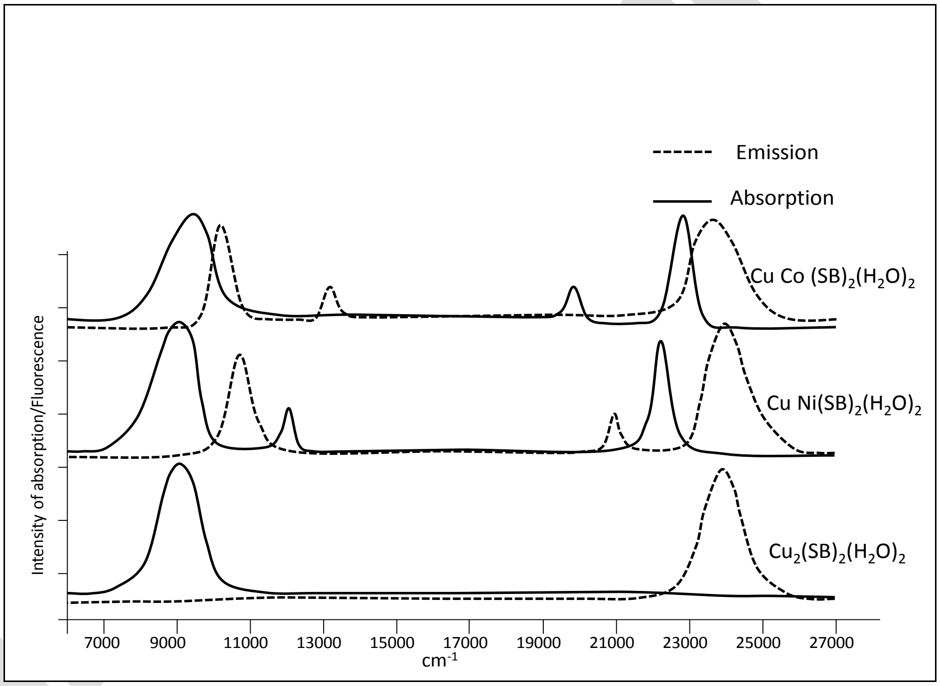
The Fluorescence spectra of complexes shown in Figure 1 were taken using a solution prepared in dimethylformamide. The study was carried out in the range of previously observed peaks in absorption spectra. All the complexes exhibited a broad band around 22000 cm,$^{-1}$ and another strong band in the vicinity of 10500 cm^{-1}. The former broadband is attributed to the coupling of $\pi \rightarrow \pi^*$ transition in the ligand to one or two of the d-d transitions observed in absorption spectra [14, 20, 21]. The emission at 10500 cm^{-1}was probably the mirror image of the absorption band observed in the nickel and cobalt containing complexes.

Table 3: Analytical data of the complexes.

System	Mol.Wt. g/mole	Color	% Yield (g)	μ_{eff} per ion B.M.	Elemental Analysis % Found (Calculated)				
					C	H	N	Cu	Ni/Co
$Cu_2(SB)_2(H_2O)_2$	585.55	Dark green	85 (0.995)	2.3	53.36 (53.33)	3.76 (3.79)	4.81 (4.78)	21.67 (21.70)	-
$Cu\ Ni\ (SB)_2(H_2O)_2$	580.70	Yellowish green	80 (0.929)	*	53.80 (53.78)	3.80 (3.82)	4.84 (4.82)	10.92 (10.94)	10.10 (10.11)
$Cu\ Co\ (SB)_2(H_2O)_2$	580.94	Brown	80 (0.929)	*	53.76 (53.75)	3.84 (3.82)	4.83 (4.82)	10.93 (10.94)	10.16 (10.14)

* Could not be calculated.

Figure 1: Absorption and emission spectra of the complexes.

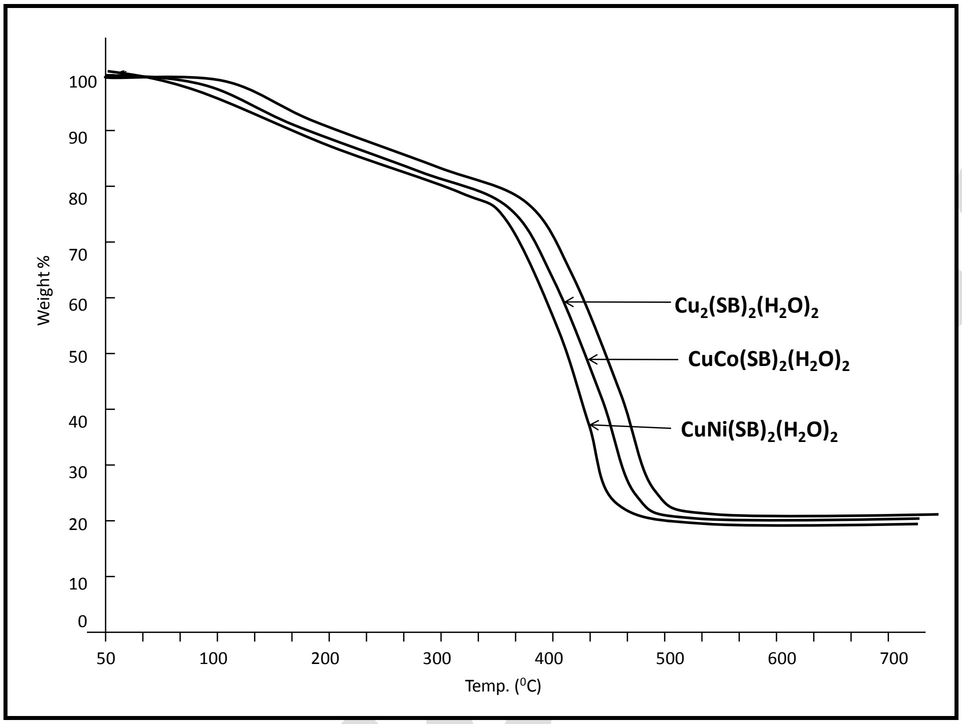


3.4. Elemental and thermal analysis

The C, H, N analysis along with metal estimation data shown in Table 3. The experimental data strongly supported the theoretical values [22]. Since the percentage of copper and nickel metal were also found to be same in CuNi $(SB)_2(H_2O)_2$, the analysis reaffirmed the presence of one copper and one nickel ion in the complex. Moreover, it suggested the presence of two water molecules in the complex.

The TGA thermograms for thermal degradation of the complexes shown in Figure 2 exhibited weight loss during all the phases. A negligible weight loss was observed below 150^{0}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_4O_2) with mass losses of (Obs. = 6.3%, Calc. =6.15%) was observed. The complexes exhibited thermal stability up to 350^{0}C after which the next step involving an accelerated weight loss of the organic fraction, with mass loss (Obs. = 60.9%, Calc. = 60%) in the region of 400^0C to 450^0C, observed.

Figure 2: TGA thermo grams of complexes.



3.5. 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 $Cu_2 (SB)_2 (H_2O)_2$ was found to be 2.3 BM for each Cu (II) ion which was slightly higher than spin only value of tetrahedral copper (1.92-2.2 BM). For the heterodinuclear complexes Cu Ni $(SB)_2 (H_2O)_2$ and Cu Co $(SB)_2 (H_2O)_2$, it was difficult to find the effective magnetic moment per each ion whereas the total effective magnetic moment were high. These higher values of the effective magnetic moment suggest the presence of some ferromagnetic interactions at room temperature [23, 24].

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 3a, 3b and 3c.

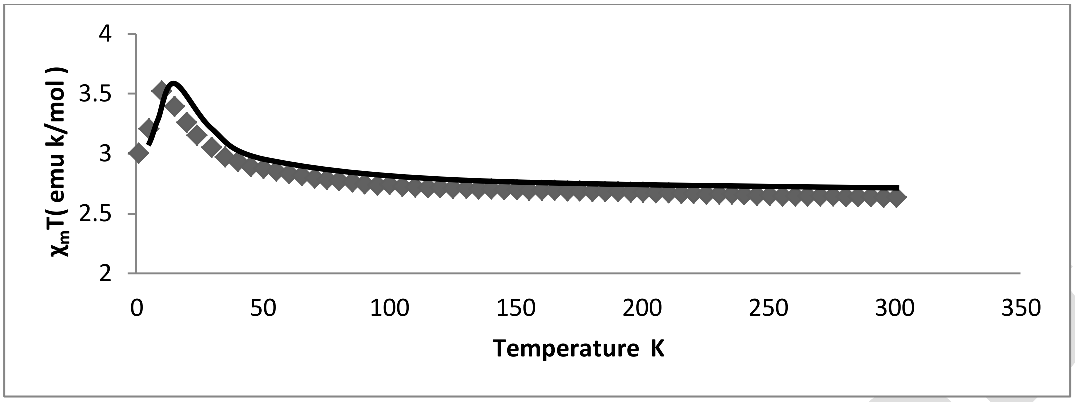
For a paramagnet, the molar susceptibility χ_m is given by Curie's law in SI units as shown in equation (4). The $\chi_m T$ values at 298 K obtained from Figures 3a, 3b and 3c were substituted in equation (5) which is another form of the equation (4) to obtain the effective magnetic moment (μ_{eff}) values at 298 K in Bohr magnetons per formula unit[25].

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

$$\mu_{eff} = \sqrt{8\,\chi_m\, T} \qquad (5)$$

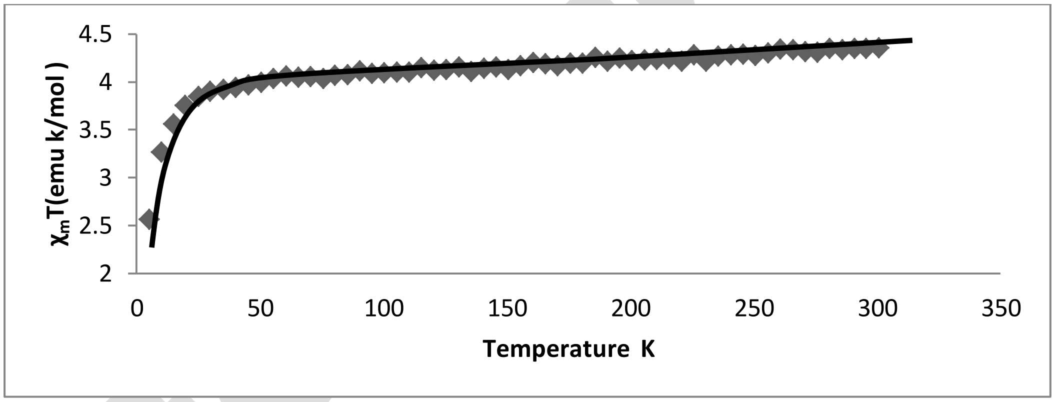
For the homodinuclear complex $Cu_2 (SB)_2 (H_2O)_2$, the $\chi_m T$ vs. T plot is shown in Figure 3a.

Figure 3a: A plot of $\chi_m T$ Vs. T for $Cu_2 (SB)_2 (H_2O)_2$



The $\chi_m T$ and μ_{eff} values at room temperature were 2.63 emu K mol^{-1} and 4.58 BM which accounted for an effective magnetic moment of 2.29 BM per each Cu (II) ion. The $\chi_m T$ product increased with decreasing temperature, reaching a maximum of 3.52 emu K mol^{-1} at 5K. This behavior is characteristic of ferromagnetic coupling between two copper ions [26].

Figure 3b: A plot of $\chi_m T$ Vs. T for Cu Ni $(SB)_2 (H_2O)_2$



In the heterodinuclear complex Cu Ni $(SB)_2 (H_2O)_2$, the value of $\chi_m T$ was 4.34 emu K mol^{-1} at 300 K (Figure 3b). The $\chi_m T$ slowly fell off upon cooling to a value of a 3.84 emu K mol^{-1} at 20 K, after which the values rapidly decreased to a value of 2.56 emu K mol^{-1} at 5 K. Here, the distribution of effective magnetic moment could not be done for the individual ions. The low temperature data indicated the presence of intramolecular antiferromagnetic exchange between two hetero centers Cu and Ni.

For heterodinuclear complex Cu Co $(SB)_2 (H_2O)$, the value of $\chi_m T$ was 5.95 emu K mol^{-1} at 300 K (Figure 3c). The $\chi_m T$ value continuously decreased with a decrease in the temperature. At 50 K, it was 5.14 emu K mol^{-1} which sharply decreased to 2.2 emu K mol^{-1} at 5 K. The low temperature data again suggested antiferromagnetism between the two hetero centers Cu and Co.

3.6. Mass spectra

Mass spectra of $Cu_2 (SB)_2 (H_2O)_2$ dissolved in acetonitrile carried out as ESI -MS showed peaks attributed to the molecular ion at m / z 584 (M^+) and m/z 586 for (M^{+2}). The spectra of Cu Ni $(SB)_2 (H_2O)_2$ and Cu Co $(SB)_2 (H_2O)_2$ both showed peaks at m / z of 580 and m / z of 579 as a molecular ion peak (M^+) as well as (M^{+2}) peak at m / z of 582 and m / z of 581. These molecular ion peaks were in line with the proposed structures of the complexes. Several peaks for fragments with m / z = 547, 457, 352, 336, 213 and 182 were also noticed in the spectrum, which corresponded to the fragments associated with a different number of H^+ ions shown in Figure 4.

Figure 3c: A plot of $\chi_m T$ Vs. T for Cu Co (SB) $_2$ (H$_2$O) $_2$

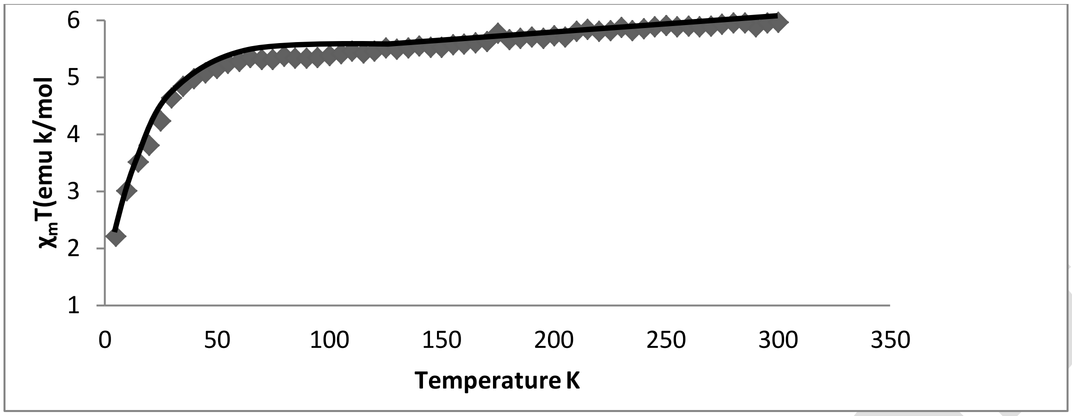
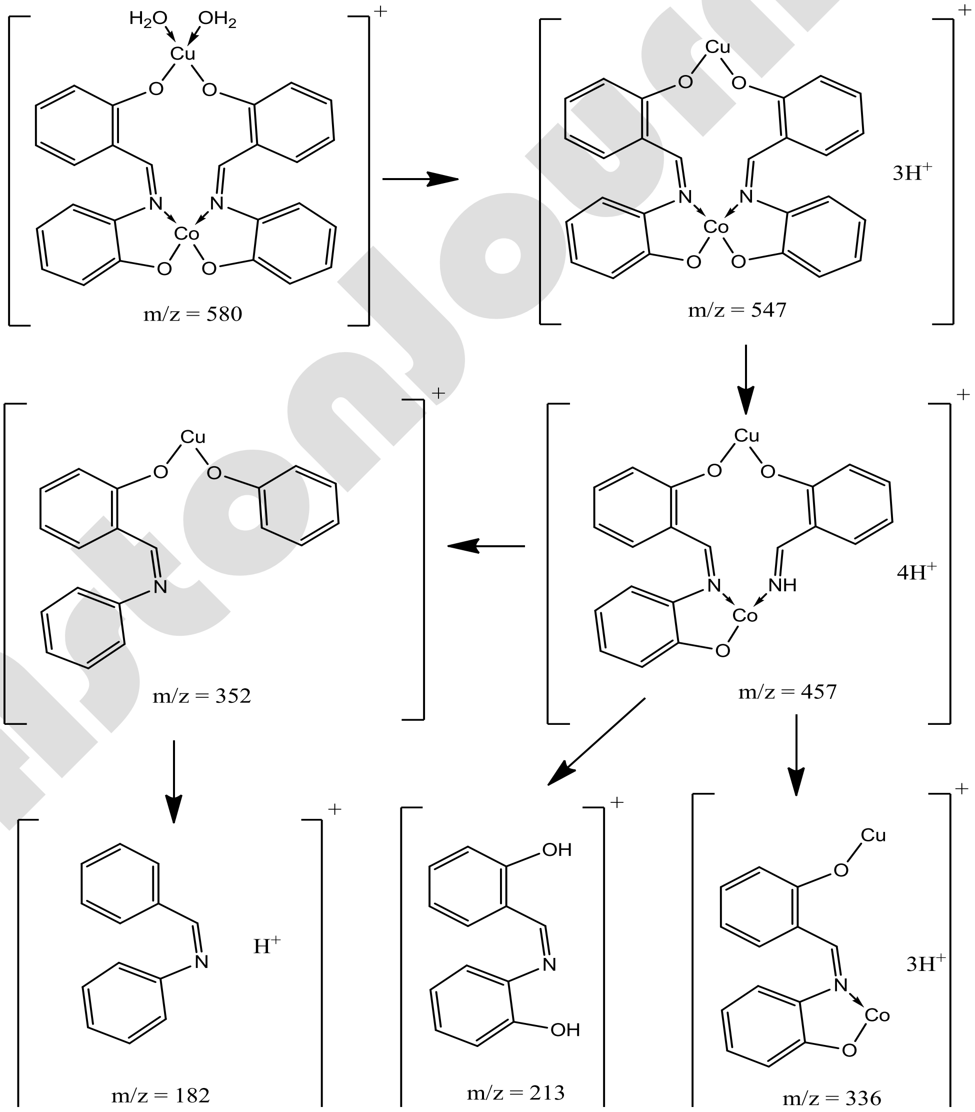


Figure 4: Fragmentation pattern for Cu Co(SB) $_2$ (H$_2$O) $_2$ complex.



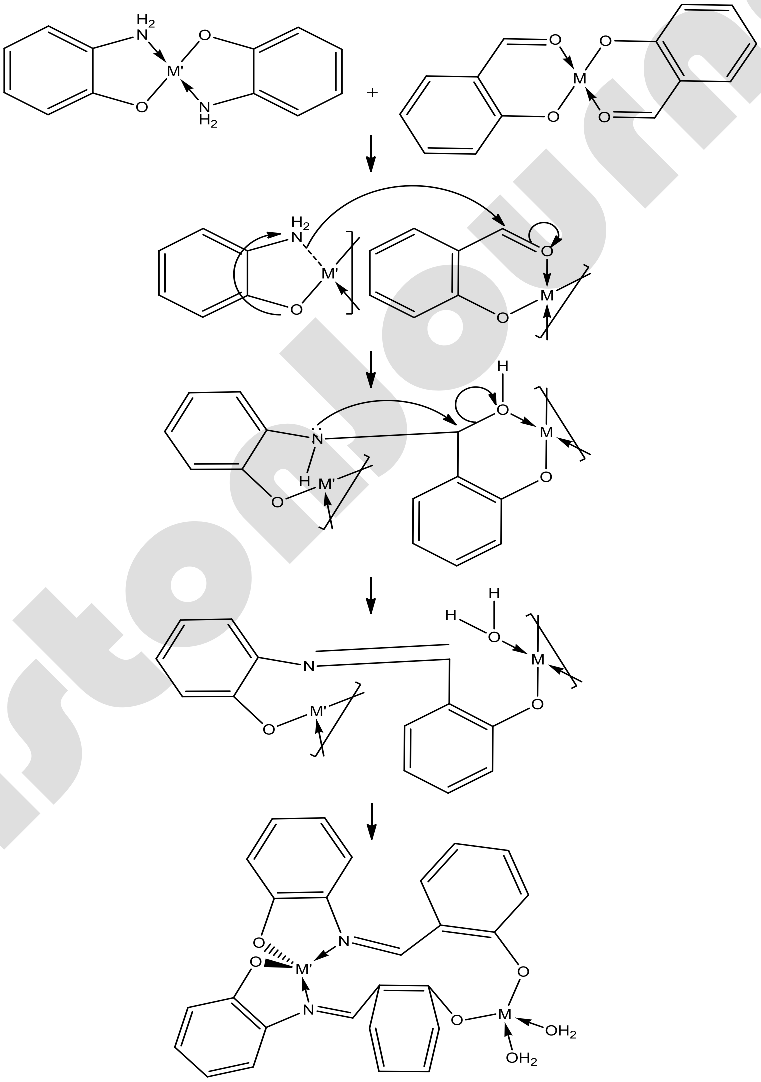
3.7. Structure and bonding

IR spectra of the samples clearly indicated the presence of imine group, M–O & 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. Inability of obtaining NMR and ESR spectra along with a very high value of the effective magnetic moment narrowed down the number of possible structures for the complex formed. Formation of dinuclear complexes was also evident from the mass spectra. The proposed structure has been obtained by minimization of energy using the molecular mechanical method.

3.8. Reaction mechanism

According to well-known mechanism of Schiff base formation between a amine and an aldehyde, the lone pair of electron on nitrogen makes a nucleophilic attack on the carbonyl carbon of the aldehyde resulting in the formation of a C-N bond and a proton transfer from amine to carbonyl oxygen. This intermediate, when catalyzed with a weak acid undergoes a loss of water molecule forming a Schiff base.

Figure 5: Mechanism for synthesis of mixed metal complexes where M = Cu (II), M' =Cu (II) / Ni (II) / Co (II).



A mechanism for the formation of the complexes under present investigation is shown in Figure 4. In this reaction, both nitrogen and carbonyl oxygen of the reacting complexes are previously coordinated to the respective metal ions. While, the metal ion coordinated to the carbonyl oxygen facilitates the nucleophilic attack by nitrogen, the coordinated nitrogen does not have the sufficient electron density required for the attack. It is thought that the electron density required by the nitrogen is made available through the oxygen atom of the amino phenol via ring electrons. Thus, due to this induction of electron density, the nitrogen becomes electron rich and makes a nucleophilic attack on the carbonyl carbon. Weakly acidic medium permits the imine formation by facilitating carbon–oxygen bond cleavage. In contrast to the classical Schiff base mechanism, here in the formation of Cu Ni $(SB)_2(H_2O)_2$, the oxygen remains coordinated to the Cu (II) ion as OH which picks up the proton released by nitrogen resulting into the coordinated water molecule. Upon increasing the pH of the solution, the imine nitrogen readily coordinates to the vicinal Ni (II) ion.

4. Conclusion

The preparation of dinuclear complexes by a novel synthetic route is strongly supported by analytical data. The formation of imine group was apparent 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 thermo gravimetric 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 dinuclear complexes via novel route is capable of opening a new era in the preparation of complexes with lot more variations.

Competing Interests

The authors have no competing interests to anyone.

Authors' Contributions

VDB is the guide under whose supervision SRR has carried out the present research work.

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