

Synthesis of Dinuclear Schiff Base Complexes of Mn(II), Fe(II) and Zn(II) via Inter-Complex Reaction

VASISHTA D. BHATT* and SAMAT R. RAM

Department of Chemical Sciences, NVPAS, Vallabh Vidyanagar-388120, Gujarat, India
vdishq@yahoo.co.in

Received 12 December 2012 / Accepted 13 January 2013

Abstract: Dinuclear complexes of Mn(II), Fe(II) and Zn(II) were synthesized by using the mononuclear complexes of such metals as precursor. These dinuclear complexes formed by the inter-complex Schiff base reaction. The physicochemical data were established by metal estimation and elemental analysis. The effective magnetic moment and electronic spectral data supported the tetrahedral environment of the metal ions. Spectroscopic methods like infrared spectroscopy, UV-visible spectroscopy and thermal analysis were used for structure elucidation of the complexes. Mass spectrometry was used for confirmation of molecular mass and fragmentation pattern of the complexes. Powder diffraction pattern suggested the crystalline nature with the tetragonal symmetry of the complexes.

Keywords: Dinuclear complex, Schiff base, Inter-complex reaction

Introduction

Plenty of research work has been done on transition metal complexes includes ordinary complexes, chelates and mixed ligand complexes^{1,2}. The development of the field has increased, since it has been recognized that many of these complexes may serve as biological model, NMR-shift reagent, catalysts and as a magnetic materials³. In the last 25 years polynuclear complexes of transition metals have begun to attract the attention given to higher nuclearity compounds. In order to synthesize tailor made polynuclear complexes, the development of new synthetic route has always remained a challenge for synthetic chemists^{4,5}. The homonuclear complexes can be prepared successfully by some self assembly methods⁶. Many methodologies have been applied to the synthesis of heteropolynuclear complexes amongst which the use of 'metal complexes as ligand' has proven to be most successful. In this method, the ligands are already bound to one metal and have unutilized functionality for further reaction with the same or different metal⁷⁻⁹. Here, a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL's)⁴.

We report here the novel method includes the reaction of two mononuclear complexes to form the homo and heterodinuclear complexes of transition metals. The mononuclear

complexes of *o*-vanillin and *o*-aminophenol exhibited coordinated amine and aldehyde groups that can undergo Schiff base reaction and form the dinuclear Schiff base complexes¹⁰. The dinuclear complexes formed by the inter-complex reaction were characterized by suitable analytical methods.

Experimental

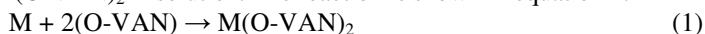
o-aminophenol and *o*-vanillin ($\geq 99.0\%$) were purchased from Sigma-Aldrich. manganese(II) acetate, iron(II) acetate, zinc(II) acetate, sodium hydroxide and solvents ($\geq 99.0\%$) were purchased from E-Merck Ltd, Mumbai (India). The purification was done according to the needs through known procedures¹¹.

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 (1:1.5:2.5). The metal composition of the complexes was carried out by following method. Manganese from homodinuclear complex Mn₂(SB)₂(H₂O)₂ was determined by back titration with standard EDTA solution. Iron(II) from homodinuclear complex *viz.* Fe₂(SB)₂(H₂O)₂ was determined by direct titration of EDTA. Manganese(II) and Iron(II) content from heterodinuclear complex Mn Fe (SB)₂(H₂O)₂ was determined by the method, determination of manganese in presence of iron. Manganese(II) and Iron(II) content from heterodinuclear complexes Zn Mn (SB)₂(H₂O)₂ and Zn Fe (SB)₂(H₂O)₂ were determined by EDTA titration followed by separation of Zinc(II) with quinaldic acid¹². 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 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) Tetrathiocyanatocobaltate(II). Magnetic study of the complexes at room temperature with variable magnetic field was carried out on LAKESHORE VSM7410 vibrating sample magnetometer.

Synthesis

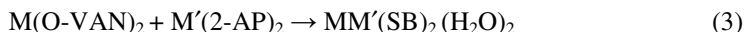
In the first step, 0.612 g of *o*-vanillin was dissolved in ~20 mL of absolute alcohol to prepare 0.2 M solution and a solution of manganese(II)/ iron(II)/ zinc(II) acetate (0.490, 0.247, 0.429 g, 0.1 M) in rectified spirit (~20 mL) were mixed and stirred for an hour to obtain a four coordinated complex *viz.* M (O-VAN)₂ in solution. The reaction is shown in equation 1.



In the second step, 0.436 g of *o*-aminophenol was dissolved in ~20 mL of absolute alcohol to form 0.2 M solution and a manganese(II)/ iron(II)/ zinc(II) acetate (0.490, 0.247, 0.429 g, 0.1 M) in rectified spirit (~20 mL) were mixed and stirred for an hour to obtain a four coordinated complex *viz.* M' (2-AP)₂ in solution. The reaction is shown in equation 2.



In the last step, a solution of M(O-VAN)₂ was added to the refluxing solution of M' (2-AP)₂. The reaction mixture was refluxed for 6 hours in a water bath to obtain the product under slightly alkaline condition created by sodium hydroxide. The precipitates were then filtered, washed with ethanol and dried over fused CaCl₂. The reaction of the third step is depicted in equation 3.



All the complexes were prepared by the above discussed method. The proposed structure of the dinuclear complex is given in Figure 1.

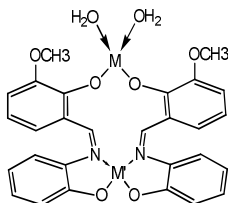


Figure 1. Proposed structure of dinuclear complex, M & M' = Mn(II), Fe(II) or Zn(II).

Physicochemical data

Mn₂(SB)₂(H₂O)₂

Homo dinuclear complex $Mn_2(SB)_2(H_2O)_2$ was obtained using above discussed method where both M and M' = Mn(II). Yield: 71.4%, μ_{eff} : (4.98 per each ion) m.p.: > 350 °C. Anal. Calc. for $C_{28}H_{26}N_2O_8$ Mn_2 (628.39) : C, 53.52; H, 4.17; N, 4.46; Mn, 17.49%. Found: C, 53.41; H, 4.01; N, 4.44; Mn, 17.27 %, mass: m/z = 628[M]⁺, 597 [M-H₄O₂ + 5H]⁺, 501 [M-H₄O₂ - C₆H₃O]⁺, 409 [M-H₄O₂ - C₇H₅O₂NMn + 5H]⁺, 376 [M-H₄O₂ - C₈H₈O₃NMn + 2H]⁺, 352 [(SB)+Mn₂+H]⁺, 244[(SB)+H]⁺.

Fe₂(SB)₂(H₂O)₂

Homo dinuclear complex $Fe_2(SB)_2(H_2O)_2$ was obtained using above discussed method where both M and M' = Fe(II). Yield: 69.37%, μ_{eff} : (4.52 per each ion) m.p.: > 350 °C. Anal. Calc. for $C_{28}H_{26}N_2O_8$ Fe_2 (630.20) : C, 53.36; H, 4.16; Fe, 17.72; N, 4.45. Found: C, 53.25; H, 4.06; N, 4.32; Fe, 17.53%, mass: m/z = 630[M]⁺, 599 [M-H₄O₂ + 5H]⁺, 503 [M-H₄O₂ - C₆H₃O]⁺, 410 [M-H₄O₂ - C₇H₅O₂NFe + 5H]⁺, 377 [M-H₄O₂ - C₈H₈O₃NFe + 2H]⁺, 354[(SB)+Fe₂+H]⁺, 244[(SB)+H]⁺.

Mn Fe(SB)₂(H₂O)₂

Hetero dinuclear complex $Mn Fe(SB)_2(H_2O)_2$ was obtained using above discussed method where both M and M' = Mn(II) and Fe(II) respectively. Yield: 67.24%, m.p.: > 350 °C. Anal. Calc. for $C_{28}H_{26}N_2O_8$ $Mn Fe$ (629.30) : C, 53.44; H, 4.16; Fe, 8.87; Mn, 8.73; N, 4.45%. Found: C, 53.35; H, 4.08; N, 4.38; Fe, 8.72; Mn, 8.50%, mass: m/z = 629[M]⁺, 598 [M-H₄O₂ + 5H]⁺, 502 [M-H₄O₂ - C₆H₃O]⁺, 409 [M-H₄O₂ - C₇H₅O₂NFe + 5H]⁺, 376 [M-H₄O₂ - C₈H₈O₃NFe + 2H]⁺, 353 [(SB)+Mn Fe+H]⁺, 244[(SB)+H]⁺.

Zn Mn(SB)₂(H₂O)₂

Hetero dinuclear complex $Zn Mn(SB)_2(H_2O)_2$ was obtained using above discussed method where both M and M' = Zn(II) and Mn(II) respectively. Yield: 67.24%, μ_{eff} : (5.70) m.p.: > 350 °C. Anal. Calc. for $C_{28}H_{26}N_2O_8$ $Zn Mn$ (638.86) : C, 52.64; H, 4.10; N, 4.38; Zn, 10.24; Mn, 8.60%. Found: C, 52.51; H, 4.03; N, 4.25; Zn, 10.00 ; Mn, 8.43%, mass: m/z = 637 [M]⁺, 605 [M-H₄O₂ + 5H]⁺, 510 [M-H₄O₂ - C₆H₃O]⁺, 418 [M-H₄O₂ - C₇H₅O₂NMn + 5H]⁺, 385 [M-H₄O₂ - C₈H₈O₃NMn + 2H]⁺, 361 [(SB)+ZnMn+H]⁺, 244[(SB)+H]⁺.

Zn Fe(SB)₂(H₂O)₂

Hetero dinuclear complex $Zn Fe(SB)_2(H_2O)_2$ was obtained using above discussed method where both M and M' = Zn(II) and Fe(II) respectively. Yield: 67.12 %, μ_{eff} : (5.11) m.p.: > 350 °C.

Anal. Calc. for $C_{28}H_{26}N_2O_8$ Zn Fe(639.77) : C, 52.57; H, 4.10; Fe, 8.73; N, 4.38; Zn, 10.22 %. Found: C, 52.49; H, 3.99; Fe, 8.65; N, 4.23; Zn, 10.11%, mass: $m/z = 638[M]^+$, 607 $[M-H_4O_2+5H]^+$, 511 $[M-H_4O_2-C_6H_3O]^+$, 418 $[M-H_4O_2-C_7H_5O_2NFe+5H]^+$, 385 $[M-H_4O_2-C_8H_8O_3NFe+2H]^+$, 362 $[(SB)+ZnFe+H]^+$, 244 $[(SB)+H]^+$.

Results And Discussion

IR spectral studies

The IR spectra of reactant complexes and dinuclear complexes compared for some similarities and dissimilarities. Significant IR bands for reactant complexes of $Mn_2(SB)_2(H_2O)_2$ and for all dinuclear complexes are summarized in Table 1. The spectra of reactant complex $M(O-VAN)_2$ showed a broad and strong band at 1629 cm^{-1} attributed to $C=O$ stretching. A broad band appearing at 1029 cm^{-1} was assigned to the presence of $-OCH_3$ group. A weak band at 454 cm^{-1} observed in the spectra was due to $M-O$ stretching frequency.

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} | $\delta_{H_2O(\text{coord.})}$ cm^{-1} |
|----------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--|
| $M(O-VAN)_2$ | - | - | 454 | - | - |
| $M(2-AP)_2$ | - | - | 452 | 546 | - |
| $Mn_2(SB)_2(H_2O)_2$ | 1604 | 3405 | 456 | 555 | 1585 |
| $Fe_2(SB)_2(H_2O)_2$ | 1606 | 3404 | 457 | 558 | 1587 |
| $MnFe(SB)_2(H_2O)_2$ | 1608 | 3405 | 455 | 560 | 1588 |
| $ZnMn(SB)_2(H_2O)_2$ | 1608 | 3400 | 455 | 559 | 1588 |
| $ZnFe(SB)_2(H_2O)_2$ | 1606 | 3400 | 456 | 558 | 1586 |

IR spectra of the reactant complex $M'(2-AP)_2$ showed a strong absorption at 1596 cm^{-1} which was assigned to coupled vibrations of NH_2 bending and $C-N$ stretching. Absorptions at 3320 cm^{-1} and 3255 cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequency respectively. A weak band at 546 cm^{-1} was observed in the complex which was assigned to the $M-N$ stretching frequency¹³⁻¹⁴.

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.

In the spectra of $MM'(SB)_2(H_2O)_2$, it was found that the peaks due to $C=O$ stretching (1629 cm^{-1}), NH_2 bending and NH_2 stretching (3320 cm^{-1} and 3255 cm^{-1}) were absent. However, emergence of a new sharp and strong peak in the region of $1600 - 1610\text{ cm}^{-1}$ was the evidence of imine formation. The stronger bands appearing at $540 - 560\text{ cm}^{-1}$ and $450 - 460\text{ cm}^{-1}$ were assigned to $M-N$ and $M-O$ stretching frequencies. The peak due to $-OCH_3$ 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 $740 - 750\text{ cm}^{-1}$ was assigned to the wagging mode of the coordinated water.

Electronic spectra

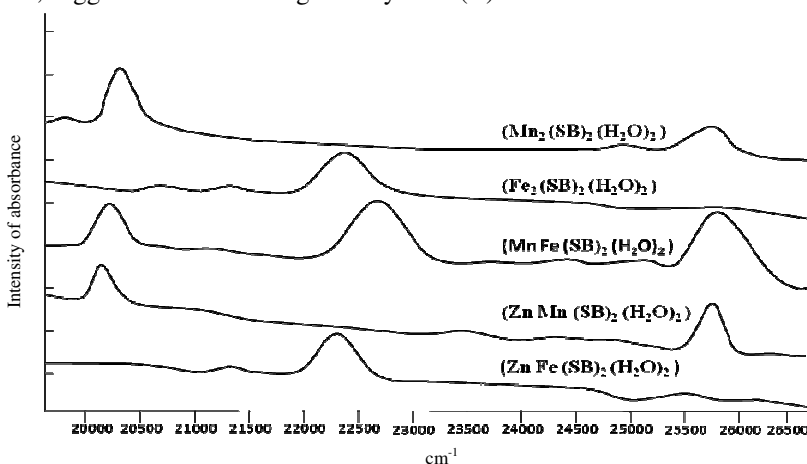
Electronic absorption spectra of all dinuclear complexes were carried out in DMSO. Absorption spectra are shown band position and their assignments are summarized in Table 2. The homodinuclear complex $Mn_2(SB)_2(H_2O)_2$ shown two bands at 25900 cm^{-1} and 20230 cm^{-1} assigned to ${}^6A_{1g} \rightarrow {}^4A_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ transition respectively, suggest the tetrahedral geometry of $Mn(II)$.

Table 2. Electronic transitions and their assignments in complexes

| S. No. | System | $\nu_1 \text{ cm}^{-1}$ | $\nu_2 \text{ cm}^{-1}$ |
|--------|---|---|---|
| 1. | $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | $25900^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}$ | $20230^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}$ |
| 2. | $\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2$ | $22360^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ | - |
| 3. | $\text{Mn Fe}(\text{SB})_2(\text{H}_2\text{O})_2$ | $25980^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}$ $22540^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ | $20300^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}$ - |
| 4. | $\text{Zn Mn}(\text{SB})_2(\text{H}_2\text{O})_2$ | $25890^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}$ | $20240^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}$ |
| 5. | $\text{Zn Fe}(\text{SB})_2(\text{H}_2\text{O})_2$ | $22300^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ | - |

The spectra of $\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2$ shown band at 22360 cm^{-1} assigned to $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition, suggest the tetrahedral environment of Fe(II). The heterodinuclear complex $\text{Mn Fe}(\text{SB})_2(\text{H}_2\text{O})_2$ shown three bands at 25980 cm^{-1} , 20300 cm^{-1} and 22540 cm^{-1} assigned to $^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g}$, $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}$ and $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ attributed to tetrahedral geometry of Mn(II) and Fe(II).

The dinuclear complex of zinc(II) with manganese(II) viz. $\text{Zn Mn}(\text{SB})_2(\text{H}_2\text{O})_2$ shown two bands at 25890 cm^{-1} and 20240 cm^{-1} attributed to tetrahedral environment of Mn(II). The spectra of complex $\text{Zn Fe}(\text{SB})_2(\text{H}_2\text{O})_2$ shown band at 22300 cm^{-1} assigned to $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition, suggest the tetrahedral geometry of Fe(II)¹⁵.

**Figure 2.** Electronic spectra of the complexes

Thermal analysis

Thermal degradation of the complexes was seen in the TGA thermograms, suggest a negligible weight loss was below 100°C , this was attributed to the presence of small amounts of adsorbed water. For all the complexes, in the first step, a loss of two coordinated water molecules (H_2O) with mass losses of (5 - 6%) was observed. The complexes exhibited thermal stability up to 350°C after which an accelerated weight loss of the organic fraction, with mass loss (75 - 76%) in the region of 400°C to 550°C was observed. The residual weight was not to be considered.

Mass spectra

Mass spectra of the complexes was carried out in a polar aprotic solvent; acetonitrile as ESI-MS. The spectra of $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ showed peaks attributed to the molecular ion at m/z of 628 (M^+) and m/z of 630 ($\text{M}+2$). This molecular ion peak was in line with the proposed structure of the complex. Several peaks for fragments with $m/z = 597 [\text{M}-\text{H}_4\text{O}_2+5\text{H}]^+$, 501

$[M-H_4O_2-C_6H_3O]^+$, 409 $[M-H_4O_2-C_7H_5O_2NMn+5H]^+$, 376 $[M-H_4O_2-C_8H_8O_3NMn+2H]^+$, 352 $[(SB)+Mn_2+H]^+$, 244 $[(SB)+H]^+$ were also noticed in the spectrum, which corresponded to the stable fragments associated with a different number of H^+ ions shown in Figure 3.

Table 3. Thermal data of the complexes

| Complex | TG Range $^{\circ}C$ | Mass loss obs. (cald) | Assignment |
|-----------------------|-------------------------|--------------------------|-------------------------------------|
| $Mn_2(SB)_2(H_2O)_2$ | 100-350 | 5.80 (5.74) | loss of coordinated water molecules |
| | 350-550 | 76.01 (76.77) | loss of organic fraction |
| $Fe_2(SB)_2(H_2O)_2$ | 100-350 | 5.79 (5.71) | loss of coordinated water molecules |
| | 350-550 | 76.05 (76.57) | loss of organic fraction |
| $Mn Fe(SB)_2(H_2O)_2$ | 100-350 | 5.81 (5.72) | loss of coordinated water molecules |
| | 350-550 | 76.76 (76.68) | loss of organic fraction |
| $Zn Mn(SB)_2(H_2O)_2$ | 100-350 | 5.79 (5.65) | loss of coordinated water molecules |
| | 350-550 | 75.65 (75.51) | loss of organic fraction |
| $Zn Fe(SB)_2(H_2O)_2$ | 100-350 | 5.77 (5.62) | loss of coordinated water molecules |
| | 350-550 | 75.22 (75.43) | loss of organic fraction |

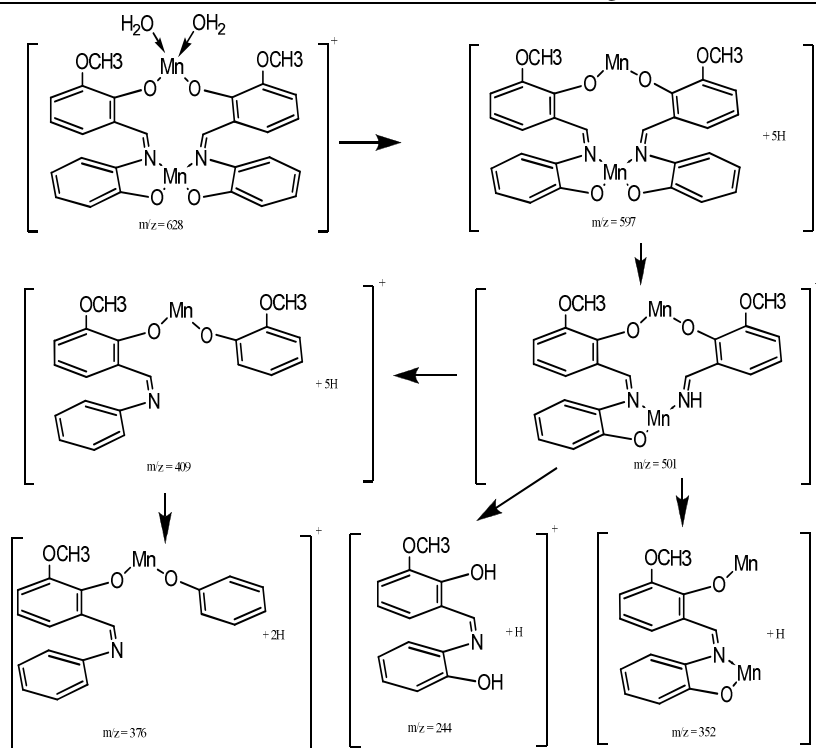


Figure 3. Fragmentation pattern for $Mn_2(SB)_2(H_2O)_2$ complex

Powder X-RD

Powder X-ray diffraction pattern showed sharp intense peaks suggests the crystalline nature of all the complexes. All the reflections for complex $Mn_2(SB)_2(H_2O)_2$ were indexed for h, k and l values (Table 4) using methods reported in the literature. The observed inter planner

spacing values *i.e.* d-spacing with 2θ angles were measured from experimental diffractogram and compared with standard reference pattern¹⁶. The complex was found to be a tetragonal crystal having unit cell parameters 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 powder diffraction pattern of all the complexes exhibited sharp peaks suggests the crystalline nature of all complexes.

Table 4. Powder x-ray diffraction data for $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$

| h k l | 2θ (obs.) | 2θ (cald.) | $\Delta 2\theta$ | d (obs.) | D (cald.) | Δd | Intensity (obs.) |
|-------|---------------------|----------------------|------------------|-------------|--------------|------------|---------------------|
| 1 0 0 | 17.425 | 17.757 | - 0.332 | 5.0899 | 4.9910 | 0.0989 | 18 |
| 1 1 0 | 25.210 | 25.214 | - 0.004 | 3.5326 | 3.5291 | 0.0035 | 100 |
| 2 0 1 | 39.912 | 39.747 | 0.165 | 2.2587 | 2.2659 | -0.0072 | 48 |
| 2 1 1 | 43.246 | 43.843 | - 0.597 | 2.0927 | 2.0632 | 0.0295 | 36 |
| 2 2 0 | 51.318 | 51.766 | - 0.448 | 1.7808 | 1.7645 | 0.0163 | 20 |
| 1 1 3 | 57.211 | 57.340 | - 0.129 | 1.6134 | 1.6055 | 0.0079 | 13 |

Magnetic studies

Magnetic properties of the complexes were carried on Gouy balance and vibrating sample magnetometer at room temperature. The magnetic moments from Gouy balance and the transitions found from visible spectra, suggests the tetrahedral geometry of the metal ions. The room temperature magnetic moments of the homodinuclear complexes $\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2$ and $\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was found to be $(\text{Mn}_2(\text{SB})_2(\text{H}_2\text{O})_2 = 4.98$ per each ion) and $(\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2 = 4.52$ per each ion) that was less than the suggested magnetic moments for tetrahedral geometry of manganese(II) and iron(II). The extensive magnetic property with the variation of magnetic field was studied on vibrating sample magnetometer at room temperature. The hysteresis curve and the magnetic moment data from Gouy balance suggest the antiferromagnetic interaction at room temperature. The magnetic moment of heterodinuclear complex $\text{Mn Fe}(\text{SB})_2(\text{H}_2\text{O})_2$ was also found to be less and gives the hysteresis curve at variable fields suggest the antiferromagnetic interactions at room temperature¹⁷⁻¹⁸. The magnetic moments of heterodinuclear complexes of zinc(II) with Manganese(II) and Iron(II) *viz.* $\text{Zn Mn}(\text{SB})_2(\text{H}_2\text{O})_2$ and $\text{Zn Fe}(\text{SB})_2(\text{H}_2\text{O})_2$ were found 5.70 B.M and 5.11 B.M respectively, that was clearly indicated the tetrahedral geometry of the Mn(II) and Fe(II) and no interactions found.

Conclusion

The preparation of dinuclear complexes by a novel synthetic route is strongly supported by analytical data. The formation of precursor complexes as well as imine in dinuclear complexes confirmed by existant and missing peaks in infrared spectra. The effective magnetic moment and electronic spectral data 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 powder diffraction pattern of all the complexes gives sharp peaks suggests the crystalline nature with tetragonal symmetry. Finally, the molecular mechanical method used for energy minimization corroborated the proposed structure of the complexes. The novel method to synthesize the dinuclear complexes is capable of opening a new era in the preparation of complexes with a lot more variations.

Acknowledgements

The authors are thankful to the UGC, New Delhi (India), for providing financial support in the form of a major research project to the corresponding author. The authors thank the Directors of Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Sophisticated Analytical Instrument Facility (SAIF) IIT Mumbai and IIT Chennai for providing analytical support. The authors also thank Dr. Basudeb Bakshi, Principal, Natubhai V. Patel College of Pure and Applied Sciences, Vallabh Vidyanagar, for providing laboratory facilities.

References

1. Dobrokhotova Z, Emelina A, Sidorov A, Aleksandrov G, Kiskin M, Koroteev P, Bykov M, Fazylbekov M, Bogomyakov A, Novotortsev V and Eremenko I, *Polyhedron*, 2011, **30(1)**, 132-141 .
2. Bhatt V D, *Inorg Chem An Indian J.*, 2008, **3(1)**, 60.
3. Cotton F A, Wilkinson G and Murillo C A, *Advanced Inorganic Chemistry*; Wiley-Interscience: New York, 1999, 23.
4. Dul M C, Pardo E, Lescouezec R, Journaux Y, Ferrando-Soria J, Ruiz-García R, Cano J, Julve M, Lloret F, Cangussu D, Pereira C L M, Stumpf H O, Pasan J and Ruiz-Perez C, *Coord Chem Rev.*, 2010, **254(19-20)**, 2281-2296.
5. Venegas-Yazigi D, Aravena D, Spodine E, Ruiz E and Alvarez S, *Coord Chem Rev.*, 2010, **254(17-18)**, 2086-2095.
6. Masoud M S, Khalil E A, Hindawy A M and Ramadan A M, *Canadian J Anal Sci Spectrosc.*, 2005, **50(6)**, 297-310.
7. Deepalatha S, Rao P S and Venkatesan R, *Spectrochim Acta Part A: Molecular Biomolecular Spectroscopy*, 2006, **64(1)**, 178-187.
8. Paital A R, Wong W T, Aromi G and Ray D, *Inorg Chem.*, 2007, **46** , 5727.
9. Murugavel R, Choudhury A, Walawalkar M G, Pothiraja R and Rao C N R, *Chem Rev.*, 2008, **108**, 3549-3655.
10. Bhatt V D and Ram S R, *Chem Sci J.*, 2012, **63**, 1-10.
11. Armarego W L F and Perrin D D, *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, 1997, 178.
12. Vogel A I, *A Text Book of Quantitative inorganic Analysis*; Longmans: London, 1989, 329.
13. Bellamy L J, *Advances in Infrared Group Frequencies*; Methuen: London, 1968, 67.
14. Nakamoto K, *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1986, 88.
15. Sathyanarayana D N, *Electronic Absorption spectroscopy and Related Techniques*; Universities Press: New Delhi, 2001, 157.
16. Aydogdu Y, Yakuphanoglu F, Aydogdu A, Sekerci M, Balci Y and Aksoy I, *Synthetic Metals*, 1999, **107(3)**, 191-198.
17. Boca R, Gembicky M, Herchel R, Haase W, Jager L, Wagner C, Ehrenberg H and Fuess H, *Inorg Chem.*, 2003, **42(22)**, 6965-6967.
18. Kahn O, *Molecular Magnetism*; Weinheim VCH Publisher: New York, 1993, 176.