
Solvent Induced Conformational Change of Mn(III) Azide Complex [Mn(L)(N₃)(Solvent)] with Chiral Schiff base (R,R)-N,N-di-salicylidene cyclohexane 1, 2-diamine(H₂L)

Tapan Kumar Si^{1*}

^{1*} Assistant professor, Department of Chemistry, Bidhan Chandra College, Asansol-713304, India.
e-mail: tapan@bccollegeasansol.ac.in

Abstract

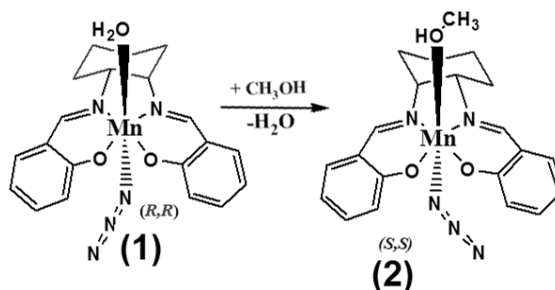
Two new mononuclear azide coordinated Mn(III) complexes [Mn^{III}(L)(N₃)(H₂O)](**1**), [Mn^{III}(L)(N₃)(CH₃OH)](**2**) with tetradentate chiral Schiff base ligand (H₂L) (H₂L=(R,R)-N,N-di-salicylidene cyclohexane 1,2-diamine) have synthesized and characterized by spectroscopic (e.g. IR, UV-vis and Circular Dichroism) as well as single crystal X-ray diffraction studies. Substitution of axially coordinated water (H₂O) molecule in compound **1** by methanol (CH₃OH), compound **2** is formed with inversion of configuration of coordinated chiral Schiff base ligand. The configurational change of Schiff base ligand has been revealed by single crystal XRD studies as well as circular dichroism analysis of its solution.

KEYWORDS: Schiff base, Inversion, Azide, Circular Dichroism

INTRODUCTION

The widespread application of transition metal complexes with multidentate Schiff base ligands in the field of bioinorganic and catalytic research have created considerable attention because of their interesting physicochemical properties¹. The manganese(III) Schiff base complexes with salen type ligands are used as effective catalysts for superoxide dismutation reaction². The Schiff base complexes of manganese (III) have also increased interest for the development of magnetic materials³, catalysts for oxidation of various organic compounds⁴ including asymmetric organic synthesis⁵. Oxygen evolving manganese (III) Schiff base complexes are also very helpful to unveil the mechanism of photosystem-II⁶. Additionally, the chirality in metal complexes enhances their pharmacological behavior for synthesis of designed drug with specific conformation and selective target binding affinity with chiral DNA and protein molecule⁷. In this respect the introduction of chirality in metal complexes and the regulation of stereochemical configuration of above-mentioned metal complexes is one of the challenging tasks in the area of biochemical research⁸. Herein, the author reports the synthesis, structural characterization and physicochemical properties of two newly synthesized

mononuclear azide coordinated Mn^{III} complexes [Mn^{III}(L)(N₃)(H₂O)](**1**) and [Mn^{III}(L)(N₃)(CH₃OH)](**2**) with chiral Schiff base (H₂L). The physicochemical studies of the complexes shows that the methanolic solution of complex **1** results the formation of complex **2** with stereochemical inversion of configuration in coordinated Schiff base ligand moiety (Scheme1). The structural change in configuration of complex **2** in both solid (Fig.1) and solution state has been studied by single crystal XRD studies and Circular Dichroism analysis respectively:



Scheme 1: Substitutions of apical H₂O ligand by CH₃OH of complex **1** results the formation of compound **2** involving the inversion of configuration.

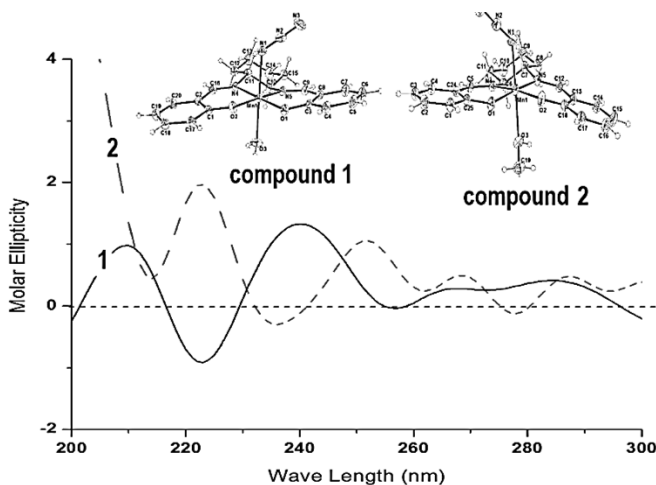


Fig.1: X-ray crystal structure and CD study of compound **1** and **2** showing inversion of configuration in diamine moiety of coordinated Schiff base in **2** with respects to **1**.

EXPERIMENTAL SECTIONS

Materials & methods:

Salicylaldehyde and Manganese (II)acetatehexahydratedimethylformamide (G.R.), methanol (G.R.) and isopropyl alcohol, Sodium azide and all other chemicals were obtained from Merck (India). and (*R,R*) *N,N*-*trans*-1,2-cyclohexanediamine was obtained from Aldrich Chemical Co Ltd. Ethanol (95%) was obtained from Bengal

Chemical and Pharmaceutical Works (Calcutta), and was lime distilled before use. The solvent used for physico-chemical studies were further purified by literature method⁹. The IR spectra were recorded as KBr pallets on a Perkin-Elmer 597 IR spectrophotometer ($4000\text{-}200\text{cm}^{-1}$) and electronic spectra ($200\text{-}800\text{ nm}$) were recorded at room temperature with a Shimadzu U-1200 spectrophotometer using 1cm quartz cell. Circular dichroism (CD) studies were performed in a JASCO(J600) microprocessor based spectropolarimeter. Molar conductance values were measured at 25°C using a thermostatically controlled systronics(India) model 335 digital conductivity bridge. Elemental analyses were performed with the help of a Perkin-Elmer 240C elemental analyzer.

Caution! Although we have experienced no problem with the compounds reported in this work, sodium azide is often explosive and should be handled with great caution.

Synthesis of ligands (H_2L)

The Schiffbase ligand N,N -bis(salicylidene)cyclohexane-1,2-diamine (H_2L) was prepared by literature method¹⁰. IR (KBr disc, cm^{-1}). $3481(\text{b})[\nu_{\text{O-H}}]$, $1629(\text{s})[\nu_{\text{C=N}}]$. UV-Vis: (λ , nm): $317(\epsilon = 9,700)$; $253(\epsilon = 25,000)$; $213(\epsilon = 56,800)$.

Synthesis of the complex $[\text{Mn}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]$ (**1**)

In the methanol solution of Schiff base H_2L (10 mM), solid $\text{Mn}(\text{II})$ acetate (10 mM) and aqueous solution of sodium azide (NaN_3) (20 mM) was added with constant stirring. After a while, a brown precipitate of $[\text{Mn}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]$ was settled down. The precipitate was filtered off and washed with water and dried. Diffraction quality single crystals were obtained by the slow evaporation of acetonitrile solution of $[\text{Mn}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$. Anal. calcd. for $\text{C}_{20}\text{H}_{24}\text{N}_5\text{O}_4\text{Mn}$: C, 53.15; H, 5.36; N, 15.50%. Found: C, 52.98; H, 5.27; N, 15.54%. IR data of the compound **1**, (KBr disc, cm^{-1}) are $3281(\text{b})[\nu_{\text{O-H}}$ of $\text{H}_2\text{O}]$, $2856(\text{w})$, $2056(\text{s})[\nu_{\text{N=N}}$ vibration of azide], $1618(\text{s})$ and $1597(\text{s})[\nu_{\text{C=N}}]$. UV-Vis(λ , nm): $555(\epsilon = 210)$; $485(\epsilon = 780)$; $398(\epsilon = 7,370)$; $340(\epsilon = 10,740)$; $272(\epsilon = 31,400)$, $235(\epsilon = 72,600)$.

Synthesis of the complex $[\text{Mn}(\text{L})(\text{N}_3)(\text{CH}_3\text{OH})]$ (**2**)

The evaporation of the saturated methanolic solution of compound $[\text{Mn}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]$ (**1**) resulted the formation of complex, $[\text{Mn}(\text{L})(\text{N}_3)(\text{CH}_3\text{OH})]$ (**2**) in crystalline form. The crystalline product was filtered off and washed with water and dried. Anal. calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_5\text{O}_3\text{Mn}$: C, 56.08; H, 5.38; N, 15.57%. Found: C, 56.17; H, 5.32; N, 15.48%. IR data of the compound **2**, (KBr disc, cm^{-1}), $3269(\text{w})[\nu_{\text{O-H}}$ of $\text{CH}_3\text{OH}]$, $2056(\text{s})[\nu_{\text{N=N}}$ vibration of azide] $1618(\text{s})$ and $1599(\text{s})[\nu_{\text{C=N}}]$, $1309(\text{s}) \nu(\text{C-O}_{\text{phenolate}})$. UV-Vis(λ , nm): $575(\epsilon = 220)$; $480(\epsilon = 700)$; $394(\epsilon = 7,280)$; $340(\epsilon = 9,690)$; $278(\epsilon = 27,250)$, $237(\epsilon = 62,300)$.

Structural analysis of complexes 1 and 2 by single crystal X-ray Diffraction.

X-ray data of [Mn(L)(N₃)(H₂O)] (1) and [Mn(L)(N₃)(CH₃OH)] (2) were collected from Bruker SMART Apex CCD area detector using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). X-ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs¹¹. The structure was solved by direct method. Data collection parameters and selected crystal data and are given in Table 1.

Table 1: Selected crystals data and data collection parameters

| Compound | 1 | 2 |
|--|--|--|
| Empirical Formula | C ₂₀ H ₂₂ N ₅ O ₄ Mn | C ₂₁ H ₂₄ Mn N ₅ O ₃ |
| Mr | 451.37 | 449.39 |
| T/K | 296 | 293 |
| $\lambda/\text{\AA}$ | 0.71073 | 0.71073 |
| Crystal System | Triclinic | Triclinic |
| Space Group | P-1 | P-1 |
| Unit Cell Dimension | | |
| a/ \AA | 8.1041(2) | 8.5258(3) |
| b/ \AA | 11.2172(3) | 9.9391(3) |
| c/ \AA | 12.4178(3) | 12.1734(4) |
| α° | 115.917(1) | 96.355(2) |
| β° | 92.526(1) | 97.330(2) |
| γ° | 99.279(1) | 96.883(2) |
| V/ \AA^3 , Z | 993.65(4), 2 | 1007.41(6), 2 |
| D _c /g cm ⁻³ | 1.509 | 1.482 |
| F(000) | 468 | 468 |
| Crystal size/mm | 0.03 x 0.03 x 0.22 | 0.03 x 0.05 x 0.20 |
| θ Range for data collection($^\circ$) | 2.0-24.0 | 2.1, 27.6 |
| Reflections collected | 12080 | 16164 |
| Independent reflections (R _{int}) | 3130(0.026) | 4598(0.042) |
| Completeness to $\theta = \theta_{\text{max}}$ (%) | 99.6 | 98.8 |
| Refinement method | | |
| Data/restraints/parameters | 2652/0/359 | 4598/0/367 |
| Goodness-of-fit on F ² | 1.101 | 1.041 |
| Final R indices [I > 2 σ (I)] | 0.0412, 0.1043 | 0.0449, 0.1060 |
| R indices (all data) | 0.0524, 0.1141 | 0.0644, 0.1154 |
| Largest diff. Peak, hole/ \AA^{-3} | 0.614, -0.493 | -0.26, 0.65 |

Circular Dichroism spectral studies of the ligand(H₂L) and the complexes 1 and 2:

The CD spectra of the ligand (H₂L) and complex 1 was taken in acetonitrile solution of concentration 5×10^{-5} (M) and while that of compound 2 was taken in methanol solution of concentration 3.0×10^{-5} (M). The range of wavelength in which the spectra were taken is 200-450 nm The unit of CD spectra is $[\theta] \times 10^{-3}$ (deg cm² dmol⁻¹) and the CD path length was 1 cm in each measurement.

RESULTS AND DISCUSSION

Synthetic aspects

Manganese (II) ion is coordinated by tetradentate (R,R) chiral Schiff base (H_2L) ligand in aqueous methanol medium and form six coordinated water soluble intermediate $[Mn^{II}(L)(H_2O)_2]$ complex which is oxidized to form $[Mn^{III}(N_3)(L)(H_2O)]$ (**1**) in presence of azide (N_3^-) ion and finally settle down as brown precipitate from the solution. This compound **1** is converted to $[Mn(N_3)(L)(CH_3OH)]$ (**2**) through exchange of H_2O by CH_3OH .

General characterizations, IR and UV spectroscopic studies

Conductometric studies show that the compounds **1** and **2** are non-electrolyte in appropriate solvents. In both the compounds, the manganese ion exists in the +3 oxidation state and both are paramagnetic at 300K. The magnetic moment values are lying in the range 4.6-4.8 BM¹². The broad stretching frequency at 3281 cm^{-1} in compound **1** indicates the presence of coordinated H_2O molecule and the vibration at 3269 cm^{-1} in compound **2** indicates the presence of coordinated CH_3OH molecule as shown in experimental section. The strong vibration at 2056 cm^{-1} appears due to N=N bond of coordinated azide ion (N_3^-) ion for compound **1** and **2**¹³. The $\nu(C=N)$ of free H_2L is obtained at 1627 cm^{-1} but it appears at 1597-1618 cm^{-1} after chelation¹⁴ in compounds **1** and **2**. The strong C-O(phenolic) vibration band at 1279 cm^{-1} for free H_2L ligand and it is shifted to higher energy region at 1309 cm^{-1} due to $\nu(C-O_{phenolate})$ for **1** and **2**¹⁰. The electronic spectra of a $d^4Mn(III)$ system in all the two complexes shows bands with shoulders around 460-600nm due to d-d transitions¹⁵. The electronic spectra ligand H_2L in acetonitrile exhibits the azomethine $\pi-\pi^*$ transition at 317 nm and the benzene $\pi-\pi^*$ transitions bands at 253 nm and 214 nm. The brown color acetonitrile solution of compound **1** exhibit intra-ligand $\pi \rightarrow \pi^*$ transition at 215nm, 234nm and 273 nm with a shoulder at 305nm. The LMCT transition occurs at 399 nm with a shoulder at 345nm¹⁶(Fig.2) while the respective bands for compound **2** are observed at 215nm, 235nm and 281 nm with a shoulder at 305nm and LMCT transition at 401nm with a shoulder at 345nm. (Fig.3).

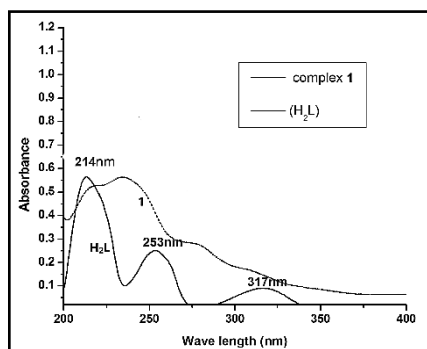


Fig.2: Electronic absorption spectra of the complex **1** and the ligand (H_2L) in acetonitrile solution ($1.0 \times 10^{-5}M$).

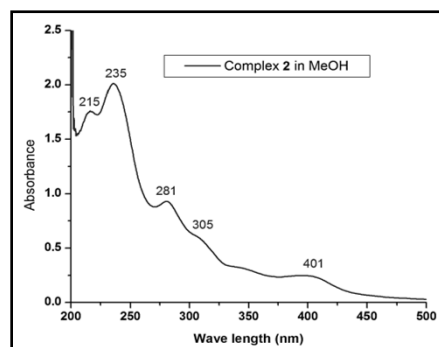


Fig.3: Electronic absorption spectra of the complex **2** in methanol solution ($1.0 \times 10^{-5}M$).

Xray crystal structure of compounds 1 and 2.

The compounds $[\text{Mn}^{\text{III}}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (1) and $[\text{Mn}^{\text{III}}(\text{L})(\text{N}_3)(\text{CH}_3\text{OH})]$ (2) crystallize in the triclinic space group P-1 with Z=2 and view of packing pattern in unit cell (100 plane) of the two complexes are shown in the Fig.4.

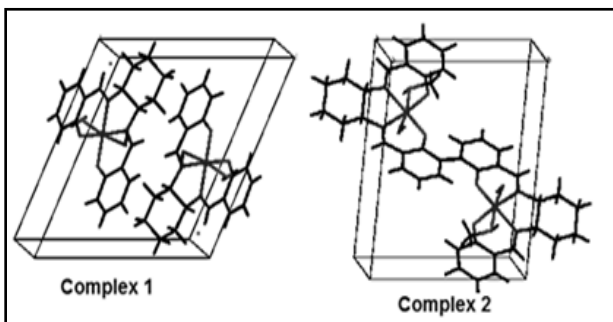


Fig.4: View of packing pattern of complex 1 and 2 in the unit cell in 100 planes.

The structural characteristics of the complexes are given below.

$[\text{Mn}^{\text{III}}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (1). In this mononuclear Mn(III) compound the Mn(1) has a six-coordinated pseudo-octahedral geometry where O(1), O(2), N(4) and N(5) atoms of the di-deprotonated Schiff base L^{2-} constitutes the equatorial plane. In the axial position the Mn(III) ion is coordinated by one N_3^- ion (via N1 atom) and one water (H_2O) molecule (via O3 atom) as terminal ligands, forming its octahedral coordination sphere (Fig.5). The bond lengths of Mn(1)–O(1), Mn(1)–O(2), Mn(1)–N(4) and Mn(1)–N(5) are 1.8707(18), 1.8753(19), 1.980(3) and 1.985(2) Å, respectively.

Due to a Jahn–Teller distortion of the Mn(III) ion¹⁷ the bond distances in the axial positions (Mn(1)–N(1) 2.257(2) Å and Mn(1)–O(3) 2.336(2) Å are significantly longer as compared to linked L^{2-} ligand. The terminal azide nitrogen atom (N3) form hydrogen bond with the hydrogen (H24) of coordinating H_2O molecules makes one-dimensional infinite chain, which is shown in Fig.6. Selected bond lengths and bond angles are listed in Table 2. Details of the hydrogen bonding are shown in the Table 4.

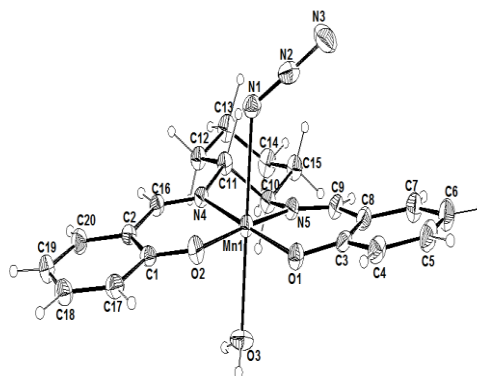


Fig.5: The Ortep view of $[\text{Mn}(\text{L})(\text{N}_3)(\text{H}_2\text{O})]$ (1) with ellipsoids at 30% probability planes.

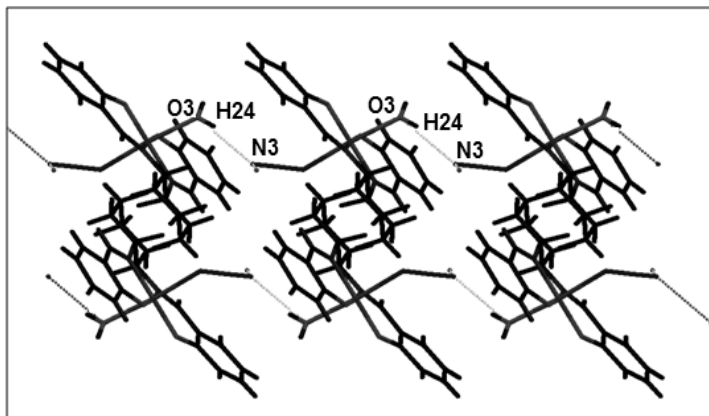
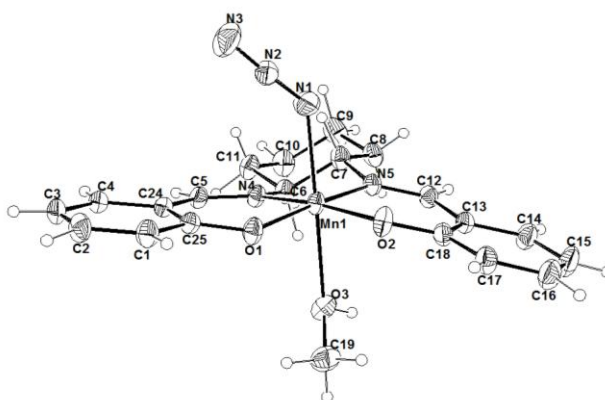


Fig. 6:Formation of infinite one dimensional chain in (001) plane due to strong hydrogen bonding between terminal azide nitrogen (N3) with the hydrogen(H24) of coordinating H₂O of compound 1.

Table 2: Important Bond lengths (Angstrom) and bond angles of compounds 1

| [Mn(L)(N ₃)(H ₂ O)] (1) | | Bonds | Angles | Bonds | Angles |
|--|------------|-------------|-----------|-------------|-----------|
| Mn1 - O1 (water) | 2.336(2) | O1 -Mn1 -O2 | 91.37(8) | O1 -Mn1 -O3 | 91.26(10) |
| Mn1 - O1 | 1.8707(18) | O1 -Mn1 -N1 | 93.36(9) | O3 -Mn1 -N4 | 87.15(10) |
| Mn1 - O2 | 1.8753(19) | O1 -Mn1 -N4 | 175.29(9) | O2 -Mn1 -O3 | 90.32(10) |
| Mn1 - N1 | 2.257(2) | O2 -Mn1 -N4 | 92.73(8) | O2 -Mn1 -N4 | 92.72(10) |
| Mn1 - N4 | 1.980(3) | O1 -Mn1 -N5 | 92.63(9) | O3 -Mn1 -N1 | 172.57(9) |
| Mn1 - N5 | 1.985(2) | O2 -Mn1 -N5 | 173.46(9) | O3 -Mn1 -N5 | 84.69(10) |
| N1 - N2 | 1.173(4) | N1 -Mn1 -N4 | 87.74(12) | N1 -Mn1 -N5 | 89.28(10) |
| N2 - N3 | 1.168(4) | N4 -Mn1 -N5 | 87.79(9) | Mn1 -N1 -N2 | 125.3(2) |
| | | N1 -N2 -N3 | 179.0(4) | | |

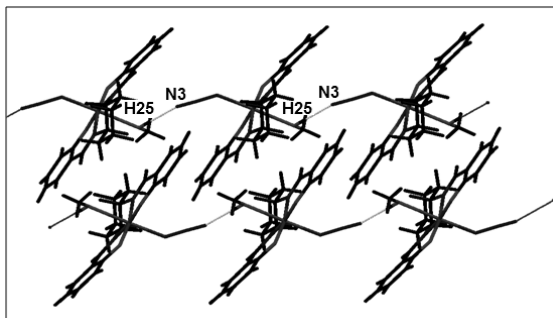
[Mn^{III}(L)(N₃)(CH₃OH)](2). In this compound the coordination geometry of Mn(III) is mononuclear pseudo-octahedral structure where O(1), O(2), N(4) and N(5) atoms of the di-deprotonated Schiff base L²⁻ constitutes the equatorial plane. In the axial position the Mn(III) is coordinated by one N(1) atom of N₃ ion and one oxygen atom (O3) of CH₃OH



molecule forming its distorted octahedral structure (Fig.7).

Fig.7:TheOrtep view of [Mn(L)(N₃)(CH₃OH)] (2)with ellipsoids at 30 % probability.

The bond lengths of Mn(1)-O(1), Mn(1)-O(2), Mn(1)-N(4) and Mn(1)-N(5) are 1.8808(16), 1.8661(17), 1.997(2), and 1.9847(18) Å respectively. Here the bond distances in the axial position (Mn(1)-N(1) 2.191(2) Å ; Mn(1)-O(3) 2.476(2) Å) are also significantly longer than the linked L²⁻ ligand due to a Jahn-Teller distortion of the Mn(III) ion. Due to



the formation of hydrogen bonding, it forms infinite one-dimensional chain and two anti parallel chains are situated closely due to pi-pi stacking interaction of aromatic ring of coordinated Schiff base (Fig.8). The Selected bond lengths and bond angles compound 2 are listed in Table 3 whereas details of the hydrogen bonding is shown in Table 5.

Fig. 8: Formation of infinite one-dimensional chain in 010 plane of compound 2 due to hydrogen bonding (O3-- H25...N3) between azide nitrogen (N3) and methanolic proton (H25).

Table 3: Important bond lengths (Angstrom) and bond angles of compound [Mn(L)(N₃)(CH₃OH)] (2)

| [Mn(L)(N ₃)(CH ₃ OH)] (2) | | Bonds | Angles | Bonds | Angles |
|--|------------|---------------|-----------|---------------|-----------|
| Mn1 - O3 (methanol) | 2.476(2) | O1 - Mn1 - O2 | 93.06(7) | O1 - Mn1 - O3 | 89.51(8) |
| | | O1 - Mn1 - N1 | 95.46(8) | O1 - Mn1 - N4 | 91.85(7) |
| Mn1 - O2 | 1.8661(17) | O1 - Mn1 - N5 | 171.23(8) | O2 - Mn1 - O3 | 88.88(7) |
| Mn1 - O1 | 1.8808(16) | O2 - Mn1 - N1 | 97.45(9) | O2 - Mn1 - N4 | 169.56(7) |
| Mn1 - N1 | 2.191(2) | O2 - Mn1 - N5 | 92.07(8) | O3 - Mn1 - N1 | 171.71(8) |
| Mn1 - N4 | 1.997(2) | O3 - Mn1 - N4 | 81.95(7) | O3 - Mn1 - N5 | 83.48(8) |
| Mn1 - N5 | 1.9847(18) | N1 - Mn1 - N4 | 91.25(9) | N1 - Mn1 - N5 | 90.92(8) |
| N1 - N2 | 1.160(3) | N4 - Mn1 - N5 | 81.98(8) | Mn1 - N1 - N2 | 132.4(2) |
| N2 - N3 | 1.147(3) | N3 - N2 - N1 | 176.8(3) | | |

Table 4 : Relevant hydrogen bonds for complex [Mn(L)(N₃)(H₂O)]

| D-H...A ∠(DHA) | d(D-H) | d(H...A) | d(D...A) |
|---|----------------|----------------|-----------------|
| O3 -- H23 .. O1 ⁽ⁱ⁾ 151(5) | 0.75(6) | 2.41(5) | 3.084(4) |
| O3 -- H23 .. O2 ⁽ⁱⁱ⁾ 139(5) | 0.75(6) | 2.49(6) | 3.088(4) |
| O3 -- H24 .. N3⁽ⁱⁱⁱ⁾ 164(6) | 0.73(5) | 2.27(6) | 2.983(5) |
| C9 -- H9 .. O4 ⁽ⁱⁱⁱ⁾ 161(3) | 0.90(3) | 2.48(3) | 3.341(8) |

Table 5 : Relevant hydrogen bonds for complex[Mn(L)(N3)(CH3OH)] (2).

| D-H...A ∠(DHA) | d(D-H) | d(H...A) | d(D...A) |
|---|---------|----------|----------|
| O3 -- H25 .. N3 ⁽ⁱ⁾ 178(5) | 0.80(3) | 2.01(3) | 2.809(4) |
| C4 -- H4 .. N3 ⁽ⁱⁱ⁾ 140(2) | 0.92(3) | 2.61(3) | 3.363(5) |
| Symmetry codes: (i) -1+x,y,z (ii) 2-x,2-y,2-z | | | |

CD SPECTRA OF COMPLEX

To assign the configurational status in solutions, the circular dichroism (CD) experiment was done. In the UV-vis spectrum of (H₂L) (Fig.2) the azomethine π - π^* transition band was observed at 317 nm and the benzene π - π^* transitions gave rise to bands at 253 nm and 214 nm. The CD spectrum of ligand H₂L displays a negative Cotton effect (CE) associated with the π - π^* transition of the azomethine chromophore, in agreement with the *R,R*-configuration¹⁸ of the diamine moiety. The band in the region 210-270 nm although appeared better resolved in the CD but is complicated by multiple Cotton

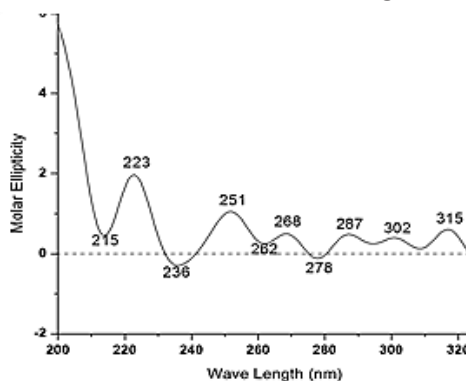


Fig.9: CD spectrum of H₂L in CH₃CN solution (1.0 × 10⁻⁴M)

Effects arising out of the benzenoid transitions involving salicyaldimine rings (Fig.9).

In the UV-vis spectra of complexes **1** (Fig.2) and **2** (Fig.3) show four absorption bands at region 214-300 nm and two extra absorption bands in the region 300-450 nm due to intraligand π - π^* transitions and LMCT transitions respectively. The CD spectrum of complex **1** (Fig.10) exhibits a negative Cotton effect (CE) associated with the π - π^* transition (at 315nm) of the

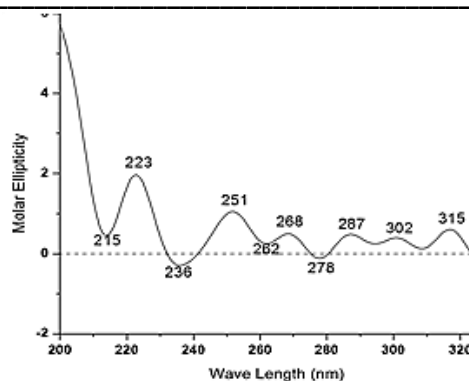


Fig.11: CD spectrum of complex **2** in methanol solution ($3.0 \times 10^{-5} \text{M}$)

azomethine chromophore, in agreement with the *R,R*-configuration of the diamine moiety while that of complex **2** (Fig.11) The

CD spectrum at the region 215-260 nm for complex **2** opposite to that of complex **1** indicating their different configuration with respect to complex **1**. The findings of the single crystal XRD analysis and the solution CD studies clearly demonstrate that a consistent change in configuration is induced by the change apical solvent molecule. The examples of such conformational change of complex influenced by the nature of coordinated solvent molecule are very rare in literature¹⁹⁻²⁰.

CONCLUSION

The physicochemical studies of two mononuclear azide coordinated Mn(III)-tetradentate chiral Schiff base complexes show that molecular configuration of the metal complex can be modulated in different solvent media with suitable coordination environment of the complex molecules. So, the synthesized chiral azidecoordinated Mn(III)-Schiff base complexes may play important role in target selective binding affinity with chiral DNA and protein by adopting specific conformation. The controlled stereochemistry of chiral Mn(III) complexes may be acted as fruitful catalysts for the asymmetric synthesis of various organic compounds.

Supplementary data:

The X-ray crystallographic data (CIF files) for the structures reported in this paper have been deposited in the

Cambridge Crystallographic Data Centre and the deposition number are CCDC

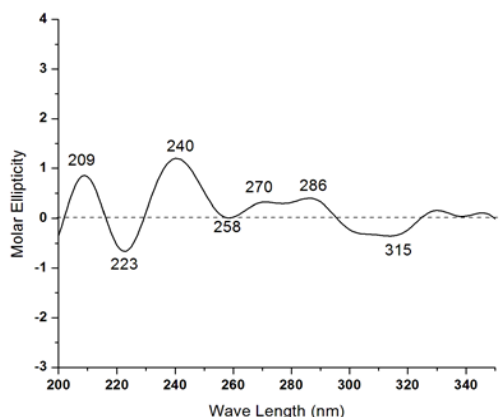


Fig.10: CD spectrum of complex **1** in CH_3CN solution ($5.0 \times 10^{-5} \text{M}$)

870102 and 870103 for the complex **1** and **2** respectively. The data can be obtained free of charge via the website www.ccdc.cam.ac.uk/conts/retrieving.html.

Acknowledgements

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REFERENCES:

- i. Mohamed G, Soliman M. (2010). Synthesis, spectroscopic and thermal characterization of sulphiride complexes of iron, manganese, copper, cobalt, nickel, and zinc salts. Antibacterial and antifungal activity. *Spectrochim Acta Part A*. **76**:341-347
- ii. Cozzi P. G. (2004). Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem Soc Rev*. **33**:410-421. (b) Dekhordi, M. N., Brodbar, A. K., Mehrgardi, M. A., Mirkhani, V. (2011). Spectrophotometric study on the binding of two water soluble Schiff base complexes of Mn(III) with ct-DNA. *J. Fluoresc.* **21**:1649-1658.
- iii. Miyasaka, H., Saitoh, A., Abe, S. (2007) Magnetic assemblies based on Mn(III) salen analogues. *Coord. Chem. Rev.* **251**: 2622-2664.
- iv. Aghmiz, A., Mostafa, N., Iksi, S. (2013). Mn(III) complexes with tridentate N,N,O-ligands as catalysts for the epoxidation of alkenes. *J. Coord. Chem.* **66**:2567-2577.
- v. Zhao, J., Zhang, Y., Han, F., Zhao, S. (2009). Asymmetric epoxidation of unfunctionalized alkenes catalyzed by sugar moiety-modified chiral salen-Mn(III) complexes. *Carbohydr. Res.* **344**:61-66.
- vi. Karacan, M. S., Somer, G. (2004). Reconstruction of the water-oxidizing complex in manganese-depleted Photosystem II by using Schiff base manganese complexes. *J. Photochem. Photobiol. A: Chem.* **163**:307-310.
- vii. Wang, B. W., Jiang, L., Shu, S. S. et al. (2015). Synthesis, Crystal Structure, and Biological Activities of Two Chiral Mononuclear Mn(III) Complexes. *Chirality*. **27**:142-50
- viii. Khan, N. H., Pandya, N., Maity, N. C. et al. (2011). Chiral discrimination asserted by enantiomers of Ni (II), Cu (II) and Zn (II) Schiff base complexes in DNA binding, antioxidant and antibacterial activities. *Eur. J. Med. Chem.* **1**:199-208.
- ix. Jeffery, G. H., Bassett, J., Mendham, J., Denny Addison R. C. (1989). *Vogel's Text Book of Quantitative Chemical Analysis, 5th edn.*, Wesley Longman Limited, UK.
- x. Si, T. K., Drew, M. G. B., Mukherjee K. K. (2011). Peroxidative bromination and oxygenation of organic compounds: Synthesis, X-ray crystal structure and catalytic implications of mononuclear and binuclear oxovanadium(V) complexes containing Schiffbase ligands *Polyhedron*. **30**: 2286-2293.
- xi. Sheldrick, G. M. (1997). *SHELXS-97 and SHELXL-97 Programs for Crystal Structure Solution and Refinement*, University of Gottingen, Gottingen, Germany.
- xii. Kara, H. (2007). A Novel Hydrogen-bonded Zigzag Chain Manganese (III) Complex: Synthesis, Crystal Structure and Magnetic Properties. *Z. Naturforsch.* **62b**: 691-695.
- xiii. Yoon, J. H., Lee, J.W., Ryu, D.W. et al. (2011). One-Dimensional End-To-End Azide-Bridged Mn(III) Complexes Incorporating Alkali Metal Ions: Slow Magnetic Relaxations and Metamagnetism. *Chem. Eur. J.*, **17**: 3028-3034.
- xiv. Yang, C., Wang, Q. L., Ma, Y. et al. (2010). Bimetallic Materials Derived from Manganese(III) Schiff Base Complexes and Pentacyanonitrosylferrate(II) Precursor: Structures and Magnetic Properties. *Inorg. Chem.* **49**:2047-2056.
- xv. Matzapetakis, M., Karligiano, N., Bino, A. et al. (2000). Manganese Citrate Chemistry: Syntheses, Spectroscopic Studies, and Structural Characterizations of Novel Mononuclear, Water-Soluble Manganese Citrate Complexes. *Inorg. Chem.* **39**: 4044-4051.
- xvi. Felicio, R. C., Canaleiro, E. T. G., Dockal, E. R. (2001). Preparation, characterization and thermogravimetric studies of [N,N'-cis-1,2-cyclohexylene bis(salicylideneaminato)]cobalt(II) and [N,N'-(±)-trans-1,2-cyclo-hexylene bis(salicylideneaminato)] cobalt(II). *Polyhedron*. **20**: 261-268.

-
- xvii. Biswas, S., Mitra, K., Schwalbe, C. H., Lucas, C. R., Chattopadhyay, S. K., Adhikary, B. (2005). Synthesis and characterization of some Mn(II) and Mn(III) complexes of N,N'-o-phenylenebis(salicylideneimine) (LH₂) and N,N'-o-phenylenebis(5-bromosalicylideneimine)(L'H₂). Crystal structures of [Mn(L)(H₂O)(ClO₄)], [Mn(L)(NCS)] and an infinite linear chain of [Mn(L)(OAc)]. *Inorg. Chim. Acta.* **358**: 2473-2481.
- xviii. Patti, A., Pedotti, S., Ballistreri, F. P., Sfrassetto, G. T. Synthesis and Characterization of Some Chiral Metal-Salen Complexes Bearing a Ferrocenophane Substituent. *Molecules.* 2009, **14**:4312-4325.
- xix. Sato, H., Morib, Y., Yamagishi, A. (2013). Conformational change of a chiral Schiff base Ni(ii) complex with a binaphthyl moiety: application of vibrational circular dichroism spectroscopy. *Dalton Trans.* **42**:6873-6878.
- xx. Sunaga, N., Haraguchi, T., Akitsu, T. (2019). Orientation of Chiral Schiff Base Metal Complexes Involving Azo-Groups for Induced CD on Gold Nanoparticles by Polarized UV Light Irradiation. *Symmetry.* **11**, 1094:1-19.