IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Chloro-bridged Mn(II) complex: Synthesis, Crystal Structure and DFT Studies

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Abstract: A new usymmetric bidentate Schiff-base ligand from p-bromo salicylaldehyde and benzylamine was prepared. The crystal structure of a chloro-bridged complex $[Mn(\mu\text{-}Cl)(L)_2]_2$ (1) was derived whose structure has been confirmed by single-crystal X-ray diffraction analysis. The complex was characterized by IR and elemental analysis. Complex 1 is crystallized in *Tetragonal* system with space group *P 4 c c* with the chlorine atoms bridging the two Mn atoms. DFT studies were carried out and the energy difference between HOMO and LUMO was calculated.

Key words: Chloro-bridged, Single crystal X-ray diffraction, DFT studies

Index Terms **- Component,formatting,style,styling,insert.**

I. INTRODUCTION

The coordination chemistry of manganese ions with N and/or O containing ligands has been receiving a great deal of attention, because of the variable structures of manganese complexes and the importance of manganese enzyme models, the possibility of magnetic coupling interactions, and the application of manganese compounds in industrial catalysis [1], [2].

The behaviour of these manganese complexes is mainly dependent on the structure and coordination mode of the ligands in addition to the oxidation number of manganese. Dinuclear chloro-bridged Mn(II) compounds with N/O donor ligands are relatively rare and only a few six-coordinated Mn(II) compounds have been structurally investigated [2], [3], [4], [5], [6].

In this study the molecular and X-ray structure of an unusual dinuclear chloro-bridged Mn(II) compound with the formula $[Mn(\mu\text{-}Cl)(L)_2]_2$ is reported along with DFT optimization.

2.EXPERIMENTAL SECTION

2.1 Materials and Methods

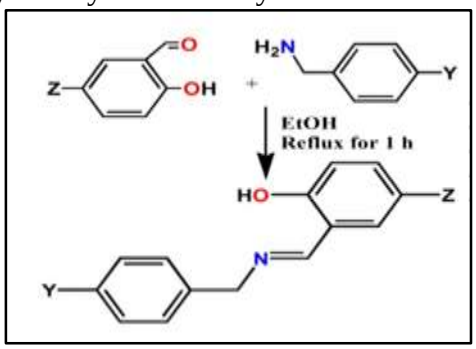
All starting materials were commercially available, reagent grade and used as received without further purification.

2.2 Physical Measurements.

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. Infrared spectra (400–4000 cm^{-1}) were recorded from KBr pellets on a Nickolet Magna IR 750 series-II FTIR spectrophotometer. ^{1}H and ^{13}C-NMR were recorded in $CDCl_3$ on a Bruker 300 MHz NMR spectrometer using tetramethylsilane ($\delta = 0$) as an internal standard.

2.3 Syntheses

2.3.1 Preparation of Ligand (HL).The bidentate Schiff base ligand HL was synthesized (**Scheme 1**) by mixing the p-bromo salicylaldehyde and benzylamine in 1:1 molar ratio in ethanol.

3. 

Scheme 1: Synthesis of ligand

2.3.2 Preparation of Complex (1). The complex was synthesized using a general procedure. In a typical procedure 0.125 g $MnCl_2$ (1 mmol) was added to a methanolic solution of HL (1.0 mmol) in 10 ml methanol and the mixture was stirred vigorously for 5 h, filtered and kept in air. After 2 days X-ray quality single crystals were obtained which were filtered, washed with water and ether and then dried in vacuum. Yield 60-70%.

$[Mn^{III}$ (μ-Cl) $L_2]_n$ (1). IR (KBr): 2044 cm^{-1}, 1618 cm^{-1}. Anal. (%): C, 49.88; H, 3.36; N, 10.17. Calcd. (%) for $C_{28}H_{22}Br_2MnCl_2$ (M. W. =699): C, 48.06; H, 3.14.

2.4 X-ray Crystallography

Single crystal X-ray data of complex **1** is collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073Å). Data collection, reduction, structure solution, and refinement are performed using the Bruker Apex-2 suite. All available reflections to $2\theta_{max}$ are harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus [7]. Reflections are then corrected for absorption, inter-frame scaling, and other systematic errors with SADABS [7]. The structures are solved by the direct methods and refined by means of full matrix least-square technique based on F^2 with SHELX-97 software package [8]. All the nonhydrogen atoms are refined with anisotropic thermal parameters. All the hydrogen atoms belonging to carbon and nitrogen atoms are placed in their geometrically idealized positions, while hydrogen atoms on oxygen atoms of coordinated water are found on the difference furior map, and all of them were constrained to ride on their parent atoms.

2.4.1 Structural description:

The single crystal X-ray diffraction showed that Mn^{III} based 1D chain complex $[Mn^{III}L_2Cl]_n$(**1**) is depicted in **Fig. 1**, crystallized in *Tetragonal* system with space group *P 4 c c*. The mononuclear metal center Mn^{III} is surrounded by two symmetry related deprotonated bidented Schiff base (between benzyl amine and p-bromo-salicylaldehyde) ligand L^{1-}(namely O1 and N1) in plane and two Cl1-atom at the two axial positions; thus to form hexa-coordinated octahedral geometry in an asymmetric unit. The metal center Mn^{III} is d^4 system and there is a strong Jahn-Teller (JT) distortion, so geometry of metal centre is distorted octahedral.This asymmetric unit is further extend to form 1D chain through μ_2-Cl bridge along crystallographic *b*-axis with base vector (0 0 1).The sole water molecule is out of coordination environment, crystallised with this 1D network. The bond distances around metal center are: Mn-O1=1.878Åwhere as Mn-N1=2.039Å. The closest Mn···Mn short contacts distance through chloro-bridged is 2.532Å. There is no such classical H-bonding found in complex **1**.

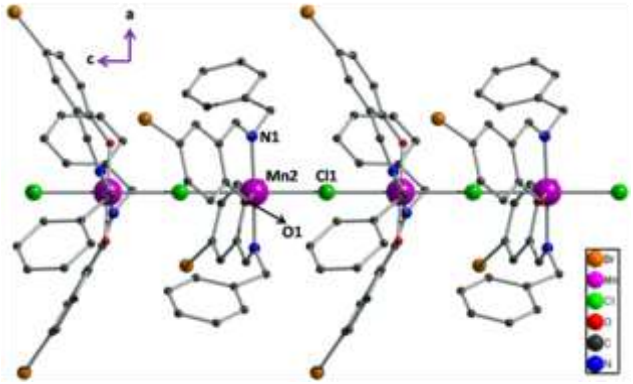


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Fig. 1: The Molecular view of 1D chain of complex **1** in crystallographic *b* axis. All H-atoms and one water molecule are omitted for clarity.

2.5 Computational details

DFT study has proven to be an important tool to obtain better insights into the geometry and electronic structure of these systems. Becke's hybrid function [9] with the Lee-Yang-Parr (LYP) correlation function [10] was used through the study. The geometry of the complex **1** was fully optimized with multilayer ONIOM model at quintet spin state accordance with repeating asymmetric unit only.

For H atoms we used 6-31G basis set; for C, N and O atoms we employed 6-31G and for Cl , Br atoms and metal centre Mn atom, we adopt 6-31G +G(d,p) as basis set for the optimization of the ground state.All the calculations were performed with the Gaussian 09W software package [11].

2.5.1 Geometry optimization

We have tabulated comparable experimental and theoretical values of bond distances and bond angles in **Table 1.** The values for energy UONIOM(B3LYP/6-31G), RMS gradient norm and the dipole moment were -8094.08249353a.u., 0.04274974a.u. and 5.9212D, respectively for this optimization. The frontier orbital diagram of the optimization of **1** is shown in **Fig. 2.**The energy difference between HOMO and LUMO is 3.191eV.

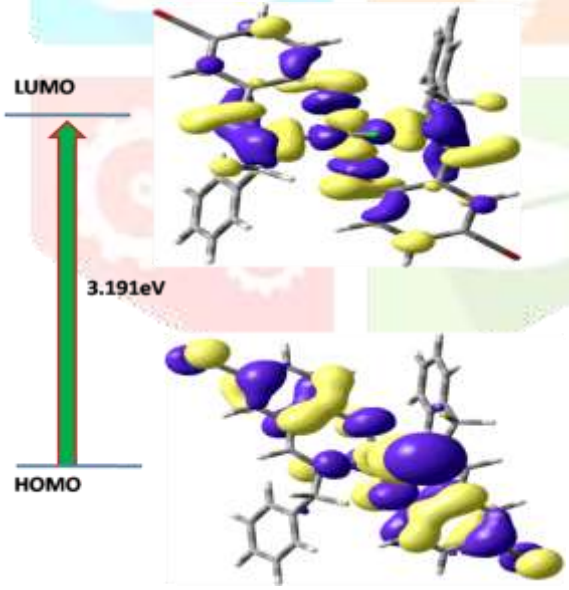

Fig. 2. The frontier orbital diagram of the optimization of **1**underUONIOM(B3LYP/6-31G).

Table 1. The comparableexperimental and theoretical values of bond distances and bond angles

Bond Type	Experimental values	Theoretical values
Mn2-O1	1.878 Å	1.8784 Å
Mn2-N1	2.039 Å	2.0381 Å
Mn2-Cl1	2.532Å	2.5301 Å
N1-Mn2-Cl1	89.03°	91.261°
N1-Mn2-O1	89.51°	89.383°
O1-Mn2-Cl1	90.23°	90.111°

3 Conclusion

A bidentate NO donor ligand affords a new μ_2-Cl bridged Mn^{III} 1D chain that has been characterized structurally. Structural analyses show that in the complex Mn^{III} atoms are in distorted octahedral

geometry where two NO donor ligands occupy the basal plane and two axial sites being occupied by the two bridging Cl ions and extended along the crystallographic *b* axis to give 1D chain.

4 ACKNOWLEDGMENT

Financial support from Swami Vivekananda Institute of Science & Technology, Kolkata – 700145, West Bengal, India is gratefully acknowledged.

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