Accepted Manuscript

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PII: S0022-2860(19)30294-7

DOI: https://doi.org/10.1016/j.molstruc.2019.03.027

Reference: MOLSTR 26296

- To appear in: Journal of Molecular Structure
- Received Date: 8 November 2018

Revised Date: 1 March 2019

Accepted Date: 8 March 2019

Please cite this article as: M. Karakoç, Bü. Dede, M. Erdem Tunçmen, F. Karipcin, Synthesis, characterization, DFT calculations and catalase-like enzymatic activities of novel hexadentate schiff base and its manganese complexes, *Journal of Molecular Structure* (2019), doi: https://doi.org/10.1016/j.molstruc.2019.03.027.

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SYNTHESIS, CHARACTERIZATION, DFT CALCULATIONS AND CATALASE-LIKE ENZYMATIC ACTIVITIES OF NOVEL HEXADENTATE SCHIFF BASE AND ITS MANGANESE COMPLEXES

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ABSTRACT

We reported the synthesis of the manganese(II) and manganese(III) complexes of a novel hexadentate Schiff base ligand (HBME) (1) obtained from the condensation of triethylenetetramine and 2 equiv. of 1-(biphenyl)-2-hydroxyimino-2-(morpholino)-1ethanone. Hexadentate Schiff base ligand reacted with manganese(II) perchlorate or manganese(III) acetate and sodium azide, to give rise to a series of mono and dinuclear complexes $[Mn(BME)_2 tren)]$ (2), $[Mn_2(BME)_2 tren(N_3)_2]$ (3) and $[Mn_2(BME)_2 tren(N_3)_4]$ (4). Synthesized molecules were characterized by elemental analyses, ICP-MS, spectroscopic studies, thermal analyses, molar conductivity and magnetic susceptibility measurements. The quantum chemical calculations of the HBME and complexes (2-4) were performed in the ground state using the DFT of B3LYP level with 6-311G(d,p) and LanL2DZ basis sets, respectively. ¹H- and ¹³C-NMR chemical shifts were calculated by using the gauge independent atomic orbital (GIAO) method and the electronic properties such as HOMO-LUMO energies were determined by the time-dependent DFT approach. The calculated spectroscopic values for the HBME were in very good agreement with experimental ones. Furthermore, catalytic activity of the complexes for the disproportionation of hydrogen peroxide was also investigated in the presence of 1-methylimidazole. All the complexes displayed catalytic ability for the disproportionation of H₂O₂ significantly, but the activities of the (3) and (4) were relatively higher than the other molecules.

Keywords: Schiff base, manganese, dinuclear complex, DFT, catalase-like activity

1. INTRODUCTION

Manganese is known to be an essential element in many biological systems and a catalytic component of several enzymes, including catalase. Its oxidation-reduction chemistry is especially important for the electron-transfer reactions of mitochondrial superoxide dismutase, bacterial catalases and photosystem II in green plant photosynthesis. Catalase, one of the three major sensitive protective enzymes in living organisms, exists in almost all aerobically respiring organisms. It protects biological systems against oxidative damage caused by hydrogen peroxide generated during aerobic metabolism through bioelectronic reduction of molecular oxygen, the latter being linked to a variety of pathological consequences such as aging, diabetes and cancer [1, 2].

Recently, Schiff base manganese complexes have been of great interest because of the remarkable structural variety and the potential applications of these compounds in magnetochemistry, catalysis and bioinorganic chemistry [3-6]. In the area of bioinorganic chemistry, these complexes are very well studied because these species may be used as synthetic models of the active site of various proteins and enzymes such as catalases [1,2], catechol oxidase [4], superoxide dismutase [7]. The behaviour of these manganese complexes is mainly dependent on the structure and coordination mode of the ligands in addition to the oxidation state of manganese [6].

In this work novel hexadentate Schiff base ligand and its neutral mononuclear and dinuclear complexes containing bridging azide ligands were synthesized and structurally characterized. Molecular geometry, vibrational frequency, ¹H- and ¹³C-NMR chemical shifts, HOMO–LUMO, molecular electrostatic potential (MEP) and potential energy surface (PES) studies

were performed using Density Functional Theory (DFT). The disproportionation of hydrogen peroxide by the complexes (2-4) was also discussed.

2. EXPERIMENTAL

2.1. Materials and Physical Measurements

All chemical reagents and solvents were purchased from Merck or Aldrich and used without further purification. The elemental analyses and metal contents were performed by using on a LECO 932 CHNS analyser and a Perkin Elmer NexION 300D ICP-Mass Spectrometer. The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectrum of the compound was registered using a Perkin Elmer Spectrum 100 FT-IR spectrometer (4000-650 cm⁻¹). ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AVANCE III 400 FT-NMR spectrometer, using CDCl₃ as a solvent and TMS as an internal standard. Melting points were determined using an EZ-Melt melting point apparatus. Magnetic susceptibility measurements were carried out using an Alfa Magnetic Susceptibility Balance at room temperature. The molar conductivities were obtained on a WTW COND 3110 conductivity meter. Thermogravimetric analyses were carried out on a Shimadzu TG DTA 60 thermal analyzer. The experiments were performed in dynamic nitrogen atmosphere (20 mLmin⁻¹) with a heating rate of 10°Cmin⁻¹ in temperature range 20-1000°C

2.2. Synthesis of ligand, HBME (1)

1-(Biphenyl)-2-hydroxyimino-2-chloro-1-ethanone was prepared according to literature [8]. Firstly, 1-(Biphenyl)-2-hydroxyimino-2-chloro-1-ethanone (1.5 mmol; 0.389 g) was dissolved in EtOH (40 mL) and the mixture was cooled to -5°C. Morpholine (3 mmol; 0.26 mL) was dissolved in EtOH (5 mL) and added dropwise to the first solution with cooling. After that period, the reaction mixture was stirred 2 h at the same temperature. Then it was allowed to

stir at ambient temperature for 2 h and diluted 100 mL distilled water. The resulting precipitate was filtered and then recrystallized from ethanol-water (1:4). The product was filtered off, washed with aqueous sodium bicarbonate (1%), distilled water, ethanol and dried on P_2O_5 .

(1): Yellow powder; yield: 88%; m.p.: 125° C. Anal. Calc. for $C_{18}H_{18}N_2O_3$: C, 69.67; H, 5.84; N, 9.03. Found: C, 69.55; H, 5.84; N, 9.00; ¹H-NMR (CDCl₃, ppm): Theo. Calc. 3.44(m, 4H, N-CH₂); 3.79 (m, 4H, O-CH₂); 7.60-8.69 (m, 9H, Ar); 12.04 (s, 1H, NOH). Found: 3.41(m, 4H, CH₂); 3.71 (m, 4H, CH₂); 7.45-8.03 (m, 9H, Ar); 8.49 (s, 1H, NOH); ¹³C-NMR (CDCl₃, ppm): Theo. Calc. 192.12 (CO); 155.67 (C=NOH); 130.97-154.97 C (Arom); 49.40-65.52 ppm C (Aliph). Found: 188.25 (CO); 147.36 (C=NOH); 127.12-146.58 C (Arom); 46.67-48.94 ppm C (Aliph); FT-IR (cm⁻¹): Theo. Calc. 3304 (OH) 3083 (CH arom), 2995, 2875 (CH aliph), 1682 (C=O), 1574 (C=N), 1248 (C-O), 989 (NOH) Found: 3278 b (OH) 3047 w (CH arom), 2959, 2858 w (CH aliph), 1661s (C=O), 1598 s (C=N), 1264 m (C-O), 981 s (NOH) (b, broad; s, strong; m, medium; w, weak).

2.3. Synthesis of complexes, (2-4)

Caution: Although no problems were encountered in the present work, perchlorates are potentially explosive and should be treated in small quantities with care.

Synthesis of $[Mn(BME)_2 tren)]$ (2)

A methanolic solution (30 mL) of HBME (2 mmol, 620 mg) was added dropwise to a methanolic solution (10 mL) of triethylenetetramine (1 mmol, 0.15 mL). The yellowish mixture was stirred at reflux temperature for 2 h. Then, a solution of $Mn(CIO_4)_2.6H_2O$ (1 mmol, 360 mg) in methanol (10 mL) was added to the mixture and stirring was continued for

another 1 h and filtered. The powder product was washed with distilled water, ethanol and dried on P_2O_5 .

(2): Black-brown powder; yield: 45%; m.p.: 189°C. Anal. Calc. for $C_{42}H_{48}N_8O_4Mn$: C, 64.36; H, 6.16; N, 14.29; Mn, 7.00. Found: C, 64.00; H, 5.89; N, 14.00; Mn, 6.50. Λ_M (DMF solution, Ω^{-1} cm² mol⁻¹): 15; μ_{eff} =5.55 B.M.; FT-IR (cm⁻¹): 3309 b (NH) 3027 w (CH arom), 2918 w (CH aliph), 1584 s (C=N), 1277 m (C–O), 1021 s (NOH).

Synthesis of $[Mn_2(BME)_2 tren(N_3)_2]$ (3)

A methanolic solution (30 mL) of HBME (2 mmol, 620 mg) was added dropwise to a methanolic solution (10 mL) of triethylenetetramine (1 mmol, 0,15 mL). The yellowish mixture was stirred at reflux temperature for 2 h. Then, a solution of $Mn(CIO_4)_2.6H_2O$ (2 mmol, 720 mg) in methanol (10 mL) was added to the mixture. After 2 h of stirring, NaN₃ (2 mmol, 130 mg) dissolved in distilled water (2 mL) was added dropwise, and the mixture turned black. After 2 h of stirring, the precipitate was filtered, the powder product was washed with distilled water, ethanol and dried on P_2O_5 .

(3): Brown powder; yield: 48%; m.p.: 285°C. Anal. Calc. for $C_{42}H_{48}N_{14}O_4Mn_2$: C, 54.71; H, 5.24; N, 21.26; Mn, 11.91. Found: C, 54.12; H, 4.97; N, 21.00; Mn, 11.61. Λ_M (DMF solution, Ω^{-1} cm² mol⁻¹): 6.2; μ_{eff} =6.36 B.M.; FT-IR (cm⁻¹): 3278 b (NH) 3024 w (CH arom), 2961 w (CH aliph), 2057 s (N₃), 1587 m (C=N), 1270 m (C–O), 1021 m (NOH).

Synthesis of $[Mn_2(BME)_2 tren(N_3)_4]$ (4)

Complex (4) was prepared by addition dropwise of a methanolic solution (10 mL) of triethylenetetramine (1 mmol, 0,15 mL) in methanolic solution (30 mL) of HBME (2 mmol,

620 mg). The resulting mixture was stirred at reflux temperature for 2 h. Then, a solution of $Mn(CH_3COO)_3.2H_2O$ (2 mmol, 536 mg) in methanol (15 mL) was added to the mixture. After 2 h of stirring, NaN₃ (4 mmol, 260 mg) dissolved in distilled water (2 mL) was added dropwise. After 2 h of stirring, the precipitate was filtered, the powder product was washed with distilled water, ethanol and dried on P₂O₅.

(4): Brown powder; yield: 40%; m.p.: 260°C. Anal. Calc. for $C_{42}H_{48}N_{20}O_4Mn_2$: C, 50.14; H, 4.80; N, 27.84; Mn, 10.92. Found: C, 50.04; H, 4.00; N, 27.50; Mn, 10.48. Λ_M (DMF solution, Ω^{-1} cm² mol⁻¹): 6.6; μ_{eff} =4.31 B.M.; FT-IR (cm⁻¹): 3239 b (NH) 3031 w (CH arom), 2930 w (CH aliph), 2050 s (N₃), 1587 m (C=N), 1268 m (C–O), 1020 m (NOH).

2.4. Computational Studies

All calculations were performed using the Gaussian 09 program [9]. Visualizations were done with the GaussView 5.0.9 program [10]. Geometry optimization and frequency calculations were performed using Becke's B3LYP [11-13] function, which consists of a three-parameter exchange function (B3) and a Lee-Yang-Parr correlation function (LYP) with 6-311G(d,p) basis set. In order to prevent the systematic errors the computed vibrational wavenumbers were scaled as 0.9682 for frequencies higher than 1700 cm⁻¹ and 1.0119 for frequencies less than 1700 cm⁻¹ for B3LYP/6-311G(d,p) basis set [14]. Molecular structural calculations of the complexes (**2-4**) were performed in gas phase at DFT/B3LYP level with LanL2DZ basis set which stands for "Los Alamos National Laboratory 2-Double–Z' [15,16]. Electronic properties and HOMO-LUMO orbitals of the HBME and its metal complexes were studied using TD-DFT/B3PW91 with same basis sets. ¹H- and ¹³C-NMR chemical shift calculations were performed using the GIAO method [17-19].

2.5. Studies on Catalase-like Function

The catalytic activities of ligand (1) and its complexes (2-4) towards the disproportionation of hydrogen peroxide were investigated by measuring the volume of evolved oxygen during the course of the reaction [20]. Volumetric measurements of evolved dioxygen during the reactions of the compounds with H_2O_2 were carried out as follows: A 50 mL three-necked round-bottom flask containing a suspension of the complexes (0.005 mmol solid sample) in DMF (10 mL) was placed in a water bath (25°C). One of the necks was connected to a burette and the others were stoppered by a rubber septum. While the solution was stirring, H_2O_2 (1.33 mmol, 0.150 mL) was injected into it through the rubber septum using a microsyringe. Volumes of evolved dioxygen were measured at 1 min time intervals by volumometry. In cases where 1-methylimidazole (50 mg) was added this was introduced into the reaction vessel before the addition of H_2O_2 (in the absence of the 1-methylimidazole the complexes were either inactive or very weak catalysts for this reaction).

3. RESULTS AND DISCUSSION

1-(Biphenyl)-2-hydroxyimino-2-(morpholino)-1-ethanone (HBME) ligand was Novel synthesized in three steps. The synthetic plan for the synthesis of the HBME is given in Scheme 1. Mono and dinuclear manganese complexes were prepared by reaction of HBME triethylenetetramine (tren), Mn(CIO₄)₂.6H₂O [for complexes (2) and (3)], with Mn(CH₃COO)₃.2H₂O [for complex (4)] and NaN₃. The complexes were insoluble in water and common organic solvents but showed maximum solubility in DMF and DMSO at room temperature. The complexes were thermally stable at least up to about 200°C. Attempts to isolate crystals suitable for X-ray diffraction were unsuccessful. Therefore, elemental analyses, ICP-MS, spectroscopic, molar conductivity, thermal and magnetic susceptibility techniques were employed in order to determine the structural characteristics of the complexes. The analytical data of the complex (2) indicated 1:2 metal-ligand stoichiometry whereas this ratio was 2:2 in (3) and (4) (Figs. 2-4). The values of the molar conductance in10⁻³ M DMF solutions were in the range 6.2-15 ohm⁻¹cm²mol⁻¹, suggesting a nonelectrolytic nature for these complexes [21].



Scheme 1. Synthetic plan for the synthesis of the HBME

3.1. ¹H- and ¹³C-NMR spectra

The ¹H- and ¹³C-NMR data of the ligand (HBME) were recorded in CDCl₃ and used as important evidence for the assigned structures. ¹H- and ¹³C-NMR chemical shift values of the HBME were also calculated at B3LYP/6-311G(d,p) level of theory. The experimental and calculated chemical shifts, expressed in ppm downfield from tetramethylsilane, are given in Experimental section and these NMR spectra are also given in Figs. S1 and S2 comparatively.

The ¹H-NMR spectrum of the HBME showed a singlet at 8.49 ppm assigned for oxime NOH proton. This proton (H27), which was adjacent to two electronegative atoms such as nitrogen and oxygen, was calculated in a slightly lower field (cal. 12.04 ppm) than the experimental result. A multiplet observed in the range 7.45-8.03 ppm may be attributed to the aromatic ring protons [22-24]. The calculated chemical shift values in aromatic rings were observed at the interval 7.60-8.69 ppm. The chemical shifts of N-CH₂ (4H) and O-CH₂ (4H) of the morpholino ring were observed at 3.41/3.44 ppm (exp./cal.) and 3.71/3.79 ppm (exp./cal.), respectively [25-27].

The ¹H-NMR spectral data of the ligand were supported by the ¹³C-NMR spectra. The chemical shift which belongs to the carbonyl carbon atom (C=O) was obtained at 188.25 ppm while shift was observed at 192.12 ppm in theoretical spectrum. The signal for the carbon atom (C=NOH) bonded to the oxime group was observed at 147.36 ppm, which also confirms the structure of the ligand. Calculated value of the oxime carbon atom (C23) by DFT was observed at 155.67 ppm. The chemical shift values for the carbon atoms of the aromatic rings were found as 127.12-146.58/130.97-154.97 ppm (exp./cal.), respectively. In the ¹³C-NMR spectrum of the HBME, the signals between 46.67 and 48.94 46 were attributed to carbon atoms of the heterocyclic morpholino ring which were calculated as 49.40-65.52 ppm. All the

protons and carbons were found to be in their expected regions and in good agreement with values previously reported [22,24,27,28]. The results strongly suggest that the proposed oxime ligand was formed. Because of the paramagnetic nature of the complexes, their ¹H and ¹³C NMR spectra could not be obtained.

3.2. FT-IR spectra

The experimental and simulated at B3LYP/6-311G(d,p) IR spectra of the HBME are presented in Fig. S3. The significant wavenumbers obtained from these spectra are given in Experimental section. The IR spectra of the free ligand and their complexes exhibited various bands in the 4000-650 cm⁻¹ region. The FT-IR spectrum of the oxime ligand showed medium band at 3278 cm⁻¹, assignable to v(OH) of oxime group; the broad nature of these bands and their low wavenumbers suggested the presence of hydrogen bonding [29]. The corresponding calculated value was 3304 cm⁻¹ which was quite consistent with the experimental value. The C=O vibrations for the ligand was observed as sharp band at 1661 cm⁻¹. The same vibration appears in the theoretical calculations at 1682 cm⁻¹. In the IR spectrum of the ligand, the stretching vibration of C=N was observed at 1598 cm⁻¹ [30-32] and the stretching vibration of N-O was observed at 981 cm⁻¹ as reported for similar ligands [33-35]. Their calculated wavenumbers were found as 1574 and 989 cm⁻¹, respectively.

The IR spectra of the HBME (1) and its metal complexes (2-4) provided information about the metal-ligand bonding. The broad stretching bands due to the -OH group of the free ligand did not appear in the IR spectra of the complexes. This means that the Schiff base was deprotonated and act as dianionic ligand. The v(N-O) stretching frequencies were shifted to $1020-1021 \text{ cm}^{-1}$ in the complexes. In addition, the bands observed in the 3209-3279 cm⁻¹

range of the complexes were due to the stretching vibrations of the N-H bond in the triethylenetetramine group of the structure.

The strong band occurred at 1661 cm⁻¹ resulting from the streching vibration of the C=O bond in the HBME ligand was disappeared with the addition of triethylentetraamine. Instead of this band, v(C=N) of Schiff base were observed in the 1584-1587 cm⁻¹ range. The presence of streching vibrations of the C=N bond in the spectra of the complexes showed that triethylenetetramine was bound to the ligand and the condensation reaction was completed. While the peaks belonging to N₃⁻ group were observed between 2050-2064 cm⁻¹ in the complexes (**3**) and (**4**), no peaks were observed in the FT-IR spectrum of complex (**2**) in this region [36,37]. The experimental and theoretical wavenumbers of N-O bond in the oxime group of the HMBE were found to be 981 and 989 cm⁻¹, respectively. The experimentally observed band was shifted to high value after the formation of the complex. This showed that the N-O group of oxime group also participated in the coordination [38-40].

When the FT-IR spectra of the ligand and its metal complexes were evaluated, the disappearance of some bands, the appearance of new bands and the shifting of the bands showed that the HBME ligand was synthesized and Mn(II) and Mn(III) ions participated coordination with the ligand. In addition, the data obtained from the spectra of the compounds were found to be consistent with the values of similar compounds in the literature [36-42].

3.3. Magnetic studies

The room temperature magnetic moments of the complexes showed that all of the complexes were paramagnetic. Measurements on the complex (2) revealed a room temperature magnetic moment of 5.55 B.M., which was compatible with a high-spin d^5 system. Such behavior is

typical of this class of compound. The measured magnetic moments of the dinuclear manganese(II) (3) and manganese(III) (4) complex was found to be as 6.36 and 4.31 B.M., respectively. Magnetic susceptibility measurements showed that these complexes were five and four-electron paramagnetics, which corresponds to the +2 and +3 oxidation states of manganese (high-spin d^5 and d^4) in these complexes. This values were in agreement with a spin value of 5.91 and 4.90 B.M. for the Mn(II) and Mn(III) complexes, respectively [43-45].

3.4. Thermal studies

In thermogravimetric analyses (TGA) the change in weight of a complex was recorded as a function of temperature during heating. The TGA curve was also supported by the derivative thermogravimetry (DTG) curves. All the complexes showed a gradual mass loss indicating decomposition by fragmentation with an increase in temperature (Figs. 1,S4,S5). The complexes were decomposing in a gradual manner rather than with the observed sharp decomposition above 230°C, which may be due to fragmentation and thermal degradation of the organic moiety. Dinuclear manganese complexes showed residues not conforming to the corresponding a metallic residue such as metal oxides or metallic manganese, even at 1000°C, indicating that the decomposition of the organic moiety remains incomplete even at this temperature. In the case of the mononuclear Mn(II) complex, the molecule showed mass loss in a gradual manner above 254°C. The continuous loss of weight was observed up to 665-900°C; after that the weight of the product of the complex was remained constant. The final weight losses in these cases were agreed with the formation of the respective MnO₂ (Fig. 1).



Figure 1. 4. TGA thermogram of complex (2) at a scanning rate of 10 °Cmin⁻¹.



Figure 2. Proposed structure of the [Mn(BME)₂tren)] (2) complex



Figure 3. Proposed structure of the $[Mn_2(BME)_2tren(N_3)_2]$ (3) complex



Figure 4. Proposed structure of the [Mn₂(BME)₂tren(N₃)₄] (4) complex

3.5. Computational Studies

3.5.1. Geometry Optimization

Geometry optimization of the HBME was performed using B3LYP functional with 6-311G(d,p) basis set in gas phase. The optimized and numbered geometry of the HBME is shown in Fig. 5. Selected calculated bond lengths, bond angles and dihedral angles are given in Table 1. The calculated bond length of C1-C2 in the benzene ring was 1.391 A° . The C5-C12 (1.483 A°) bond between the two benzene rings in biphenyl was observed longer than the carbon-carbon bond in the aromatic rings. The lengths of the C15-C22 bond between the biphenyl-carbonyl groups and C22-C23 bond between carbonyl-oxime groups were found to be 1.490 A° and 1.504 A°, respectively, which were in agreement with the lengths of the single bonds. The C23-N24 double bond length was calculated to be shorter (1.298 A°) than the single bond as expected.



Figure 5. Optimized geometric structure of the HBME computed at B3LYP/6-311G(d,p) level

If all four neighbouring atoms lie on same plane in a molecule, the dihedral angle is equal to 0° or 180°. The calculated value for the C6-C5-C12-C13 dihedral angle was found as 141.1 A°. This result revealed that two benzene ring in the biphenyl moiety of the HBME weren't lying in the same plane. Furthermore, dihedral angles C22-C23-N28-C29 and C31-O37-C34-C30 were computed as -58.7 A° and -59.3 A°, respectively. The molecular structure of HBME showed that the morpholino ring was deviated from carbonyl and oxime carbon atom planes. On the other hand, it was found that morpholino ring was not in linear geometry.

Table 1. Some selected calculated bond lengths (Å), bond and dihedral angles ($^{\circ}$) for the

HBME (1)					
Bond lengths (Å)					
C1-C2	1.391				
С3-Н9	1.084				
C5-C12	1.483				
C16-C17	1.388				
C16-H18	1.081				
C15-C22	1.490				
C22-O25	1.232				
C22-C23	1.504				
C23-N24	1.298				
N24-O26	1.367				
O26-H27	0.981				
C23-N28	1.404				
C30-C34	1.530				
С29-Н33	1.092				
С34-Н39	1.092				
C31-O37	1.421				
C34-O37	1.429				
Bond angles	5 (⁰)				
C3-C1-C2	120.2				
Н9-С3-С4	120.2				
C2-C5-C6	118.3				
C5-C12-C13	121.0				
C5-C12-C17	121.1				
C13-C12-C17	117.9				
C13-C14-C15	120.8				
C14-C15-C16	118.5				
C16-C15-C22	124.1				
C15-C22-O25	119.4				

HBME computed at B3LYP/6-311G(d,p) level

122.6 120.3 107.5
120.3 107.5
107.5
117.1
110.6
es (°)
-0.2
-179.9
141.1
-0.9
156.2
164.6
15.8
-58.7
87.9
-59.3

The molecular geometries of the complexes (2-4) were also optimized in gas phase using DFT based B3LYP method along with LanL2DZ basis set. The numbering schemes for the (2), (3) and (4) are given in Figs. 6, 7 and 8, respectively. Hydrogen atoms were neglected in order to allow the representation of the complexes to be simple. Some selected calculated bond lengths, bond angles and dihedral angles are also given in Table 2.



Figure 6. Optimized geometric structure of the complex (2) computed at B3LYP/LanL2DZ

level

3

Figure 7. Optimized geometric structure of the complex (3) computed at B3LYP/LanL2DZ

level



Figure 8. Optimized geometric structure of the complex (4) computed at B3LYP/LanL2DZ

level

A slight elongation in C5-C12, C23-N24, C23-N28 bond lengths and a slight shortening in C24-O26 bond length was observed in all three complexes after the coordination was completed. In addition, it was observed that the C23-N24-O26 bond angle of the oxime group increased slightly after the oxygen atom of this group was coordinated with manganese ions. N22 atom was found in the equatorial position while the O54 atom was found in the axial position of the Mn(II) ion in complex (2). The calculations showed that N22-Mn55-O54 and O53-Mn55-N28 bond angles were 89.8 and 171.2°, respectively. The calculated bond length and bond angle values for the metal complex (2) indicated the octahedral geometry around the Mn(II) ion. The four equatorial positions of Mn(II) ion were occupied by amine nitrogen, oxime oxygen and two imine nitrogen atoms, while two axial positions were occupied by amine nitrogen and oxime oxygen atoms.

N22-Mn55-O53, N25-Mn55-N60, N31-Mn56-O54 and N28-Mn56-N60 angles were calculated to be close to 90° degrees in complex (**3**). Mn55 and Mn56 ions were found in distorted square pyramidal coordination and surrounded by five atoms (imine nitrogen, oxime oxygen, amine nitrogen and two azide nitrogen atoms). According to the calculated bond angles around the Mn(II) in complex (**3**), it was found that one of the azide molecule lay in the perpendicular plane. Furthermore, the Mn55-N59-Mn56-N60 dihedral angle of the four-membered ring formed by Mn55 and Mn56 ions and two azide bridges was calculated to be 26.4°. This value showed that the atoms of the four-membered ring deviated slightly from linearity and weren't lay in the same plane.

The complex (4) was six coordinated with slightly distorted pentagonal pyramidal environment around the Mn(III) ions. The Mn(III) was coordinated with amine nitrogen, imine nitrogen, oxime oxygen and three azide nitrogen atoms. Amine nitrogen atom was coordinated perpendicular to the Mn(III), while all other atoms were in the equatorial position of the metal ion. The N22-Mn55-O53 and N31-Mn56-O54 bond angles were calculated as 76.0 and 77.1°, respectively. The N25 and N28 atoms were in the axial positions of the Mn(III) ions and therefore the N25-Mn55-N66 and N28-Mn56-N63 bond angles were calculated to be close to 90°. Furthermore, dihedral angles of N66-Mn55-N60-Mn56, N63-Mn56-N60-Mn55 and Mn55-N59-Mn56-N60 were calculated as 179.6, 179.8 and 0.2°, respectively. This result showed that the four-membered ring composed of two Mn(III) ions and two azide nitrogen atoms was planar and that the ring atoms lay in the same plane.

Table 2. Some selected calculated bond lengths (Å), bond and dihedral angles (°) for the (2),

(2)		(3)		<mark>(4)</mark>		
Bond lengths (Å)						
C1-C2	<mark>1.402</mark>	C1-C2	<mark>1.401</mark>	C1-C2	<mark>1.398</mark>	
C3-C7	<mark>1.499</mark>	C3-C7	<mark>1.492</mark>	C3-C7	<mark>1.482</mark>	
C11-C12	<mark>1.398</mark>	C11-C12	<mark>1.399</mark>	C11-C12	<mark>1.397</mark>	
C10-C13	<mark>1.504</mark>	C10-C13	<mark>1.494</mark>	C10-C13	<mark>1.515</mark>	
C13-C14	<mark>1.473</mark>	C13-C14	<mark>1.483</mark>	C13-C14	<mark>1.482</mark>	
C14-N15	<mark>1.322</mark>	C14-N15	<mark>1.319</mark>	C14-N15	<mark>1.303</mark>	
<mark>N15-O53</mark>	<mark>1.343</mark>	N15-O53	<mark>1.352</mark>	N15-O53	<mark>1.317</mark>	
<mark>C14-N16</mark>	<mark>1.416</mark>	C14-N16	<mark>1.417</mark>	C14-N16	<mark>1.437</mark>	
<mark>N16-C17</mark>	<mark>1.492</mark>	N16-C17	<mark>1.484</mark>	N16-C17	<mark>1.449</mark>	
C17-C18	<mark>1.555</mark>	C17-C18	<mark>1.529</mark>	C17-C18	<mark>1.533</mark>	
C20-O19	<mark>1.455</mark>	C20-O19	<mark>1.457</mark>	C20-O19	<mark>1.409</mark>	
N25-Mn55	<mark>2.133</mark>	N25-Mn55	<mark>1.767</mark>	N25-Mn55	<mark>2.064</mark>	
N28-Mn55	<mark>2.131</mark>	N22-Mn55	<mark>1.949</mark>	N22-Mn55	<mark>2.028</mark>	
N22-Mn55	<mark>2.048</mark>	O53-Mn55	<mark>1.797</mark>	O53-Mn55	<mark>1.926</mark>	
N31-Mn55	<mark>2.036</mark>	<mark>N59-Mn55</mark>	<mark>1.931</mark>	<mark>N59-Mn55</mark>	<mark>2.334</mark>	
<mark>O53-Mn55</mark>	<mark>1.923</mark>	N60-Mn55	<mark>2.010</mark>	N60-Mn55	<mark>1.965</mark>	
<mark>O54-Mn55</mark>	<mark>1.928</mark>	N28-Mn56	<mark>1.794</mark>	N66-Mn55	<mark>1.451</mark>	
		N31-Mn56	<mark>1.965</mark>	<mark>N28-Mn56</mark>	<mark>2.024</mark>	
		O54-Mn56	<mark>1.818</mark>	N31-Mn56	<mark>2.025</mark>	
		N59-Mn56	<mark>1.916</mark>	<mark>O54-Mn56</mark>	<mark>1.931</mark>	
		N60-Mn56	<mark>2.010</mark>	N59-Mn56	<mark>2.362</mark>	
				N60-Mn56	<mark>1.819</mark>	
>				<mark>N63-Mn56</mark>	<mark>1.302</mark>	
Bond angles (°)						
C1-C6-C5	<mark>119.2</mark>	<mark>C1-C6-C5</mark>	<mark>119.0</mark>	<mark>C1-C6-C5</mark>	<mark>120.0</mark>	
C2-C3-C4	<mark>117.2</mark>	<mark>C2-C3-C4</mark>	<mark>117.2</mark>	C2-C3-C4	<mark>118.8</mark>	
<mark>C3-C7-C8</mark>	<mark>121.6</mark>	C3-C7-C8	<mark>121.7</mark>	<mark>C3-C7-C8</mark>	<mark>120.7</mark>	
C3-C7-C12	<mark>121.7</mark>	C3-C7-C12	<mark>121.7</mark>	C3-C7-C12	<mark>120.6</mark>	

(3) and (4) at the B3LYP/LanL2DZ level

C9-C10-C11	<mark>117.4</mark>	C9-C10-C11	<mark>117.8</mark>	C9-C10-C11	<mark>117.5</mark>
C11-C10-C13	<mark>121.6</mark>	C11-C10-C13	<mark>121.5</mark>	C11-C10-C13	<mark>122.3</mark>
C10-C13-C14	<mark>118.4</mark>	C10-C13-C14	<mark>118.7</mark>	C10-C13-C14	<mark>120.4</mark>
C13-C14-N16	<mark>123.9</mark>	C13-C14-N16	<mark>118.1</mark>	C13-C14-N16	<mark>124.1</mark>
C14-N15-O53	<mark>124.8</mark>	C14-N15-O53	<mark>122.6</mark>	C14-N15-O53	123.1
C14-N16-C17	<mark>121.7</mark>	C14-N16-C17	<mark>116.9</mark>	C14-N16-C17	<mark>122.9</mark>
C21-C20-O19	<mark>109.8</mark>	C21-C20-O19	<mark>111.7</mark>	C21-C20-O19	109.2
N22-Mn55-O54	<mark>89.8</mark>	N22-Mn55-O53	<mark>90.9</mark>	N22-Mn55-O53	<mark>76.0</mark>
O53-Mn55-N28	<mark>171.2</mark>	N25-Mn55-N60	<mark>91.3</mark>	N25-Mn55-N66	<mark>93.5</mark>
		N59-Mn55-N60	<mark>79.6</mark>	N59-Mn55-N60	<mark>84.2</mark>
		N59-Mn56-N60	<mark>79.9</mark>	N59-Mn56-N60	<mark>86.2</mark>
		Mn55-N59-Mn56	<mark>97.1</mark>	Mn55-N60-Mn56	<mark>115.4</mark>
		N31-Mn56-O54	<mark>89.2</mark>	Mn55-N59-Mn56	<mark>74.3</mark>
		N28-Mn56-N60	<mark>97.2</mark>	N31-Mn56-O54	<mark>77.1</mark>
				N28-Mn56-N63	<mark>90.6</mark>
		Dihedral angles	(⁰)	L	
C6-C1-C2-C3	<mark>0.6</mark>	C6-C1-C2-C3	<mark>0.1</mark>	C6-C1-C2-C3	0.2
C4-C3-C7-C8	<mark>-170.7</mark>	C4-C3-C7-C8	<mark>168.1</mark>	C4-C3-C7-C8	<mark>-178.2</mark>
C9-C10-C13-N22	121.8	C9-C10-C13-N22	<mark>-123.6</mark>	C9-C10-C13-N22	<mark>154.8</mark>
C11-C10-C13-C14	<mark>141.1</mark>	C11-C10-C13-C14	<mark>-128.8</mark>	C11-C10-C13-C14	<mark>161.1</mark>
C13-C14-N16-C21	<mark>162.7</mark>	C13-C14-N16-C21	<mark>-162.3</mark>	C13-C14-N16-C21	<mark>171.9</mark>
C21-C20-O19-C18	-72.5	C21-C20-O19-C18	<mark>-57.6</mark>	C21-C20-O19-C18	<mark>69.1</mark>
N15-O53-Mn55-N28	154.3	N15-O53-Mn55-N25	<mark>106.1</mark>	N15-O53-Mn55-N25	<mark>-136.8</mark>
N25-Mn55-O54-N46	<mark>159.4</mark>	N46-O54-Mn56-N28	<mark>-99.2</mark>	N46-O54-Mn56-N28	130.8
N22-Mn55-N31-C44	10.8	C23-N22-Mn55-N60	<mark>-5.9</mark>	C24-N25-Mn55-N66	147.2
		C30-N31-Mn56-N60	<mark>-141.6</mark>	C29-N28-Mn56-N63	<mark>-166.4</mark>
¥ ′		Mn55-N59-Mn56-N60	<mark>26.4</mark>	N66-Mn55-N60-Mn56	179.6
				N63-Mn56-N60-Mn55	<mark>179.8</mark>
				Mn55-N59-Mn56-N60	0.2
	1				

3.5.2. Frontier molecular orbital (FMOs) analysis

The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the HBME and its metal complexes (2-4) were calculated in the gaseous phase using B3PW91 method with 6-311G(d,p) and LanL2DZ basis sets, respectively. HOMOs and LUMOs are known as frontier molecular orbitals (FMOs) and appear at the outermost boundaries of electrons in the molecule. In general, HOMO expresses the ability of the molecule to electron-donate, while LUMO relates to the ability of the molecule to accept electrons. The energy gap between HOMO and LUMO is an important parameter for determining the chemical stability of a molecule. Molecular orbital surfaces and energy levels for the HOMO and LUMO of the HBME and complexes (2-4) are shown in Figs. 9-12.



E(HOMO) = -5.841 eV





E(HOMO) = -4.713 eV



computed at DFT/B3PW91/LanL2DZ level



Figure 11. Molecular orbital surfaces and energy levels for the HOMO and LUMO of the (3)

computed at DFT/B3PW91/LanL2DZ level



Figure 12. Molecular orbital surfaces and energy levels for the HOMO and LUMO of the (4) computed at DFT/B3PW91/LanL2DZ level

As seen from the Fig. 9, the HOMO of the HBME molecule was mainly localized on the morpholino ring, while the LUMO was accumulated on the biphenyl moiety. This showed that the transfer of electron density in the molecule was essentially from the morpholino ring to the biphenyl side. On the other hand the energy gap between HOMO and LUMO provides important information for the estimation of properties such as softness, hardness chemical stability etc. of a molecule. The calculated energy values of HOMO and LUMO were -5.841 and -2.701 eV, respectively.

Hard molecules have a large HOMO-LUMO gap, and soft molecules have a small HOMO-LUMO gap. If electron transfer or rearrangement is necessary for the reaction, soft molecules are more reactive than hard molecules [46]. HOMO-LUMO energy gap for HBME was found to be 3.140 eV. This calculated energy gap was smaller compared to similar oxime type compounds in the literature [47-50]. This energy gap means that the HBME molecule can be active in chemical and biological processes.

On the other hand, the calculated HOMO-LUMO gap values were found to be 1.746, 1.630 and 1.083 eV for the complexes (2), (3) and (4), respectively. The HOMO-LUMO gaps of the complexes (2-4) were calculated to be smaller than the HBME ligand. The smaller the HOMO-LUMO energy gap, the more easily the electrons are excited from the ground to the excited state, and this gap closely affects the chemical and biological activity and conductivity of molecules. The calculated HOMO-LUMO gap values of the metal complexes were different in the order of (4) < (3) < (2). This result means that the complex (4) has the potential to be more active in chemical and biological areas and better semiconductor than the complexes (2) and (3).

3.5.3. Molecular electrostatic potential (MEP) surface

The MEP surface was used to estimate the reactive behavior of the synthesized HBME molecule. The MEP diagram provides information on how the charge distribution is in the molecule, and also helps to predict regions for the possible nucleophilic and electrophilic attack. The MEP surface of the HBME was calculated using B3LYP/6-311-G(d,p) level of theory and given in Fig. 13. The red area in the diagram shows the region rich in electrons and is more predispositions to electrophilic attack. On the other hand, the blue color zone represents the electron-poor region and is susceptible to nucleophilic attack. The green colored zone corresponds to the charge potential between the red and blue regions [51].



Figure 13. 3D Molecular electrostatic potential surface of the HBME computed at B3LYP/6-311G(d,p) level

The electronically richest region was found to be the O26 atom in the oxime group from the MEP surface of the HBME molecule. The negative charge density at this oxygen atom also supported the reason why the ligand was participated the coordination through the oxime oxygen atom. The H27 atom bound to the electronegativity high oxygen atom (O26) was more readily ionizable from the ligand and the ligand can more strongly attacked the metal ions with the oxime oxygen atom. Although not as much as on the O26 atom, there was also a negative charge density on the O37 atom in the morpholino ring. A green color was observed at the biphenyl structure and there were no significant negative or positive charges. This was due to the presence of a resonance effect in the benzene rings of the biphenyl structure and thus the dispersion of the charge in the aromatic rings.

3.5.4. Conformer analysis

We carried out the potential energy surface analysis of the HBME on the rotations of C15-C22-C23-N28 and C22-C23-N28-C30 dihedral angles, scanning from -180° to 180° in steps of 10°. Potential energy surface diagram was calculated by DFT calculations using 6-311G(d,p) basis set (Fig. 14). The most stable conformer (C1) was computed with the energy of -1031.5682 a.u. (-28070.414 eV). C15-C22-C23-N28 and C22-C23-N28-C30 dihedral angles for this conformer was found to be -113.89° and 164.66°, respectively. The energy of the most unstable conformer (C2) of the HBME molecule was found to be -1031.5348 a.u. (-28069.505 eV). In this conformer C15-C22-C23-N28 dihedral angle was found to be -6.10°, while the C22-C23-N28-C30 dihedral angle was computed as 4.66°. It was observed that the HBME was more unstable when the oxime and carbonyl group were in the same direction in the HBME molecule. The O25-C22-C23-N24 dihedral angle between the oxime and the carbonyl group was calculated as -12.11°. The morpholino ring and biphenyl group, both of which had a bulky structure, were closer to each other in this conformation and this made the structure more unstable. However, in the C1 conformer of the HBME, the O25-C22-C23-N24 dihedral angle was calculated as 109.12°, which reduced the steric effect between biphenyl and morpholine moieties and made the molecule more stable.



Figure 14. Potential energy surface of the HBME computed at B3LYP/6-311G(d,p) level

3.6. Catalase-like Activity

The effects of the oxime ligand (1) and its metal complexes (2–4) to dispropotionate H_2O_2 into H_2O and O_2 was examined in N,N-dimethylformamide at ambient temperature. The catalytic activities of the synthesized molecules (1-4) were investigated in the presence and absence of the base 1-methylimidazole by measuring the pressure of evolved oxygen during the course of the reaction. Because none of the compounds exhibited catalytic activity on their own. All the complexes displayed catalytic ability for the disproportionation of H_2O_2 in the presence of 1-methylimidazole but the activity of dinuclear complexes (3, 4) were relatively higher than the other compounds.



Figure 15. The time course of the O₂ evolution of for the compounds in the presence 1methylimidazole

The time course of the O_2 evolution of for the compounds in the presence 1-methylimidazole is shown in Fig. 15. The H₂O₂ disproportionate efficiency of the complexes in the presence 1methylimidazole according to the total number of molecules of H₂O₂ disproportionated by one molecule follows the order: (**3**) > (**4**) > (**2**) > (**1**). The ligand (**1**) and the mononuclear manganese(II) complex (**2**) were less effective for the catalytic decomposition of when compared to dinuclear complexes (**3**) and (**4**). Furthermore, the reaction rates of the disproportionation reaction were calculated and the obtained values are given in Table 3. The highest rate constant was obtained as 3.55×10^{-3} molL⁻¹s⁻¹ in the disproportionation reaction of hydrogen peroxide. This result showed that (**3**) had the best catalytic activity among the studied complexes.

Compound	Reaction Rate $(molL^{-1}s^{-1})$
1	0.12×10^{-3}
2	1.25×10^{-3}
3	3.55×10^{-3}
4	2.76×10^{-3}

Table 3. Reaction rates of disproportionation reaction of the hydrogen peroxide in thepresence of the (1-4)

In the absence of heterocyclic base, the complexes decomposed hydrogen peroxide slowly but the decomposition of H_2O_2 was enhanced in the presence of a heterocyclic base such as 1methylimidazole because of its strong π -donating ability [52]. On the other hand heterocyclic bases themselves caused only a very slight disproportionation of the peroxide. Thus, the reactivity of dinuclear complexes was greatly enhanced. In the catalytic process the electron transfer occurs between metal ions in the dimer structure such as copper and manganese. The inter-molecular Mn(II)–Mn(II), Mn(III)–Mn(III) coupling are possibly active centers for H_2O_2 dismutation in the dinuclear Mn system [53,54]. As a result of catalase-like activity studies, the present dinuclear manganese(II) and (III) complexes (**3**) and (**4**) have found that a high disproportionation efficiency.

Conclusions

Novel hexadentate Schiff base (HBME) and its manganese complexes of the type $[Mn(BME)_2tren)]$ (2), $[Mn_2(BME)_2tren(N_3)_2]$ (3) and $[Mn_2(BME)_2tren(N_3)_4]$ (4) were synthesized and characterized by elemental analysis, ICP-MS, FT-IR, ¹H- and ¹³C-NMR, thermal analyses, magnetic susceptibility and molar conductivity measurements. The conductance data indicated that these complexes were non-electrolytes. The thermal degradation of the (2) was carried out in three steps, resulting in the remaining MnO₂ solid. Two consecutive steps were observed in the decomposition of (3) and (4) and the

decompositions of these complexes were still continuing even at 1000 °C. The theoretical calculations for the HBME ligand and complexes (2-4) were performed using DFT method with B3LYP/6-311G(d,p) and B3LYP/LanL2DZ levels, respectively. Comparative study of experimental ¹H- and ¹³C-NMR spectra of the HBME with theoretical ones showed good correlation. The scaled wavenumbers were found to be in good agreement with the experimental wavenumbers. Furthermore, catalytic activities of the (1-4) for the disproportionation of H₂O₂ (catalase-like activity) were investigated and it was found that (3) and (4) were more active compared to (1) and (2).

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- Novel Schiff base ligand and its mono- and dinuclear manganese complexes were synthesized and characterized
- The molecular structure parameters and spectroscopic properties were calculated using DFT/B3LYP and DFT/B3PW91 methods
- HOMO, LUMO and PES analyses were performed
- Catalase-like enzymatic activities of the complexes were studied