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Structural investigation of the catalytic activity of Fe(III) and Mn(III) Schiff base complexes



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ABSTRACT

Two novel manganese (III) and iron (III) complexes of an *N*,*N*-bis(1-naphthalidimine)-*o* phenylene diamine ligand have been successfully synthesized and characterized by various analytical techniques including single crystal X-ray structure analysis. The ligand crystallizes in the monoclinic system with space group P_{2_1}/c . The detailed analyses of Hirschfeld surface and fingerprint plots provide insight into the nature of non-covalent interactions in the ligand. Experimental data have been complemented and interpreted in the light of Density Functional Theory calculation was performed using the B3LYP method concerning molecular geometries, vibrational frequencies and electrochemical potentials. Cyclic voltammetry in dimethylformamide revealed reversible redox processes in both complexes, suggesting possible catalytic reactivity involving electron transfer process for these complexes. The catalytic efficiency and selectivity of manganese (III) and iron (III) complexes was tested in the oxidation of cyclohexene with molecular oxygen. The results show that the catalytic performance depends on the nature of metal, the most efficient catalyst in the presence of O₂beingthe iron (III) complex. A plausible mechanism for cyclohexene oxidation by complexes is proposed and discussed hereafter.

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1. Introduction

Schiff base ligands are well known for coordinating many elements and stabilizing these in various oxidation states. Schiff bases have been used in the preparation of many potential drugs and possess a broad spectrum of biological activities [1–3] and previous reports have established that after complexation of transition metal ions the antimicrobial activity was generally increased [4]. Amidst ligand for transition metals, pincer ligands play an important role and their complexes have attracted tremendous interest due to their high stability, activity and versatility [5].

The chemistry of iron and manganese complexes has been widely investigated due to their involvement in a variety of biological redox systems including peroxidases [6], catalases [7], superoxide dismutases [8], dioxygenases [9] and lipoxidases [10]. Manganese and iron chelate complexes are attractive because of their potential use as catalysts in oxidation reactions [11]. Hence, they are effective catalysts in alkanes [12] amines [13], alcohols [14] and sulfides [15] oxidation and electron transfer in a range

* Corresponding author. E-mail address: kamel_ouari@univ-setif.dz (K. Ouari). of metabolic reactions [16], electrochemical sensors and electroluminescent devices [17] or novel magnetic molecular materials [18].

Iron (III) and manganese(III) complexes, by comparison to other transition metal ions, are usually considered as the most important representative class of complexes exhibiting catalytic and electrocatalytic activity in the epoxidation of alkenes [19–21]. For both metals, the generally accepted catalytically active species for the epoxidation reactions with different substrates and oxygen atom donors are metal-oxo species.

Oxidation reactions are critical to numerous chemical transformations, and thus the development of oxidation reactions that rely on renewable and environmentally friendly oxidants is a concern for all areas of chemistry [22,23]. Indeed, molecular oxygen is an ideal oxidant in many ways as the only byproduct of its reduction is water. Dioxygen is non-toxic under most conditions, and its reduction potential is more than sufficient to drive many chemical transformations [24–27]. The coordination of O_2 to a transition metal center also facilitates oxygen transport and storage in living organisms [28–30]. One of the first discovered dioxygen activating heme enzymes, cytochrome P-450 [31], has provided many clues about the catalytic cycles of dioxygen activation and oxygen



transfer reactions. Design of metal catalysts to mimic bio-oxidative activity of cytochrome P-450 has continued to be an active area of research [32].

Hereafter, we report on the synthesis and characterization of iron(III) and manganese(III) complexes containing *N*,*N*-bis(1-naph-thalidimine)-*o*-phenylenediamine ligand as well as their applications in the catalytic oxidation of cyclohexene by molecular oxygen. The experimental characterization can be correlated and explained with DFT calculation as well as the origin of the electron transfers observed by cyclic voltammetry.

2. Experimental

2.1. Materials and measurements

The melting points for the ligand LH₂ and its complexes of LFe (III)Cl and LMn(III)Cl were determined with a Kofler Bench 7779 apparatus. Infrared spectra were recorded using KBr pellets on a Shimadzu FTIR IRAffinity-1 spectrophotometer. Electronic spectra were measured on a ShimadzuUV-1800 double-beam spectrophotometer using DMF as solvent. Elemental analyses were carried out on an Elementar-Vario EL III CHNSO analyser.¹HNMR spectra were recorded on a Bruker Advance 500 MHz spectrometer usingDMSO-d₆ as solvent and tetramethylsilane (TMS) as internal standard. Mass spectrum of the ligand LH₂is obtained on a Bruker Daltonics Flex Analysis spectrometer with MALDI-TOF procedure using dithranol as a matrix. The molar conductivities of the compounds were carried out on conductivitymeter MeterLab CDM-210 apparatus.

The electrochemical properties of the structures were investigated at room temperature in DMF solutions containing tetra-*n*butyl ammonium perchlorate (TBAP), 0.1 M, as supporting electrolyte. A classical three electrodes cell was used with glassy carbon (GC) working electrode (WE), a platinum counter electrode and a saturated calomel electrode (SCE) reference electrode. All potential values are given versus SCE and the ligand and complexes solutions were 10^{-3} M and the scan rate used in all the voltammograms was set to 100 mV s⁻¹.

2.2. X-ray crystallography

Single crystals of LH₂ ligand were grown by slow evaporation of DMSO solution at room temperature. The crystals were placed in oil and a red prism single crystal of dimensions $0.40 \times 0.38 \times 0.28 \text{ mm}^3$ was selected.

X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-K α radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software) [33] from reflections taken from tree sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-97 [34]. The refinement and all further calculations were carried out using SHELXL-97 [35]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F². A semi-empirical absorption correction was applied using SADABS in APEX2 [36]; transmission factors: T_{min}/T_{max} = 2.69/28.01.

2.3. Quantum chemical calculations

The Theoretical calculations were performed using the Gaussian 09 W program, based on Density Functional Theory (DFT) [37] with Beck's three parameters hybrid functional exchange [38], with 6-

31G (d. p) basis sets, and Lee-Yang-Parr correlation functional (B3LYP) [39,40].

2.4. Hirshfeld surface analysis

The Hirshfeld Surface (HS) and a 2D fingerprint scatter plots for LH₂were obtained using the Crystal Explorer 17.5 package [41]. The normalized contact distance (d_{norm}) based on both d_e and d_i (where d_e is distance from a point on the surface to the nearest nucleus outside the surface and d_i s distance from a point on the surface to the nearest nucleus inside the surface) and the vdW radii of the atom. Graphical plots of the molecular Hirshfeld surfaces mapped with d_{norm} used a red-white-blue color scheme; where red show shorter contacts, white constitute the contact around vdW separation and blue depict longer contacts.

2.5. General procedure of the oxidation reaction

In a typical experiment, 10 mmol of the manganese and iron catalysts were dissolved in 10 mL of DMF and 10 mmol of cyclohexene in the presence of molecular oxygen (O_2), the reaction is carried out under bubbling with a needle introduced into the mixture. The reaction mixture was refluxed while being stirred for 6 h.

A blank experiment in the absence of the complex was performed and no oxidation products were observed. In gas chromatography, the retention times for the starting materials and the products were determined by comparison with authentic samples. The conversion percentiles (%) are calculated by the following equation, in which $C_{initial}$ and C_{final} are initial and final concentration of the substrate, respectively.

%Conversion = $100(C_{initial} - C_{final})/C_{initial}$

2.6. Synthesis

2.6.1. Synthesis of the ligand LH₂

The ligand was prepared by adapting literature methods [42,43]. A mixture of 0.5 mmol(0.054 g) of 1,2-diaminobenzene and 1 mmol (0.172 g) of 2-hydroxy-1-naphthaldehyde, in 10 mL of methanol was refluxed with constant stirring under nitrogen atmosphere for 3 h to yield an abundant orange precipitate that was collected by filtration. The precipitate was washed successively with methanol (3 \times 6 mL) and diethyl ether (3 x6 mL), recrystallized from DMSO-Ethanol and dried under vacuum overnight. Crystals suitable for X-ray analysis were obtained by slow evaporation of DMSO. The Schiff base ligand was characterized by elemental analysis and spectroscopic methods. Yield: 67%, mp: 221 °C. $\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1})$ = 11.98.Analysis calculated:C₂₈-H₂₀O₂N₂.0.5MeOH:C, 79.15; H, 5.13; N, 6.48%; found: C, 78.47; H, 5.14; N, 6.29%. Selected IR data (KBr pellets, σ cm⁻¹): 3440 (O–H), 1616 (C=N), 1537 (C=C), 1179(C–O); UV–Vis: DMF, λ nm, [ε M⁻¹ cm⁻¹]: 269[11300], 316[9650], 350[8130], 364[7880], 410[4580]; ¹HNMR (DMSO *d*₆, δ ppm): 9.69 (s, CH=N), 7.05-8.55 (m, Ar-H); ¹³CNMR (DMSO *d*₆, δ ppm): 157 (C=N), 169 (C-O), 100-150 (C-Ar); MS (MALDI-TOF, dithranol): [MH]⁺ = 417.16 (Scheme 1).

2.6.2. Synthesis of the complexes

2.6.2.1. Synthesis of LFe(III)Cl. Title complex were obtained by the general procedure given in the following literature methods [44,45]. FeCl₂·4H₂O0.5 mmol (0.099 g) were dissolved in methanol 5 mL was added to a 5 mL methanol solution containing LH₂ 0.5 mmol (0.208 g). The mixture was refluxed and stirred for 2 h under nitrogen atmosphere. A brown compound precipitated out, washed with methanol and diethyl ether, and then recrystallized



Scheme 1. Synthesis of the ligand (LH₂) and the corresponding complexes.

from DMSO/methanol. Yield: 78%; mp > 300 °C. $\Lambda(\Omega^{-1} \text{ cm}^2 \text{-} \text{mole}^{-1})$ = 11.67. Analysis calculated for C₂₈H₁₈O₂N₂Fe·H₂O: C, 68.87; H, 4.13; N, 5.74. Found: C, 68.98; H, 4.30; N, 5.59%; IR (KBr pellets, σ cm⁻¹): 3452 (O–H), 1598 (C=N), 1535(C=C), 1187 (C–O); UV–Vis: DMF, λ nm, [ϵ M⁻¹ cm⁻¹]: 266[3750], 341 [2770], 409[1790], 476[1240].

2.6.2.2. Synthesis of LMn(III)Cl. To a 5 mL methanolic solution of MnCl₂0.5 mmol (0.063 g,), a methanolic solution of the ligand LH₂ 0.5 mmol (0.208 g) was added dropwise. The mixture was refluxed and stirred for 2 h under nitrogen atmosphere and then filtered. The precipitate, washed with methanol and diethyl ether, was re-crystallized from DMF-methanol. Yield: 70%; mp > 300 °C. $\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}) = 26.41.\text{Analysis calculated:C}_{28}\text{H}_{18}\text{N}_2\text{O}_2\text{-Mn} \cdot 0.5\text{H}_2\text{O}$: C, 70.30; H, 4.00; N, 5.86. Found: C, 69.79; H, 4.26; N, 5.44%; IR (KBr pellets, $\sigma \text{ cm}^{-1}$): 3439 (O–H), 1607 (C=N), 1536 (C=C), 1181 (C–O); UV–Vis: DMF, $\lambda \text{ nm}$, [$\epsilon \text{ M}^{-1} \text{ cm}^{-1}$]: 270 [5380], 340[4350], 412[2850], 472[2030].

3. Results and discussion

3.1. Elemental analysis and molar conductance

The analytical data are in good agreements with the proposed structures of the Schiff base ligand and their complexes, corroborating the occurrence of a half-molecule of methanol in the LH_2 ligand. However, the complexes show a ligand–metal of stoichiometric ratio of 1:1 affording mononuclear compounds with the presence of a molecule of water and a half one for respectively the LFe(III)Cl and LMn(III)Cl complexes.

The observed molar conductance of the ligand and the complexes in DMF (10^{-3} M) solution are in the range11.67-26.41 Ω^{-1} cm² mol⁻¹, the molar conductance values are non-electrolytic nature for the complexes, the Schiff base ligand is also regarded as a non-electrolyte [46].

3.2. Infrared spectra

The IR spectra of LH_2 and their complexes were analyzed in the region 4000–400 cm⁻¹. The spectra of ligand and complexes display IR absorption bands at 1616 and 1594 cm⁻¹, respectively, which are attributed to C=N transitions of the azomethine moiety [47]. The shift band of the LFe(III)Cl and LMn(III)Cl complexes towards lower wave number indicates coordination of the imine

nitrogen to the metal center [48]. In addition, the stretching vibration of C–O, $v_{C-O/naphtholate}$, appears at 1179 cm⁻¹ in the ligand form, whereas in the complexes LFe(III)Cl and LMn(III)Cl, it is shifted to higher energy by 20 cm⁻¹ suggesting that the metallic center causes an increase of the electronic density in the vicinity of the oxygen. This behavior can be interpreted as a result of coordination of both deprotonated oxygen of naphtolic group to the metal center giving N₂O₂ tetra-coordinated complexes [49]. The DFT calculations strongly corroborate the experimental results and our hypotheses (Table 1).

3.3. Electronic absorption spectra

In the spectrum of the ligand (Fig. 1), the band located at 460 nm is assigned to the $n \rightarrow \pi^*$ transition from the azomethine (CH=N) group [50]. In the spectra of the metal complexes, these $n \rightarrow \pi^*$ transitions, are shifted to lower frequencies indicating that the imine nitrogen atoms are involved in coordination to the metal ion. The bands at higher energies 260 and 310 nm are associated with the aryl $\pi \rightarrow \pi^*$ transitions. The spectra of the complexes show tow intense bands in the high-energy, at 345 and 410 nm, attributed to L \rightarrow M charge transfer bands (MLCT) [51].

3.4. NMR spectra

The ¹H NMR spectrum of the ligand (Fig. 2 (a)) exhibits a multiplet in the region 6.60–8.80 ppm assignable to aromatic protons (CH-Ar) of the benzene and naphthalene ring. The sharp singlet at 9.69ppmis due to azomethine proton (CH=N). The phenolic proton is not observed because of the exchange with the water present in the DMSO d_6 .

The ¹³C NMR spectrum of the ligand is in agreement with the different types of magnetically nonequivalent carbons (Fig. 2(b)). The resonance around 157 ppm can be assigned to the azomethine carbon (-C=N-). The signal observed at 169 ppm corresponds to the naphtholate (-C=O-). The carbon atoms of the benzene and naphthalene ring occurring over a broad range 110–140 ppm.

3.5. Mass spectrometry

The mass spectra of the ligand were recorded in MALDI TOF ionization mode (Fig. 3). The protonated molecular ion peak $[MH]^+$ of the ligand appears at m/z = 417.16, which is in good agreement with the proposed formula.

LH ₂			LFeCl			LMnCl			Assignments
Exp	Calculated		Exp	Calculated		Exp	Calculated		
	Unscaled	Scaled		Unscaled	scaled		Unscaled	scaled	
1616	1630	1581	1598	1553	1506	1607	1677	1626	C=N
1179	1213	1176	1187	1208	1151	1181	1230	1145	С—О
1537	1526	1490	1535	1534	1487	1536	1590	1542	C=C
3440	3116	3336	-	-	-	-	-	-	-OH
-	-	-	493	485	470	556	577	560	M-N
-	-	-	552	551	534	476	445	431	M-O



Selected experimental and theoretical infrared frequencies (cm⁻¹) and their assignments for LH₂, LMnCl and LFeCl.

Fig. 1. Electronic spectra of the ligand and the corresponding complexes in DMF.

3.6. Structural data

The ligand LH₂has been characterized by X-ray diffraction. Its solid state structure matches the optimized theoretical structure obtained by DFT calculation, whereas the molecular structures of LMn(III)Cl and LFe(III)Cl were only obtained by DFT calculations. Fig. 4 summarizes the geometry of the ligand and the calculated geometries of the complexes. Table 2 summarizes the crystal data, the data collection and the structure refinement parameters and Fig. 5shows the unit cell of the ligand LH₂.

The XRD analysis proves that the asymmetric unit of LH_2 ligand (Fig. 4a) is very far from a planar geometry; the two naphthalene moieties and the single aryl belong to three different plans, as shown in Fig. 4b. The angles between the plans are 28.57° , 39.02°

and 41.83°, but the molecule of LMn(III)Cl (Fig. 4c) is less distorted. Fig. 4d shows that the angles between the plans are 14.92° , 27.76° and 42.60° in the case of the LMn(III)Cl complex, a strikingly different situation than in the LFe(III)Cl complex (Fig. 3e) in which planarity with an out of the plane positioning of the Fe is observed (Fig. 4f).

Some characteristic bond distances and angles are listed in Table 3.

EThe LH₂ unit cell is shown in the Fig. 5. The crystal is monoclinic with P21/c space group and the cell parameters are a = 13.353(4) Å, b = 7.561(2) Å, c = 24.350(8)Å and β = 90.959 (10)°. The filling rate of the LH₂ unit cell is about four molecules (Z = 4), the unit cell is characterized by (x y z) identity, an inversion center at the point (000), a glide plane perpendicular to direction [010] with glide component [0 0 ½] and finally 2-fold screw axis with the direction [010] at the points (0 y¼) with screw component [0 ½ 0].

3.7. Hirshfeld surface analysis

The Hirshfeld Surface (HS) demonstrates the intermolecular interactions in the crystalline structures. The Fig. 6 shows the HS of the ligand LH₂mapped over the ranges: $d_{\text{norm}}[-0.1792, 1.2866]$ Å, shape index [-1.0, 1.0] Å and curvedness [-4.0, 0.4] Å.

The red spots correspond to the closer $O \cdots H/H \cdots O$ contacts due to the N—H···O hydrogen bonds. The white areas mark the places where the distance between the neighbouring atoms is close to the sum of the Van derWaals radii of the considered atoms, they indicate H···H interactions. The blue areas illustrate the domain where the neighbouring atoms are farthest apart to interact with each other (Fig. 6 (a)).

Fig. 7a illustrates the 2D fingerprint of the totality contacts contributing to the HS of the LH_2 ligand. The graph shown in Fig. 6b represent the $H \cdots O / O \cdots H$ contacts between the hydrogen atoms located inside the HS and the oxygen atoms located at the external



Fig. 2. NMR spectra of LH₂ligand in DMSO d_6 : (a) ¹HNMR, (b) ¹³CNMR.



Fig. 3. Molecular cluster of the masse spectrum of LH_2 ligand, MALDI-TOF in dithranol.

and reciprocal. It is characterized by two symmetrical points situated at the top and left and at the bottom right in the region 1.07 Å < ($d_e + d_i$) < 2.57 Å, these O···H contacts represent 13.3% of all the intermolecular contacts.

The graph shown in Fig. 7c illustrates the 2D fingerprint associated with the hydrogen atoms ($r_{vdW} = 1.20$ Å). It is characterized by extremity that points to the origin diagonally and corresponding to $d_i \approx d_e \approx 1.2$ Å, which reveals the presence of closer H···H contacts within the LH₂ crystal. They have the largest contribution to the total HS (45.9%). The decomposition of the 2D fingerprint also shows other contacts: C···H (24.9%, Fig. 7d), C–N (2.07%), C–O (0.4%), C–S (0.2%), H–S (0.9%) and H–N (0.3%).

3.8. Experimental hydrogen bonds

The hydroxyl groups are involved in intramolecular O— $H \cdots N$ hydrogen bonds influencing the molecular conformations. The amino hydrogen atom forms the center of intramolecular hydrogen bonds, which includes the N— $H \cdots O$ hydrogen bond of 2.5499(16) Å within the keto amino part. The proton transfer from the hydro-



Fig. 4. Molecular structures (a) asymmetric unit of the ligandLH₂provided by hydrogen bonds (b) optimized structure of LMn(III)Cl (c) optimized structure of LFe(III)Cl.

Data collection and structure refinement parameters.

Compound	LH ₂ .DMSO
Molecular formula	C ₃₀ H ₂₆ N ₂ O ₃ S
Molecular weight (g/mol)	494.59
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.353 (4)
b (Å)	7.561 (2)
c (Å)	24.350 (8)
β(°)	90.959 (10)
V (Å ³)	2458.43(13)
Z	4
D _{calc} (g.cm ⁻³)	1.336
Crystal size (mm ³)	$0.40\times0.38\times0.28$
Crystal description	Prism
Crystal color	Red
Temperature (K)	173(2)
Radiation Mo-Kα1	λ = 0.71073 Å
Absorption coefficient (mm ⁻¹)	0.168
F(000)	1040
Reflections collected/unique	17304/5917
R _{int}	0.0173
Range/indices (h, k, l)	$-16 \rightarrow 17; -9 \rightarrow 9; -32 \rightarrow 32$
Teta _{limit}	1.53 → 28.01
No. of observed data	4939
I > 2Sigma(I)	
No. of variables	328
No. of restraints	0
Goodness of fit on F ²	1.032
R_1 , w R_2 $[I \ge 2$ Sigma (I)] ^a	0.434, 0.1090
R_1 , w R_2 (all data) ^a	0.0543, 0.1196



Fig. 5. Unit cell of the ligand LH₂.

xyl oxygen atom of the parent aromatic aldehyde to the imino nitrogen atom requests a small amount of energy, this proton transfer causes a remarkable conformation changes within the molecule, especially in the π -electron distribution [52].

Table 4 summarizes the intramolecular hydrogen bonds with corresponding donors and acceptors angles and bond lengths.

The planarity within the naphthaldimine part of the molecule is preserved since the pseudo aromatic six membered chilate rings formed by intramolecular hydrogen bonds (H10⁻O1⁻C17⁻C8⁻C7⁻-N1 and O2⁻C28⁻C19⁻C18⁻N2⁻H2N) are almost coplanar with corresponding naphthalene rings (C17 to C8 and C28 to C18). The twisting of the naphthaldimine moiety toward the phenyl ring is described by torsion angles C7⁻N1⁻C1⁻C6 and C18⁻N2⁻C6⁻C1 being 148.23 (1) and 160.2 (1)° respectively.

4. 3D network

The structure of the 3D network of LH₂ ligand is enriched by weak contacts maintaining the stability and the structural cohesion. Fig. 8 shows the 3D network in the views (a) along the *b* axis (b) according to the *a*, *b* plan (c) along the *c* axis. Along the *b* axis, LH₂ molecules form chains in which they are attached by $H \cdots H$

and C···H contacts. In addition, the DMSO molecules play a crucial role in the chain as shown in Fig. 8b. The contact between LH_2 and DMSO molecules is maintained via O···H and C···H links, along the c axis the contact C···C makes the molecules parallel with a distance 7.562 Å, (Fig. 8 (c)).

5. Quantum calculations results

5.1. Molecular electrostatic potential (MEP)

The total electron density surfaces mapped with electrostatic potential for LH_2 , LFe(III)Cl and LMn(III)Cl are shown in Fig. 9, the surface of LH_2 exhibits a positive potential in the most geometric zones, and the most negative potential indicated by a red color is principally centered on the oxygen atoms, those sites can host nucleophilic ions as transition metal ions, a weak negative potential around the cycle indicated by a yellow color can be observed.

Furthermore, the surfaces of LMn(III)Cl and LFe(III)Clare very comparable. The Fe(III) and Mn(III) are coordinated to the oxygen and nitrogen atoms, where as the apical chlorine bears a strong negative charge indicated by a red color, the comparison with the ligand surface, the potentials generated by the cycle are more positive for the both complex molecules. The non-homogeneity of the potential distributions for the three molecules results in different values of the dipolar moment 2.644, 5.471 and 5.796 Debye for LH₂, LMn(III)Cl and LFe(III)Cl respectively.

5.2. Molecular orbitals (MOs)

The molecular orbitals and their relative energies give an important idea on electronic properties and chemical reactions [53]. The Fig. 10 shows the calculated orbitals for LH₂, LMnCl, LFeCl- α channel and LFeCl- β channel. It can be seen that all electrons of various molecular orbitals are almost delocalized on the whole molecular structure except for hydrogen atoms.

The gap energy is defined as the energy difference between the HOMO and LUMO. The calculated energies are 3.17, 2.965, 2.861 and 3.094 eV, for LH₂, LMnCl, LFeCl- α channel and LFeCl- β channel respectively, these high values indicate that the molecules are stable. Other characteristic physicochemical parameters are summarized in Table 5.

6. Electrochemical study

The electrochemical measurements have been carried out, for the ligand LH_2 and the complexes LFe(III)Cl and LMn(III)Cl, in DMF solution, for their high solubility, under nitrogen saturated atmosphere in the potential range 1600 to -2200 mV/SCE at scan rate 100 mV/s. The Fc⁺/Fc, redox couple of ferrocene, was used as an internal standard.

The cyclic voltammogram of the ligand shows irreversible anodic and cathodic peaks (Fig. 11), appearing at $E_{pa1} = -1.6$, $E_{pa2} = 0.9$, $E_{pa3} = 1.2$ V/SCE and at $E_{pc1} = -1.5$, $E_{pc2} = -1.7$ V/SCE respectively. These irreversible waves are attributed to the oxidation of the π bonds of the naphtholate moiety and the benzene ring.

The voltammetric study of LFe(III)Cl complex, in the range 100 to -500 mV/SCE, shows a reversible redox couple at $E_{1/2} = -320 \text{ mV/SCE}$, assignable to the Fe^{III}/Fe^{II} couple [54]. Fig. 12a shows multiple scans that resulted in superposable cyclic voltammograms of the redox couple. Minimal variation is observed for the potential E_p when the scanning speed increases, which is characteristic of a reversible system. A linear relationship is observed between the cathodic and the anodic peak currents and the square root of the scanning speed $(v^{1/2})$ in the range 10 to 100 mV/s (Fig. 12(c)). The value $\Delta E_p = (E_{pa} - E_{pc})$ is 80 mV/SCE

Selected experimental and theoretical bond lengths (Å) and angles values (°).

LH ₂			LMn(III)Cl		LFe(III)Cl	
Selected bonds	X-ray (Å)	Calc. (Å)	Selected bonds	Calc. (Å)	Selected bonds	Calc. (Å)
C1-N1	1.410(17)	1.41	Mn-O1	1.858	Fe-01	1.873
C6-N2	1.409(17)	1.41	Mn-O2	1.826	Fe-O2	1.873
C7-N1	1.298(17)	1.298	Mn-N1	1.898	Fe-N1	1.922
C17-01	1.327(18)	1.328	Mn-N2	2.042	Fe-N2	1.922
C18-N2	1.311(17)	1.311	Mn-Cl	2.208	Fe-Cl	2.284
C28-02	1.290(18)	1.291	01-C17	1.291	01-C17	1.32
			02-C28	1.32	02-C28	1.32
			N1-C7	1.333	N1-C7	1.329
			N2-C18	1.301	N2-C18	1.329
			N1-C1	1.416	N1-C1	1.426
			N2-C6	1.408	N2-C6	1.426
Selected angles	X-ray (°)	Calc. (°)	Selected angles	Calc. (°)	Selected angles	Calc. (°)
C2-C1-N1	122.70(12)	122.66	02-Mn-01	94.2	02-Fe-O1	87.78
C6-C1-N1	120.00(13)	117.52	O1-Mn-N1	94.15	O1-Fe-N1	91.35
C5-C6-N2	122.26(13)	122.26	O1-Mn-N2	172.22	O2-Fe-N1	163.73
C1-C6-N2	117.69(12)	117.69	O2-Mn-N1	132.89	O1-Fe-N2	163.75
N1-C7-C8	121.31(13)	121.31	N1-Mn-N2	80.16	N1-Fe-N2	84.93
01-C17-C8	122.53(13)	122.53	O2-Mn-N2	85.95	O2-Fe-N2	91.35
01-C17-C16	117.18(13)	117.18	N1-Mn-Cl	107.58	N1-Fe-Cl	94.74
N2-C18-C19	122.15(13)	122.15	N2-Mn-Cl	87.19	N2-Fe-Cl	94.73
02-C28-C19	122.81(13)	122.8	O1-Mn-Cl	99.66	O1-Fe-Cl	101.35
02-C28-C27	118.91(14)	118.91	O2-Mn-Cl	116.47	O2-Fe-Cl	101.36
C7-N1-C1	120.95(12)	120.95				
C18-N2-C6	124 23(12)	124 23				



Fig. 6. Hirshfeld surfaces mapped with (a) d_{norm} , (b) shape index and (c) curvedness of LH₂.

and the intensity ratio i_{pa}/i_{pc} is 0.83, these values reveal a reversible redox process, a typical behavior for an electron transfer process controlled by diffusion.

The cyclic voltammetric studies of LMn(III)Cl complex exhibit a reversible redox couple at $E_{1/2} = -115$ mV/SCE corresponding to Mn^{III}/Mn^{II} [55]. These results are consistent with a reversible one-electron reduction of the LMn(III)Cl complex (Fig. 12b). The variation of peak current parameters as a function of scan rate is plotted in Fig. 12c.This is slightly smaller than the corresponding value for the one-electron reduction in LMn(III)Cl complex.

The electrochemical responses of the two LFe(III)Cl and LMn(III) Cl complexes are almost identical which indicate that the electroactive species, in DMF, for the iron and the manganese complexes have probably the same redox character. It is mentioned that a similar process in Fe(III)/Fe(II) has been observed in the iron (III) mononuclear compounds derived from the related Schiff base ligand [56].

Furthermore, the DFT calculation can predict the reduction and oxidation potentials, since the first reduction and oxidation occurs at the HOMO and LUMO and the other oxidation reduction occurs at the other molecular orbitals, generally, a correlation between cyclic voltammetry waves and frontier orbitals energies can be established. The HOMO and LUMO energies of the ligand LH₂ and

both complexes LFe(III)Cl and LMn(III)Cl can be calculated using the oxidation and reduction waves respectively following the empirical relations $E_{HOMO} = -[E_{oxydation}-E_{1/2(ferrocene)} + 4.8]$ eV and $E_{LUMO} = -[E_{reduction}-E_{1/2(ferrocene)} + 4.8]$ eV.

For the ligand, all oxidation and reduction peaks correspond to the removing or addition of electrons from or to the conjugated π system, the potentials are summarized in Table 6, which illustrate that the waves affect the first and the second levels of FMOs. The first oxidation/reduction affects mostly the orbitals around the naphthalene moieties and the second affects the orbitals around the benzene rings in Fig. 10.The comparison of experimental and theoretical values of oxidation and reduction potentials is illustrated in Table 6. Moreover, the experimental and theoretical gap are 2.4, 2.9 and 3.17, 3.94 respectively.

In the LFe(III)Cl complex, the redox couple observed at $E_{1/2} = -0.32$ V corresponds to the addition of an electron in α -LUMO, $E_{LUMO} = -[E_{-0.32}-E_{1/2(ferrocene)} + 4.8] = -3.6$ eV, indicating that the first oxido-reduction event takes place at the metallic center Fe(III) in Fig. 10.

Also, the manganese complex has almost a comparable calculated molecular orbital energies as the ligand, in addition, the theoretical and experimental gaps of the ligand LH₂ and the manganese complex are nearly equal (Table 5), according to the



Fig. 7. (a) Fingerprint plots Full contact, (b) resolved into $0\cdots H$, (c) resolved into $H\cdots H$ and (d) resolved $C\cdots H$ for the ligand LH_2 .

Table 4 Hydrogen-bond geometry (Å, °)of LH₂.

$D - H \cdots A$	D—H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	$D{-}H{\cdots}A$
$\begin{array}{c} N_2 - H_2 N \cdots O_2 \\ O1 - H1 \cdots N1 \end{array}$	0.88	1.84	2.5499(16)	135.7
	0.84	1.79	2.5384(16)	147.6



Fig. 8. 3D network in the views (a) along the b axis (b) according to the b, a plan (c) along the c axis.



Fig. 9. Total electron density map with electrostatic potential of LH₂, LMnCl and LFeCl.



Fig. 10. Frontiers Molecular Orbitals plots.

presentations HOMO, LUMO, HOMO-1 and LUMO + 1 of complex LMn(III)Cl, the orbitals of the metal and of the ligand are overlapped, Fig. 10. Thus DFT calculation corroborates the experimental electrochemical data.

7. Chemical reactivity

The reactivity of our compounds could be discussed mostly on the basis of its electronic orbitals and their energies [57] which clearly control the various steps of the catalytic cycle. The high val-

S. Bendia, R. Bourzami, J. Weiss et al.

Table 5

Calculated HOMO and LUMO energies and some related physicochemical parameters.

Compound	LH ₂	LMnCl	LFeCl-α	LFeCl-β
Electronic band energies				
E _{HOMO} (eV)	-5.200	-5.265	-5.952	-5.756
E _{HOMO-1} (eV)	-5.675	-5.693	-5.962	-6.169
E _{HOMO-2} (eV)	-6.092	-5.856	-6.469	-6.442
E _{LUMO} (eV)	-2.030	-2.300	-3.091	-2.662
E _{LUMO+1} (eV)	-1.737	-2.174	-2.648	-2.507
E _{LUMO+2} (eV)	-0.658	-1.906	-2.295	-2.252
Energy gap (Δ) (eV)	3.17	2.965	2.861	3.094
Electrochemical parameters				
Dipolar moment (Debye)	2.644	5.471	5.796	5.796
Ionization potential (I)	5.20	5.265	5.952	5.756
Electron affinity (A)	2.03	2.30	3.091	2.662
Global hardness (η)	1.585	1.452	1.430	1.547
Global softness (σ)	0.631	0.688	0.699	0.646
Electronegativity (χ)	3.615	3.782	4.521	4.209
Global electrophilicity (ω)	3.491	4.925	7.146	5.725
Chemical potential (µ)	-0.069	-0.066	-0.055	-0.059
Energy gap (Δ) (eV) Electrochemical parameters Dipolar moment (Debye) Ionization potential (I) Electron affinity (A) Global hardness (η) Global softness (σ) Electronegativity (χ) Global electrophilicity (ω) Chemical potential (μ)	3.17 2.644 5.20 2.03 1.585 0.631 3.615 3.491 -0.069	2.965 5.471 5.265 2.30 1.452 0.688 3.782 4.925 -0.066	$\begin{array}{c} 2.861 \\ 5.796 \\ 5.952 \\ 3.091 \\ 1.430 \\ 0.699 \\ 4.521 \\ 7.146 \\ -0.055 \end{array}$	3.094 5.796 5.756 2.662 1.547 0.646 4.209 5.725 -0.059

 $I = -E_{HOMO}, A = -E_{LUMO}, \chi = -[1/2(E_{LUMO} + E_{HOMO})], \eta = 1/2(E_{LUMO} - E_{HOMO}), \omega = \chi^2/2 \eta, \sigma = 1/\eta, \mu = -1/2(A + I).$



Fig. 11. Cyclic voltammogram of LH₂in 0.1 M TBAP/DMF at 100 mV/s.

ues of the respective HOMO energies (E_{HOMO}) –5.265 and –5.952 eV for LMn(III)Cl and LFe(III)Cl complexes reflect a low donor character whereas the low values of the respective LUMO energies (E_{LUMO}) –2.300 and –3.091 eV reflect an acceptor character in chemical transformations. The relatively small gap 2.965 and 2.861 eV implies low kinetic stability and high chemical reactivity [56] and the negative HOMO and LUMO energies indicate that the complexes are globally predisposed to act as reducing agents. Furthermore, the high values of dipolar moment (μ) 5.796 and 5.471 D of the LMn(III)Cl and LFe(III)Cl complexes is an indicator of a high polarity of the covalent bonds correlating with the molecular distribution of electrons [57].

Also, the catalytic rates, for the investigated LM(III)Cl complexes, are linked to the redox potential of the M^{+3}/M^{+2} couple during the catalytic cycle. According to the mechanistic hypothesis, the Lewis acidity of the metal (III) center in the metal (II)-oxo intermediate significantly affects the redox potential of the complexes and, therefore, the degree of the catalytic reactivity [58].

Hence, a relationship between the catalytic properties of the complexes and the redox potentials can be established. Since the electronic effects control the reactivity in the catalytic cycle, cyclic voltammetry is a useful tool to investigate the mechanism of the catalysis and for the understanding of the structure/reactivity relationship in our LM(III)Cl complexes. When the half-wave potential values, $E_{1/2}$, approaching the zero value, the activity of the complexes is appreciable in the aerobic oxidation [59]. Herein, The $E_{1/2}$ values of the complexes LMn(III)Cl and LFe(III)Cl are respectively –115 and –320 mV/SCE, therefore, this would imply that a window of $E_{1/2}$ values exists and these values initially favor the fixation of molecular oxygen by the complexes prior to the start of the effective catalysis.

8. Catalytic reactions

The catalysts LFe(III)Cl and LMn(III)Cl complexes oxidize the cyclohexene molecule in presence of molecular oxygen and give the cyclohexene oxides as 2-cyclohexen-1-one,2-cyclohexen-1-ol and epoxy-cyclohexane (Table 7 and Fig. 13). Both the catalysts



Fig. 12. Cyclic voltammograms in DMF/0.1 M TBAP of (10⁻³ M) (a): LFe(III)Cl, (b):LMn(III)Cl. (c): Plot of cathodic currents vs. the square root of sweep rate (v^{1/2}).

Experimental and calculated potential.

Compound	LH ₂					
	E _{pa1}	E _{pa2}	E _{pa3}	E _{pc1}	E _{pc2}	
Experimental Theoretical	-1.60 /	0.90 0.90	1.20 1.37	-1.50 -2.27	-1.77 -2.56	

Table 7

Catalytic oxidation of cyclohexene with O2 by LFe(III)Cl and LMn(III)Cl complexes.

Catalyseurs	Time (h)	Conversion (%)	Products (%)	Products (%)		
			Epoxy-cyclohexane	2-Cyclohexen-1-ol	2-Cyclohexen-1-one	
LFe(III)Cl	6	96	20	16	64	
LMn(III)Cl	6	97	23	17	60	
Oxidant free	6	-	-	-	-	



Fig. 13. Oxidation of cyclohexene using LFe(III)Cl and LMn(III)Cl catalysts.

are selective to cyclohexen-1-one over the two other oxidation products and this result is revealed by gas chromatography.

From the GC data, it is observed that the LFe(III)Cl and LMn(III) Cl complexes exhibited the highest yield for cyclohexen-1-one, 64 and 60%, respectively. The iron and manganese complexes are included in the family of "best" catalysts for the oxidation of olefins [55]. Thus, screening for oxidation catalysis using molecular oxygen as the terminal oxidant identified the iron and the manganese complex as the oxidation catalysts is worthy of continued development.

The electron-rich cyclohexene has a greater reactivity than the terminal olefins. This reflects the electrophilic nature of the oxygen of the iron-oxo intermediate to the cyclohexene. The proposed mechanism of cyclohexene oxidation catalyzed by the LFe(III)Cl and LMn(III)Cl complexes consists of 3 steps and involves the binding of molecular oxygen and substrate to the iron and manganese



Fig. 14. Formation of different intermediate species during the cyclohexene oxidation.



Fig. 15. Electronic energies of the cyclohexene and their oxides.

complexes (Fig. 14). Cyclohexene is also a very useful model substrate to study catalytic systems involving Fe^{III}/Fe^{II} and Mn^{III}/Mn^{II} system.

Theoretically, the molecular structures of cyclohexene, epoxycyclohexane, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were optimized and the electronic energies of the optimized geometries were estimated, Fig. 15 shows the electronic energies of the cyclohexene and their oxides, the figure shows clearly that the 2-cyclohexene-1-onemolecule is the most stable with the energy -8399,34 eV, this result explains the high selectivity of oxygen for this last, in addition the molecules 2-cyclohexene-1-ol and epoxy-cyclohexane have slightly higher electronic energies about -8326,69 eV and 8330,77 eV respectively which explain the comparable selectivity and their weak selectivity comparatively to 2cyclohexen-1-one, finally, the high conversion can be explained by the high electronic energy of cyclohexene about -6385,15 eV which proves that this molecule is much less stable than his oxide molecules.

9. Conclusion

Iron and manganese complexes of tetradentate N₂O₂ Schiff base ligand have been prepared with high purity and good yield ~70%. Spectroscopic analysis confirmed the composition and the structure of the obtained compounds. The X-ray structural study reveals that the ligand LH₂ crystallizes in the monoclinic system in the presence of a DMSO molecule. The results of HS analysis indicate that the major interactions are found to be H...H interaction with contributions of 45.9% of the total area. The geometry of LH₂ and the vibrational frequencies of all the compounds are confirmed by the DFT calculations. The complexes show reversible redox processes with $E_{1/2(FeIII/FeII)} = -320$ mV/SCE and $E_{1/2(MnIII/MnII)} = -$ -115 mV/SCE by cyclic voltammetry. The corresponding iron and manganese complexes are efficient catalysts in the oxidation reaction of cyclohexene in presence of O₂ and the formation of cyclohexene-1-one is the main product. Among all possible products, cyclohexene-1-one shows the highest stability as suggested by the low energy (-8399,34 eV) ,obtained from DFT calculations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- [1] A.T. Taher, H.H. Georgey, H.I. El-Subbagh, Eur. J. Med. Chem. 47 (2012) 445-451.
- [2] T. Plech, M. Wujec, U. Kosikowska, A. Malm, B. Kapron, Eur. J. Med. Chem. 47 (2012) 580–584.
- [3] P. Zoumpoulakis, C. Camoutsis, G. Pairas, M. Sokovic, J. Glamoclija, C. Potamitis, A. Pitsas, Bioorg. Med. Chem. 20 (2012) 1569–1583.
- [4] A. Tarushi, E. Polatoglou, J. Kljun, I. Turel, G.P. Dimitris, P. Kessissoglou, DaltonTrans. 40 (2011) 9461–9473.
- [5] S. Murugesan, K. Kirchner, Dalton Trans. 45 (2016) 416-439.
- [6] P. Baborova, M. Moder, P. Baldrian, K. Cajthamlova, T. Cajthaml, Res. Microbiol. 157 (2006) 248–253.
- [7] J.W. Whittaker, Arch. Biochem. Biophys. 525 (2012) 111-120.
- [8] F.C. Friedel, D. Lieb, I. Ivanovic-Burmazovic, J. Inorg. Biochem. 109 (2012) 26-32.
- [9] M.W. Vetting, L.P. Eackett, L. Que, J.D. Lipscomb, D.H. Ohlendorf, J. Bacteriol. 186 (2004) 1945.
- [10] E.H. Oliw, Prostaglandins Other Lipid Mediat. 68-9 (2002) 313-323.
- [11] N.S. Venkataramanan, G. Kuppuraj, S. Rajagopal, Coord. Chem. Rev. 249 (2005) 1249–1268.
- [12] J.R. Lindsay-Smith, Y. Iamamoto, F.S. Vinhado, J. Mol. Catal. A: Chem. 252 (2006) 23–30.
- [13] T.C.O. Mac Leod, V. Palaretti, V.P. Barros, A.L. Faria, T.A. Silva, M.D. Assis, Appl. Catal. A: Gen. 361 (2009) 152–159.
- [14] S. Tollari, A. Fumagalli, F. Porta, Inorg. Chim. Acta 247 (1996) 71-74.
- [15] A. Rezaeifard, M. Jafarpour, G.K. Moghaddam, F. Amini, Bioorg. Med. Chem. 15 (2007) 3097–3101.
- [16] G.B. Shulpin, G. Suss-Fink, L.S. Shulpina, J. Mol. Catal. A: Chem. 170 (2001) 17– 34.
- [17] C.W. Tang, S.A. Van Slyke, C.H. Chen, J. Appl. Phys. 65 (1989) 3610-3616.
- [18] H. Miyasaka, A. Saitoh, S. Abe, Coord. Chem. Rev. 251 (2007) 2622-2664.
- [19] J. Bernadou, B. Meunier, Adv. Synth. Catal. 346 (2004) 171-184.
- [20] M.M.Q. Simões, C.M.B. Neves, S.M.G. Pires, M.G.P.M.S. Neves, J.A.S. Cavaleiro, Pure Appl. Chem. 85 (2013) 1671–1681.
- [21] G.G.A. Balavoine, Y.V. Geletii, D. Bejan, Biol. Chem. 1 (1997) 507-521.
- [22] G. Franz, R.A. Sheldon, Oxidation, Ullmann's Encyclopedia Of Industrial Chemistry, Wiley-VCH, Weinheim, 2004.
- [23] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329–2363.
- [24] F. Cavani, J.H. Teles, ChemSusChem. 2 (2009) 508-534.
- [25] P.M. Osterberg, J.K. Niemeier, C.J. Welch, J.M. Hawkins, J.R. Martinelli, T.E. Johnson, T.W. Root, S.S. Stahl, Org. Process Res. Dev. 19 (2015) 1537–1543.
- [26] E.I. Solomon, S.D. Wong, L.V. Liu, A. Decker, M.S. Chow, Curr. Opin Chem. Biol. 13 (2009) 99–113.
- [27] E.I. Solomon, M.L. Neidig, Chem. Commun. 105 (2005) 2227–2252.
- [28] J.B. Wittenberg, B.A. Wittenberg, J. Exp. Biol. 210 (2007) 2082-2090.
- [29] J.A. Hoy, H. Robinson, J.T. Trent Jr., S. Kakar, B.J. Smagghe, M.S. Hargrove, J. Mol. Biol. 371 (2007) 168–179.
- [30] S.N. Vinogradov, L. Moens, J. Biol. Chem. 283 (2008) 8773-8777.
- [31] P.R. Ortiz de Montellano, Cytochrome P450: Structure, Mechanism and
- Biochemistry, 3rd ed., Kluwer Academic/Plenum Publisher, New York, 2005. [32] T. Mlodnika, B.R. James, in: Metalloporphyrins Catalytzed Oxidations, Kluwer,
- Dordrecht, The Netherlands, 1994, pp. 121–144. [33] M86-E01078 APEX2 User Manual, Bruker AXS Inc., Madison, USA, 2006.
- [34] G.M. Sheldrick, SHELXS-97 program for crystal structure determination, Acta Crystallogr. A 46 (1990) 467–473.
- [35] G. Sheldrick, SHELXL-97, Universit€at Göttingen, Göttingen, Germany, 1999.
- [36] M. Dolaz, V. McKee, A. Gölcü, M. Tümer, Spectrochim. Acta, Part a 71 (2009) 1648–1654.
- [37] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) 1133-1138.
- [38] A.D. Becke, J. Chem. Phys. 98 (1993) 5648-5652.
- [39] C. Lee, W. Yang, R.G. Parr, Phys. Rev. 37 (1998) 785-789.
- [40] B. Miehlich, A. Savin, A. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200–206.
 [41] M.J. Turner, J.J. McKinnon, S.K. Wolff, D.J. Grimwood, P.R. Spackman, D.
- Jayatilaka, M.A. Spackman, CrystalExplorer17.5 (2017), http://hirshfeldsurface. net.
- [42] S. Bendia, K. Ouari, L. Karmazin, IUCrData 2 (2017) x170169.
- [43] S. Narang, R. Mehta, S.N. Upadhyay, Ind. Eng. Chem. Res. 52 (2013) 3967-3973.

S. Bendia, R. Bourzami, J. Weiss et al.

- [44] K. Ouari, S. Bendia, J. Weiss, C. Bailly, Spectrochim. Acta, Part A 135 (2015) 624-631.
- [45] Y. Tanaka, A. Onoda, S. Okuoka, T. Kitano, K. Matsumoto, T. Sakata, H. Yasuda, T. Hayashi, Chem. Cat. Chem. 10 (4) (2018) 743–750.
- [46] H. Demirelli, M. Tümer, A. Gölcü, Bull. Chem. Soc. Jpn. 79 (6) (2006) 867–875.
- [47] A. Rambabu, M.P. Kumar, S. Tejaswi, N. Vamsikrishna, J. Shivaraj, Photochem. Photobiol. B 165 (2016) 147–156.
- [48] M. Merzougui, K. Ouari, J. Weiss, J. Mol. Struct. 1120 (2016) 239-244.
- [49] S.A. Patil, S.N. Unki, A.D. Kulkarni, V.H. Naik, P.S. Badami, Spectrochim. Acta, Part A 79 (2011) 1128–1136.
- [50] M. Khorshidifard, H.A. Rudbari, B. Askari, M. Sahihi, M.R. Farsani, F. Jalilian, G. Bruno, Polyhedron 95 (2015) 1–13.
- [51] G. Grivani, A. Ghavami, V. Eigner, M. Dusek, A.D. Khalaji, Chin. Chem. Lett. 26 (2015) 779–784.

- [52] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, J. Chem. Soc. Prekin trans. I I (1987) S1–S19.
- [53] Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, London, 1976.
- [54] S. Majumder, S. Dutta, L.M. Carrella, E. Rentschler, S. Mohanta, J. Mol. Struct. 1006 (2011) 216–222.
- [55] M. Amirnasr, M. Bagheri, K. Mereiter, C. R. Chimie 16 (2013) 1091-1097.
- [56] R. Kannappan, S. Tanase, I. Mutikainen, U. Turpeinen, J. Reedijk, Polyhedron 25 (2006) 1646–1654.
- [57] S. Majumder, S. Hazra, S. Dutta, P. Biswas, S. Mohanta, Polyhedron 28 (2009) 2473–2479.
- [58] J.E. Solomon, M.J. Baldwin, M.D. Lowery, Chem. Rev. 92 (1992) 521–542.
- [59] A.A. El-Taras, I.M. EL-Mehasseb, A.E.M. Ramadan, C.R. Chimie 15 (2012) 298– 310.