

Synthesis and Characterization of Hybrid Dual Metallic Complexes of Schiff Base Containing (Cd and Mn/Fe/Co/Ni) Derived from Isatin and 1,4-Phenylenediamine As Novel Organometallic Catalysts for Rapid and Efficient Epoxidation of Alkenes

Abeer Salim Mohammed*, Jassim M Alyass, Khalaf Ibrahim Khallow

Department of Chemistry, College of Education for Pure Sciences, University of Mosul, Iraq

Received 3 February 2022; received in revised form 28 March 2022; accepted 13 April 2022 (DOI: [10.30495/IJC.2022.691408](https://doi.org/10.30495/IJC.2022.691408))

ABSTRACT

In the current study, a new methodology for the epoxidation of alkenes was developed. In this regard, the required ligand was synthesized from the reaction of isatin and 1,4-phenylenediamine to afford (3Z,3'Z)-3,3'-(1,4-phenylenebis(azaneylylidene))bis(indolin-2-one) ligand. Then, the two coordinate ligands were metallated using Cd and Mn/Fe/Co/Ni to obtain a series of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni). The prepared complexes were characterized using FT-IR spectroscopy, UV-Vis spectroscopy, CHNS analysis, and magnetic susceptibility. Then, the prepared hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) are used in the epoxidation of different alkenes to afford corresponding epoxides in moderate to good yields. The synthesized complexes were checked relative to recoverability and leaching of metal to the medium of the reaction.

Keywords: Organometallic, Catalyst, Epoxidation, Alkene, Complex.

1. Introduction

Oxiranes (epoxides or oxacyclopropanes) are important intermediate in organic synthetic and can be used under acidic and basic conditions [1-3]. The epoxides can be employed for the most widely used and practical methodology for the synthesis of 1,2-difunctional compounds through the nucleophilic and electrophilic ring-opening of epoxides using a Lewis acid or base. **Scheme 1** shows different organic reactions on epoxides under various conditions.

In the last two decades, the organometallic catalysts including ligands bearing N and O donor atoms have attracted much attention due to their versatile application in the fields of organic synthesis and catalysis in both industrial and academic applications [14-16]. In the human body, the Cytochrome P-450 enzyme can selectively oxidize the incorporation of an O atom into many substrates in different bioorganic reactions [17, 18]. Recently, different research groups synthesized various organometallic catalysts with the same performance such as Cytochrome P-450 enzyme

[19-23]. Recently, organometallic catalysts have been developed for the oxidation of alkenes for different applications (**Scheme 2**). Transition metal complexes are known as powerful organometallic catalysts for the epoxidation of alkenes in the presence of NaClO, NaIO₄, H₂O₂, PhIO, and KHSO₅ as single atom oxygen donors [24-28]. But, up to now, the catalytic activity of these organometallic complexes decreased due to the inactivation of metals and leaching of them to the medium of the reaction. Herein, we synthesized a series of dual hybrid organometallic catalysts containing Cd and Ni/Co/Fe/Mn for highly epoxidation of alkenes with sodium periodate.

2. Experimental

2.1. General

All of the reagents, compounds, and solvents were used without further purification and purchased from Sigma-aldrich and Merck chemical companies. The melting points of the synthesized ligands and complexes were measured with a Thermo-scientific micro apparatus in capillary tubes and are uncorrected. FT-IR spectra were

*Corresponding author:

E-mail address: abeersalim1971@uomosul.edu.iq (A. S. Mohammad)

recorded with Nicolet-860 spectrometer using KBr pellets in the range of 400-4000 cm^{-1} . The electronic spectra of complexes were obtained with UV-Vis A20 Shimadzu spectrophotometer. The CHNS analysis were measured using 2400 CHNS organic elemental analyzer. The analysis of the final products including epoxides was performed by gas chromatography (GC) with the following conditions; Column: CP-SIL 8CB, L=25 m, d= 0.32 mm, film=1.20 μm , inlet: injector 250 $^{\circ}\text{C}$, split injection, injected volume 0.1 μL carrier gas: N_2 , pre-column pressure 75 kPa oven: 185 $^{\circ}\text{C}$ (3 min), 25 $^{\circ}\text{C}/\text{min}$, isotherm 240 $^{\circ}\text{C}$ (180 min) detector: FID, integration: Varian CP-3800, n-Decane: Internal Standard. All of the final products from the epoxidation of alkenes were purchased from Aldrich Chemical Company and used to determine signal and retention times relative to the solvent.

2.2. Preparation of (3Z,3'Z)-3,3'-(1,4-phenylenebis(azanelylidene))bis(indolin-2-one) Ligand

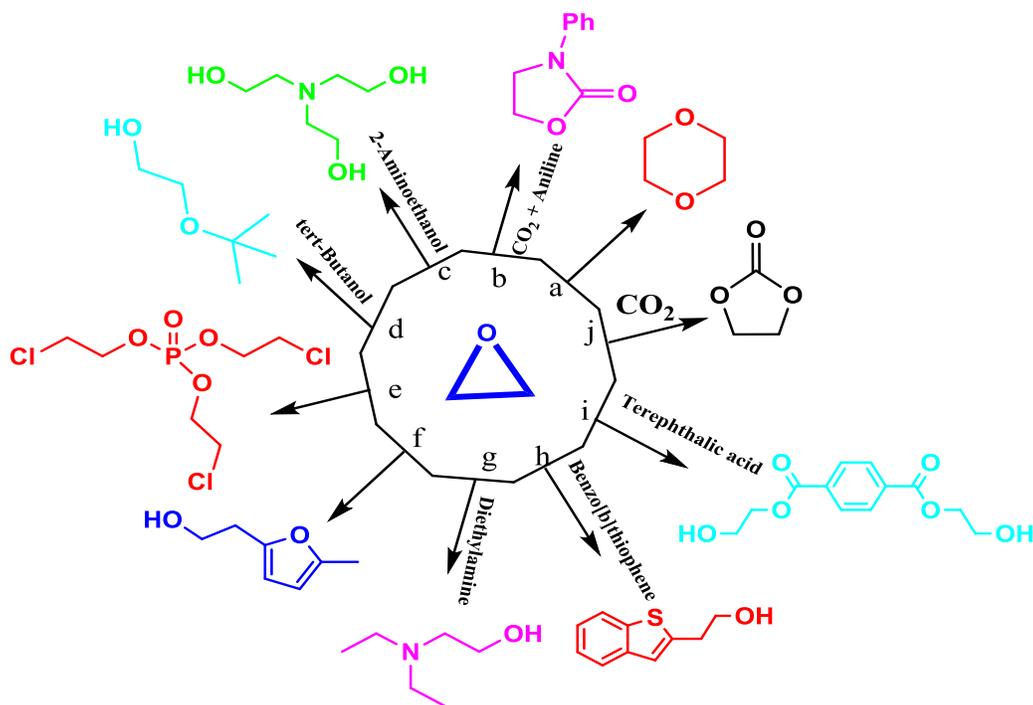
The required ligand was prepared by the mixture of isatin (0.29 g, 2 mmol) and *p*-phenylenediamine (0.11 g, 1mmole) in the presence of the catalytic amount of glacial acetic acid in ethanol for 4 h under reflux conditions [34-36]. The prepared ligand was purified and recrystallized from ethanol following solvent evaporation.

2.3. Preparation of Complexes

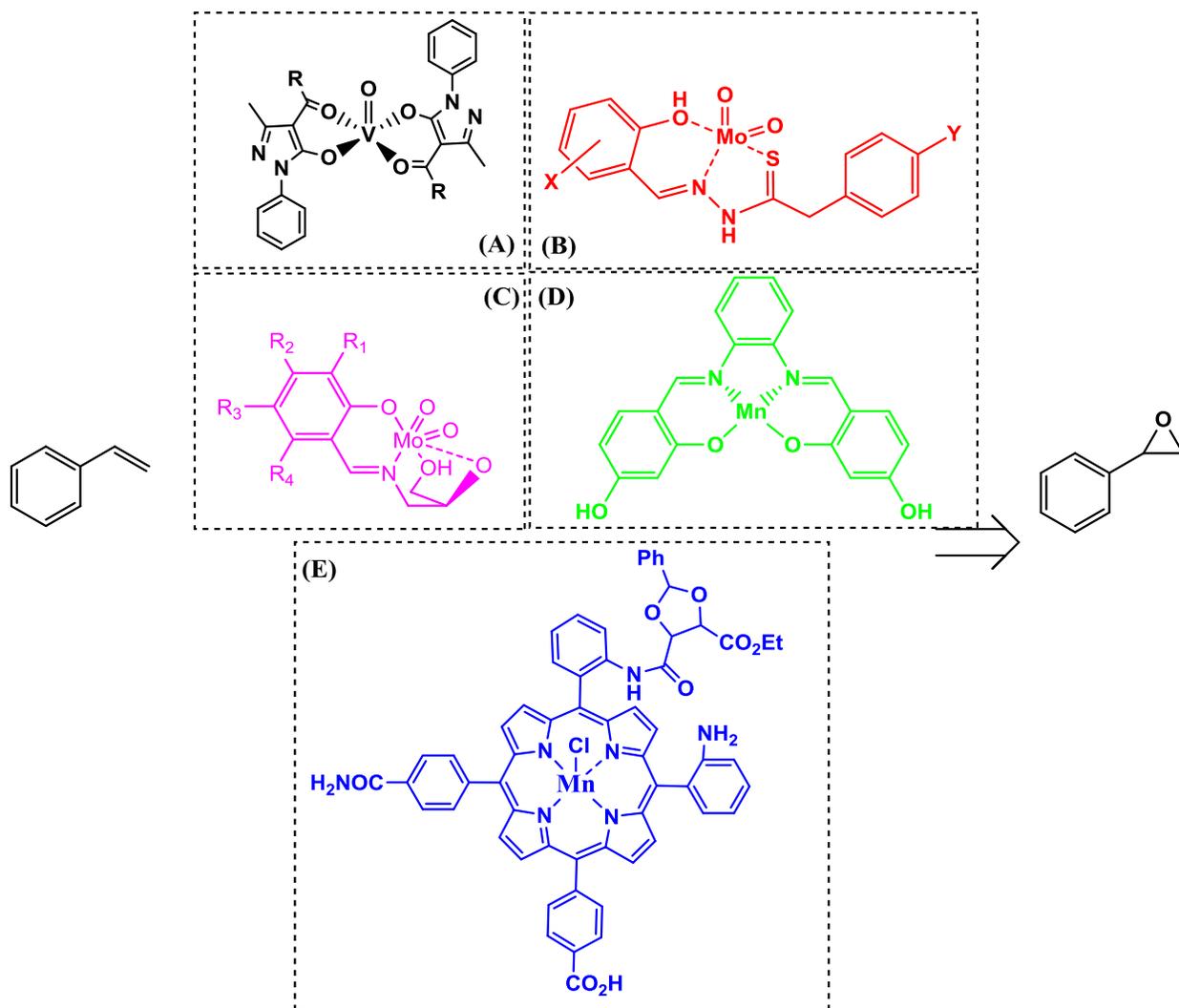
A general method has been performed for the synthesis of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) as follows: The ethanol solutions (20ml) of each of the following metal chlorides (1 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared. Then, the ethanolic solution of metal chloride was added to the ligand ethanol solution (20ml) (0.36 g, 1mmol) and stirred for 2 h. In the following, the reaction mixture was heated and another ethanolic solution (20ml) of cadmium chloride (1mmol) was added for an extra 2 h. The final complexes were dried, washed multiple times with warm ethanol and then stored overnight under 40 $^{\circ}\text{C}$ [34, 35].

2.4. General Procedure for the epoxidation of alkenes using hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni)

In a 25 mL flask equipped with a condenser and magnetic stirring bar, a mixture of alkene (1.0 mmol), NaIO_4 (1 mmol), and complexes (I-IV) (250 mg) in 10 mL of $\text{H}_2\text{O}:\text{EtOH}$ (2:1) was refluxed. The progress of the reaction was monitored by GC. After completion of the reaction, the complexes were filtered and washed with chloroform and dichloromethane (15 mL). The obtained product was purified on a silica-gel plate to afford the pure product.



Scheme 1. Different organic reactions on epoxides as an important intermediate. a) [4], b) [5], c, e) [6], d) [7] f) [8], g, h) [9], i) [10], j) [11-13]



Scheme 2. Different organometallic catalysts for epoxidation of alkenes (A): Two oxovanadium(IV) complexes containing 4-acyl-5-pyrazolonate- κ^2 -O,O' bidentate ligands [29], (B): [4-(p bromophenyl)thiosemicarbazone of salicylaldehyde (H2L1), 4-(p-X-phenyl)thiosemicarbazone ligand [30], (C): Chiral cis-dioxidomolybdenum(VI) complexes [31] (D): manganese Schiff base complex (derived from 2,4-dihydroxybenzaldehyde and 1,2-phenylenediamine) [32] (E): Mn(TCPP-R*)Cl (chiral Mn(III)-porphyrin complex) [33].

3. Results and Discussion

Scheme 3 shows the principle route for epoxidation of alkenes using NaIO_4 in the presence of the hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni). The prepared complexes were characterized by FT-IR spectroscopy, UV-Vis spectroscopy, and CHNS analyzer. First, the preliminary ligand was prepared from the reaction of 1,4-phenylenediamine and isatin in the presence of the catalytic amount of glacial acetic acid in ethanol under reflux conditions (**Scheme 4**). The chemical structure of the prepared ligand was investigated and approved using FT-IR spectroscopy, and CHNS analyzer. After the preparation of ligand, the hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) were provided as follows: the ethanolic solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared and added to the 20 mL of ethanolic solution of ligand. Then, 20 mL of cadmium chloride (1mmol) was added to the previous solution for an extra 2 h under reflux conditions. The Chemical structure of the prepared hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) was shown in **Fig. 1**.

To confirm the synthesis of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni), the complexes were characterized using FT-IR spectroscopy, UV-Vis spectroscopy, CHNS analysis, melting point, magnetic moment, and molar quality in DMF. The FT-IR of the ligand and hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) were shown in **Fig. 2** and its comparison together shows that

the metals were coordinated to the ligand (**Fig. 2**). In the regions 3415, 1739 and 1614 cm^{-1} allocated to the stretching of (N-H), (C=O) and (C=N), the free ligand showed significant spectra (**Fig. 2a**). The spectra for the isatin unit (N-H) were shown to be unchanged or slightly altered ($\Delta\nu=1-5$) relative to that of the complexes and therefore no evidence of N-H interaction with the metal ion was reported. The C=O and azomethine (C=N) spectra of the isatin group in the ligand showed significant differences in the lower values of $\Delta\nu= 33-49$ and $\Delta\nu= 17$, respectively, compared to those of the complexes and indicated the presence of both nitrogen and oxygen atoms in metal ion (II) coordination (**Fig. 2b-e**) [37-39].

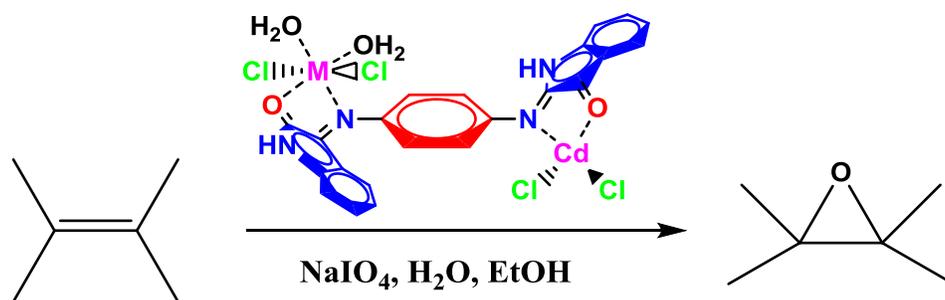
The appearance of large bands in the range 3356-3365 cm^{-1} revealed the involvement of the organized water molecules in the prepared complexes. In the complex spectra, two slightly weaker bands allocated as the OH rocking(r) and wagging (both) disturbances at 757-763 and 628-665 cm^{-1} were observed. Normally the M-Cl connection occurs in the 200-300 cm^{-1} range and this area is beyond the device's reach. In the low-frequency field, the spectra of the synthesized complexes exhibited new bands that were not present in the corresponding ligand, at 500-628 and 420-460 cm^{-1} respectively attributed to the stretching of (M-O) and (M-N) [37-39].

The electronic spectra for the initial ligand display bands of absorption at 333.33 and 220.26 nm which can be attributed to the transformation of the aromatic ring in the C=O and C=N chromophores [40-42]. The second

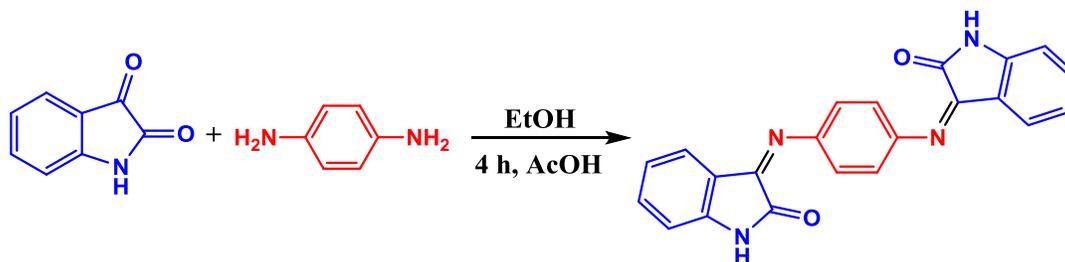
band was observed to be moved with higher intensity to a longer wavelength in the ready complexes. This transfer can be described as arising from the donation of electron density from the Schiff base's lone pair of electrons to metal ions [41] (**Fig. 3**) [43].

The physical and elemental analysis of synthesized ligand and hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) including chemical structure, melting point, color, and CHN analyzer were summarized in **Table 1**. Also, the complexes are soluble at room temperature in DMF and DMSO. The values of molar conductivity in DMF at 10^{-3} M were within the distance (30-47) of level one-to-one. $\text{Mol}^{-1}.\text{cm}^{-1}$ applies to the non-electrolytic activity of all complexes.

In addition to many low absorptions typical of d^5 electronic structure, the Mn (II) system electronic spectra had d-d transitions in the octahedral high spin complex (μ_{eff} . 5.77 BM.) attributable to spin and Laporte prohibited. The very soft bands emerge from promoting an electron to give different excited states that include just three unpaired electrons with very small intensities and are covered by transitions intra-ligand. The absorption band at 21459, 35335 cm^{-1} can be applied to the $6A_1g \rightarrow 4T_2g$ (G) and ligand load pass to metal respectively. A broad band in the spectrum of the Fe (II) complex was found at 10940 cm^{-1} and credited to a transformation of $5T_2g \rightarrow 5E_g$ which is in good agreement with the octahedral structure around the Fe (II) ion. Two spins allowed transitions located in the



Scheme 3. Epoxidation of alkenes using NaIO_4 in the presence of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni)



Scheme 4. Synthesis of ligand using Isatin and p-phenylenediamine

spectrum of the Co (II) complex at 9210 cm^{-1} and 21882 cm^{-1} as a consequence of the transformations between $4T_{1g}(F) \rightarrow 4T_{2g}(F)$, and $4T_{1g}(F) \rightarrow 4T_{1g}(P)$, respectively. This is a clear indication that six octahedral geometry guides the system. The Ni (II) complex exhibits three absorption bands, 9728 , 13054 and 21456 cm^{-1} and attributed to the $3A_{2g}(F) \rightarrow 3T_{2g}(F)$, $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ and $3A_{2g}(F) \rightarrow 3T_{1g}(P)$ transitions

respectively in accordance with the octahedral arrangement. Furthermore, Cd (II) did not show any electronic d-d transformations in the visible region but displayed bands of absorption at 40160 , 40000 , 40650 and 42016 cm^{-1} in the complexes comprising the ions Mn (II), Fe (II), Co (II) and Ni (II), respectively due to the conversion of charges (MLCT) [43-46]. **Table 2** summarized the presented data.

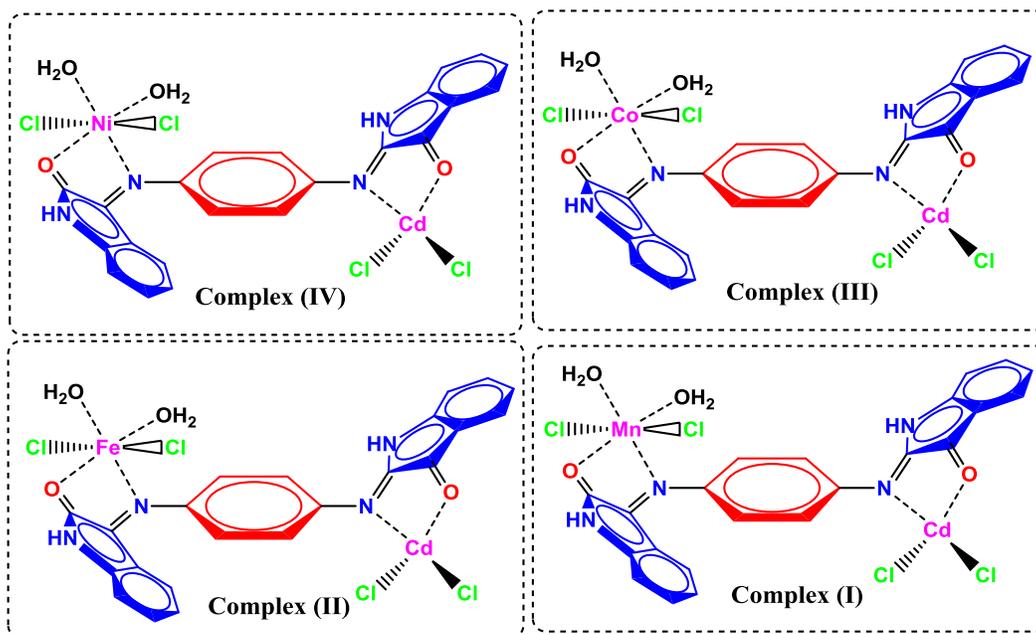


Fig. 1. The chemical structure of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni)

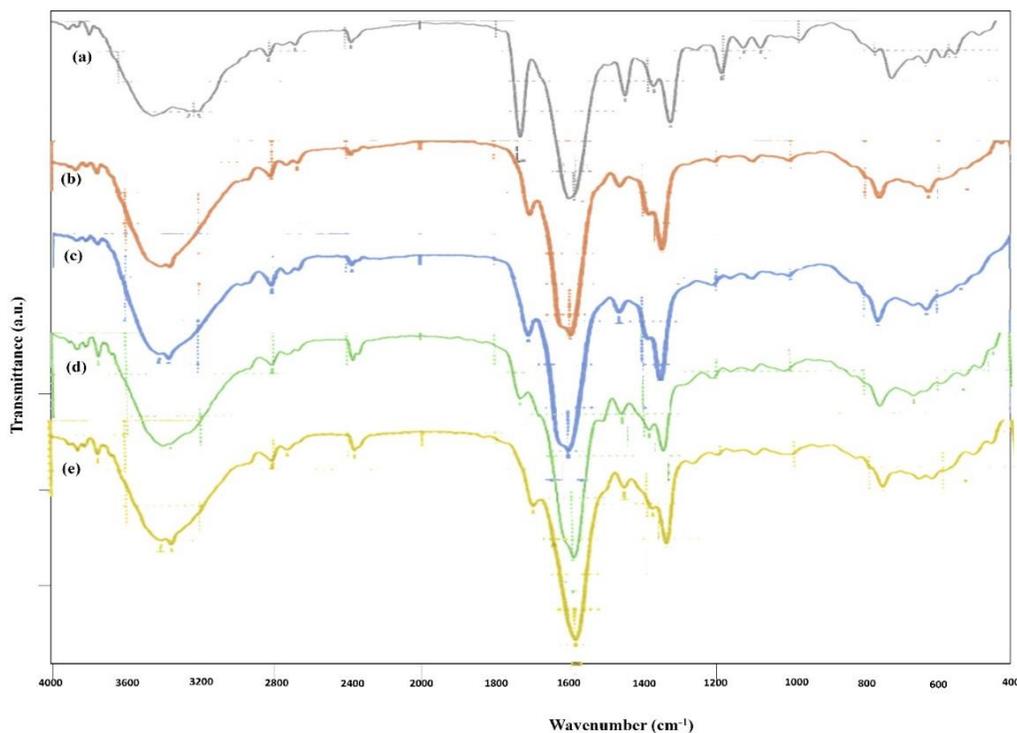


Fig. 2. FT-IR spectra of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) and ligand [a: ligand b: complex 1, c: complex 2, d: complex 3, e: complex 4]

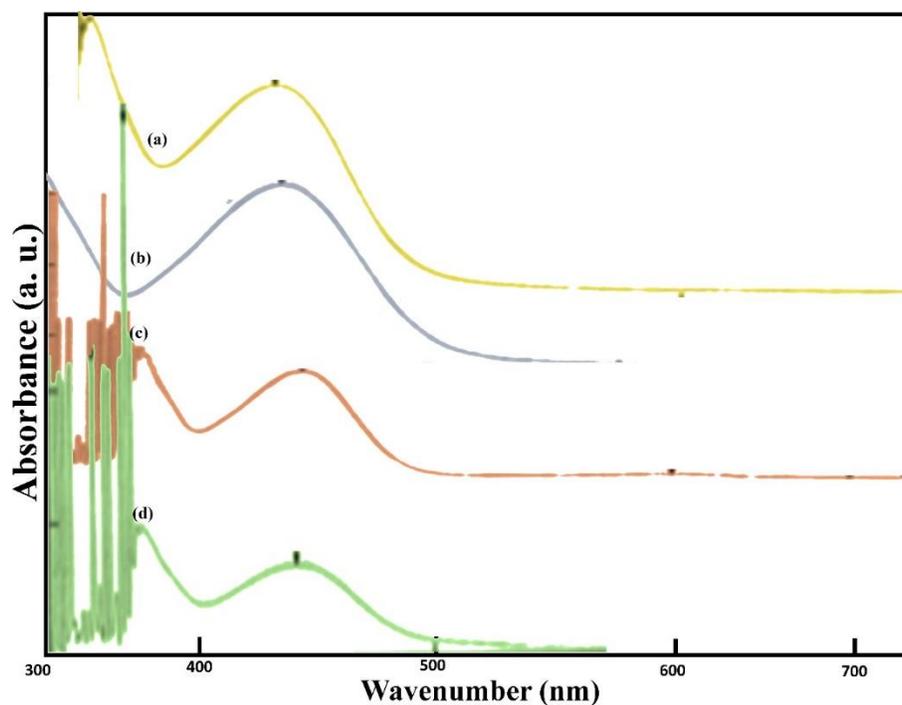
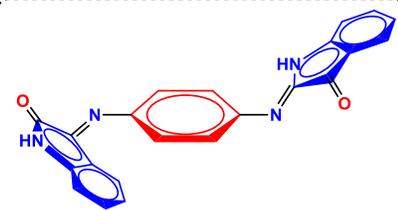
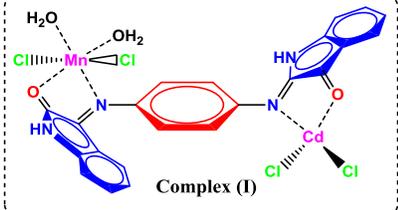
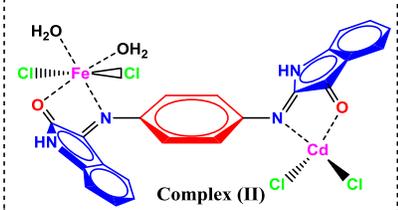


Fig. 3. The electronic spectra of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) [a: complex 1, b: complex 2, c: complex 3, d: complex 4]

Table 1. Physical and elemental analysis of synthesized ligand and hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni)

Complex/Ligand	Melting Point	Color	CHN Analyzed (Found)		
			C	H	N
	225-227	Yellow Turmeric	72.13(72.09)	3.82(3.88)	15.30(15.12)
 Complex (I)	244-246	Red Brown	37.13(37.11)	2.55(2.54)	7.87(7.84)
 Complex (II)	223 (decompose)	Brown	37.09(37.06)	2.55(2.52)	7.87(7.81)

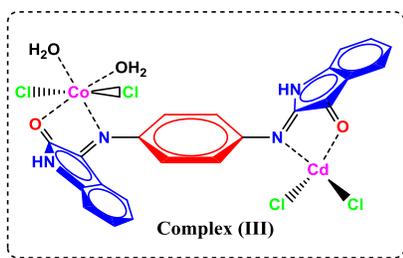
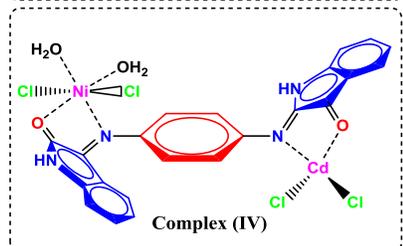
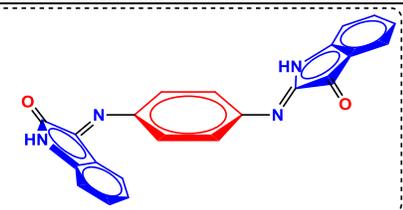
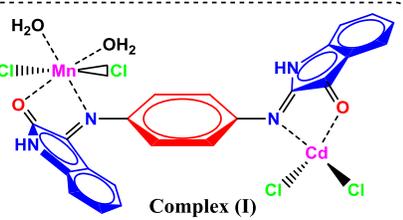
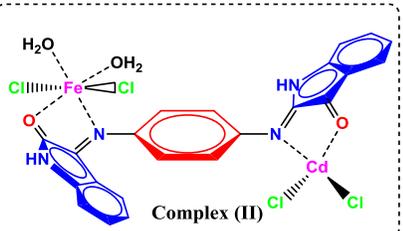
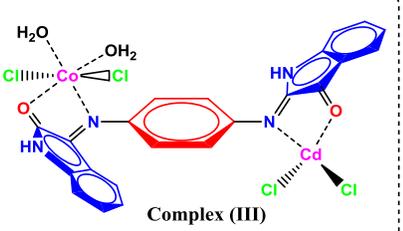
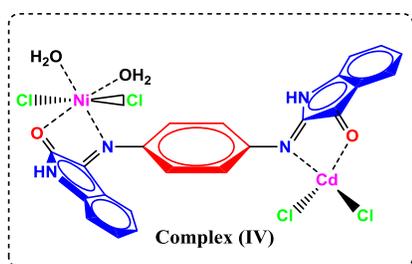
 <p>Complex (III)</p>	263 (decompose)	Deep Brown	36.93(36.63)	2.58(2.55)	7.83(7.80)
 <p>Complex (IV)</p>	243 (decompose)	Reddish Brown	36.94(36.51)	2.54(2.51)	7.83(7.82)

Table 2. Magnetic moment and molar quality in DMF for ligand and complexes

Complex/Ligand	Bands (cm ⁻¹)	Assignment	Λ (DMF)	μ_{ef}	Geometry	
					Metal	Cd
	23474 33898	n→π* π→π	-	-	-	-
 <p>Complex (I)</p>	21459 35335 40160	⁶ A _{1g} → ⁴ T _{1g} (G) C.T.(Mn) C.T.(Cd)	36	5.77	Oct.	Td
 <p>Complex (II)</p>	10940 35087 40000	⁵ T _{2g} → ⁵ E _g C.T.(Fe) C.T.(Cd)	30	4.80	Oct.	Td
 <p>Complex (III)</p>	9210 -- 21882 35587	⁴ T _{1g} → ⁴ T _{2g} (F) ⁴ T _{1g} → ⁴ A _{2g} (F) ⁴ T _{1g} → ⁴ T _{1g} (P) C.T.(Co)	45	4.09	Oct.	Td



97283
13054
21456
37593
42016

$A_2g(F) \rightarrow {}^3T_2g(F)$
 ${}^3A_1g(F) \rightarrow {}^3T_1g(F)$
 ${}^3A_1g(F) \rightarrow {}^3T_1g(P)$
C.T.(Ni)
C.T.(Cd)

47

3.32

Oct.

Td

After preparation and characterization of four types of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni), firstly, the epoxidation of styrene using NaIO_4 as an oxidant in the presence of complex I was selected as the model reaction for the optimization of the reaction conditions such as oxidant, solvent, type of complex, and catalyst amount (**Table 3**). The model reaction was performed using different solvents including water, CH_3CN , ethanol, methanol, and various ratio of water and ethanol/methanol/acetonitrile (**Table 3**, entries 1-10). The obtained results showed that the mixture of water and ethanol (2:1) was found to be the most efficient medium of the reaction. Then, the model reaction was performed in the presence of different oxidants including NaIO_4 , H_2O_2 , NaOCl , and tert-butOOH as oxidants (**Table 3**, entries 11-13). Among the oxidant experiments, NaIO_4 was selected as the best oxidant. Also, the catalytic amount of complex was investigated and the 250 mg of complex I was obtained as the optimum amount of complex (**Table 3**, entries 14-16). In addition, the optimization reaction conditions were investigated for other types of complexes (**Table 3**, entries 17-19).

With optimization results in hand, the generality and scope of this methodology were evaluated in the epoxidation of different alkenes (**Table 4**). As shown in **Table 4**, the final products were obtained in 62-91% from the epoxidation of different alkenes including electron-donating, electron-withdrawing, and long chain terminal alkenes. As we know from the previously reported literature, other products may be formed during epoxidation of alkenes such as aldehydes, carboxylic acids, and alcohols [47-49]. It is important that in this research the selectivity of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) especially complex I was to be efficient compared to other complexes.

For completion of our observation and study, the metal leaching was investigated during the reusability experiments. The observation results showed that Mn, Fe, Co, and Ni content decreased by only 3.1, 4.5, 6.0, and 5.7 ppm for Complex I, II, III, and IV, respectively, after the 4th catalytic cycle. Therefore, these results showed that the hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) are satisfactory, efficient and organometallic catalysts for the epoxidation of alkenes (**Table 5**).

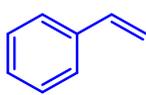
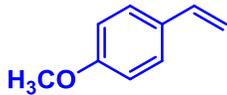
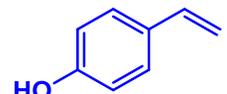
Table 3. Optimization of reaction conditions^a

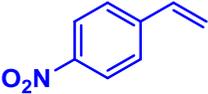
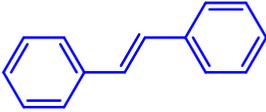
Entry	Oxidant	Solvent	Type of Catalyst	Catalyst amount (mg)	Time (h)	Yield (%) ^b
1	NaIO_4	H_2O	Complex I	150	2.5	63
2	NaIO_4	CH_3CN	Complex I	150	2.5	59
3	NaIO_4	EtOH	Complex I	150	2.5	48
4	NaIO_4	MeOH	Complex I	150	2.5	55
5	NaIO_4	$\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (1:1)	Complex I	150	2.5	71
6	NaIO_4	$\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (2:1)	Complex I	150	2.5	73

7	NaIO ₄	H ₂ O/ EtOH (1:1)	Complex I	150	2.5	75
8	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex I	150	2.5	77
9	NaIO ₄	H ₂ O/ MeOH (1:1)	Complex I	150	2.5	56
10	NaIO ₄	H ₂ O/ MeOH (2:1)	Complex I	150	2.5	60
11	H ₂ O ₂	H ₂ O/ EtOH (2:1)	Complex I	150	2.5	49
12	NaOCl	H ₂ O/ EtOH (2:1)	Complex I	150	2.5	56
13	tert- ButOOH	H ₂ O/ EtOH (2:1)	Complex I	150	2.5	53
14	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex I	200	2.5	80
15	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex I	250	2.5	86
16	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex I	300	2.5	83
17	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex II	250	2.5	83
18	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex III	250	2.5	82
19	NaIO ₄	H ₂ O/ EtOH (2:1)	Complex IV	250	2.5	85

a) Reaction conditions: Styrene (1 mmol), oxidant (1 mmol), Solvent (10 mL). Room temperature b) GC Yields based on the starting compound.

Table 4. Epoxidation of alkenes with NaIO₄ in the presence of hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni)

Entry	Alkene	Type of complex	Yield (%) ^b	Other products	Yield (%) ^c	Time (h)	TOF (h ⁻¹)
1		I	86	4	2.5	983	
		II	83	6	2.8	847	
		III	82	7	3.0	781	
		IV	85	8	2.4	1012	
2		I	90	2	1.8	1428	
		II	88	8	1.9	1323	
		III	78	8	2.0	1114	
3		IV	80	9	2.2	1039	
		I	83	1	1.8	1317	
		II	75	5	2.4	892	
		III	88	9	3.0	838	

		IV	91	3	3.2	812
		I	88	3	2.7	931
4		II	79	9	2.9	778
		III	83	5	3.0	790
		IV	80	3	3.1	737
		I	69 ^d	2	3.4	580
5		II	62 ^d	8	3.8	466
		III	65 ^d	6	3.4	546
		IV	63 ^d	7	3.7	486
		I	80 ^e	2	1.8	1270
6		II	78 ^e	6	1.9	1173
		III	81 ^e	9	2.0	1157
		IV	81 ^e	16	2.4	964
		I	86	3	2.2	1117
7		II	88	4	2.6	967
		III	84	8	2.7	888
		IV	79	6	2.7	836
		I	88	2	3.0	838
8		II	90	9	2.7	952
		III	78	7	2.4	928
		IV	76	6	2.2	987

a) Reaction conditions: Alkene (1 mmol), NaIO₄ (1 mmol), Room temperature, Catalyst (250 mg), Solvent (H₂O: EtOH) (2:1) (10 mL), b) GC yield based on the starting material c) Other products such as aldehyde, alcohol, carboxylic acid. d) Yields refer to Trans products based on ¹H NMR spectra. e) Yields refer to cis products.

a)

Table 5. The reusability of the hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) in the epoxidation of styrene (metal leaching (ppm), Yield%, %Recovered catalyst, ND: Not Detected)

Run	First	Second	Third	Fourth
Complex I (Mn)	ND, 86%, 99%	1.0, 86%, 99%	ND, 85%, 97%	3.1, 80%, 99%
Complex II (Fe)	0.6, 83%, 98%	ND, 83%, 99%	ND, 82%, 99%	4.5, 79%, 99%
Complex III (Co)	ND, 82%, 99%	ND, 82%, 98%	0.9, 80%, 99%	6.0, 73%, 99%
Complex IV (Ni)	ND, 85%, 99%	0.3, 83%, 97%	ND, 83%, 99%	5.7, 77%, 99%

4. Conclusions

In conclusion, these catalytic systems were highly efficient and organometallic systems for epoxidation of various alkenes with sodium periodate at room temperature. The prepared complexes were characterized using FT-IR spectroscopy, UV-Vis spectroscopy, CHNS analysis, and magnetic

susceptibility. Then, the prepared hybrid dual metallic complexes containing (Cd and Mn/Fe/Co/Ni) are used in the epoxidation of different alkenes to afford corresponding epoxides in moderate to good yields. The synthesized complexes were checked relative to recoverability and leaching of metal to the medium of the reaction.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We acknowledge the support of this work by the department of chemistry of University of Mosul.

References

- [1] Z. Yan, J. Tian, K. Wang, K.D.P. Nigam, G. Luo, Microreaction processes for synthesis and utilization of epoxides: A review, *Chem. Eng. Sci.*, 229 (2021) 116071.
- [2] L. Guo, K.J. Lamb, M. North, Recent developments in organocatalysed transformations of epoxides and carbon dioxide into cyclic carbonates, *Green Chem.*, 23 (2021) 77-118.
- [3] G.-G. Gu, L.-Y. Wang, R. Zhang, T.-J. Yue, B.-H. Ren, W.-M. Ren, Synthesis of polyethers from epoxides via a binary organocatalyst system, *Polymer Chemistry*, 12 (2021) 6436-6443.
- [4] S.M. Sadeghzadeh, R. Zhiani, S. Emrani, Spirulina (*Arthrospira*) platensis Supported Ionic Liquid as a Catalyst for the Synthesis of 3-Aryl-2-oxazolidinones from Carbon Dioxide, Epoxide, Anilines, *Catal. Lett.*, 148 (2018) 119-124.
- [5] B. Wang, E.H.M. Elageed, D. Zhang, S. Yang, S. Wu, G. Zhang, G. Gao, One-Pot Conversion of Carbon Dioxide, Ethylene Oxide, and Amines to 3-Aryl-2-oxazolidinones Catalyzed with Binary Ionic Liquids, *ChemCatChem*, 6 (2014) 278-283.
- [6] L. Wang, H. Li, S. Xin, P. He, Y. Cao, F. Li, X. Hou, Highly efficient synthesis of diethyl carbonate via one-pot reaction from carbon dioxide, epoxides and ethanol over KI-based binary catalyst system, *Appl. Catal., A*, 471 (2014) 19-27.
- [7] H.V. Ashburn, A.R. Collett, C.L. Lazzeli, Some β -Alkoxyethyl Esters of p-Aminobenzoic Acid, *J. Am. Chem. Soc.*, 57 (1935) 1862-1863.
- [8] G. Dannhardt, W. Kiefer, G. Lambrecht, S. Laufer, E. Mutschler, J. Schweiger, H.G. Striegel, Regioisomeric 3-, 4- and 5-aminomethyl isoxazoles: synthesis and muscarinic activity, *Eur. J. Med. Chem.*, 30 (1995) 839-850.
- [9] L.E.J. Kennis, F.P. Bischoff, C.J. Mertens, C.J. Love, F.A.F. Van den Keybus, S. Pieters, M. Braeken, A.A.H.P. Megens, J.E. Leysen, New 2-substituted 1,2,3,4-tetrahydrobenzofuro[3,2-c]pyridine having highly active and potent central α 2-antagonistic activity as potential antidepressants, *Bioorg. Med. Chem. Lett.*, 10 (2000) 71-74.
- [10] H. Zahn, R. Krzikalla, Synthese von einheitlichen, linearen oligoestern vom poly-glykol-terephthalat-typ, *Die Makromolekulare Chemie*, 23 (1957) 31-53.
- [11] W.-L. Dai, L. Chen, S.-F. Yin, W.-H. Li, Y.-Y. Zhang, S.-L. Luo, C.-T. Au, High-Efficiency Synthesis of Cyclic Carbonates from Epoxides and CO₂ over Hydroxyl Ionic Liquid Catalyst Grafted onto Cross-Linked Polymer, *Catal. Lett.*, 137 (2010) 74-80.
- [12] M. North, C. Young, Reducing the Cost of Production of Bimetallic Aluminium Catalysts for the Synthesis of Cyclic Carbonates, *ChemSusChem*, 4 (2011) 1685-1693.
- [13] W. Cheng, Z. Fu, J. Wang, J. Sun, S. Zhang, ZnBr₂-Based Choline Chloride Ionic Liquid for Efficient Fixation of CO₂ to Cyclic Carbonate, *Synth. Commun.*, 42 (2012) 2564-2573.
- [14] D.-Y. Wang, R. Liu, W. Guo, G. Li, Y. Fu, Recent advances of organometallic complexes for rechargeable batteries, *Coord. Chem. Rev.*, 429 (2021) 213650.
- [15] A. Asif, R.Y. Nadeem, M.A. Iqbal, S. Bibi, M. Irfan, Organometallic complexes of neodymium: an overview of synthetic methodologies based on coordinating elements, *Reviews in Inorganic Chemistry*, 41 (2021) 77-130.
- [16] P.T. Truong, S.G. Miller, E.J. McLaughlin Sta. Maria, M.A. Bowring, Large Isotope Effects in Organometallic Chemistry, *Chemistry – A European Journal*, 27 (2021) 14800-14815.
- [17] M.C. Stipp, A. Acco, Involvement of cytochrome P450 enzymes in inflammation and cancer: a review, *Cancer Chemother. Pharmacol.*, 87 (2021) 295-309.
- [18] D. Machalz, S. Pach, M. Bermudez, M. Bureik, G. Wolber, Structural insights into understudied human cytochrome P450 enzymes, *Drug Discovery Today*, 26 (2021) 2456-2464.
- [19] B. Large, N.G. Baranska, R.L. Booth, K.S. Wilson, A.-K. Duhme-Klair, Artificial metalloenzymes: The powerful alliance between protein scaffolds and organometallic catalysts, *Current Opinion in Green and Sustainable Chemistry*, 28 (2021) 100420.
- [20] P. Ebensperger, C. Jessen-Trefzer, Artificial metalloenzymes in a nutshell: the quartet for efficient catalysis, *Biol. Chem.*, (2021).
- [21] V. Carreras, N. Tanbouza, T. Ollevier, The Power of Iron Catalysis in Diazo Chemistry, *Synthesis*, 53 (2021) 79-94.
- [22] N. Awasthi, R. Yadav, D. Kumar, Metabolism of 8-aminoquinoline (8AQ) primaquine via aromatic hydroxylation step mediated by cytochrome P450 enzyme using density functional theory, *J. Organomet. Chem.*, 957 (2022) 122154.
- [23] L. Liu, A. Corma, Isolated metal atoms and clusters for alkane activation: Translating knowledge from enzymatic and homogeneous to heterogeneous systems, *Chem*, 7 (2021) 2347-2384.
- [24] D. Sadhukhan, P. Ghosh, S. Ghanta, Spectroscopic evidence of chirality in tetranuclear Cu(II)-Schiff base complexes, catalytic potential for oxidative kinetic resolution of racemic benzoin, *Inorganic and Nano-Metal Chemistry*, 51 (2021) 1714-1724.
- [25] T. Linker, The Jacobsen–Katsuki Epoxidation and Its Controversial Mechanism, *Angewandte Chemie International Edition in English*, 36 (1997) 2060-2062.

- [26] T. Hamada, T. Fukuda, H. Imanishi, T. Katsuki, Mechanism of one oxygen atom transfer from oxo (salen) manganese(V) complex to olefins, *Tetrahedron*, 52 (1996) 515-530.
- [27] V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. Moghbel, Rapid and efficient oxidative decarboxylation of carboxylic acids with sodium periodate catalyzed by manganese (III) Schiff base complexes, *Bioorg. Med. Chem.*, 12 (2004) 903-906.
- [28] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, M.S. Saeedi, Efficient epoxidation of alkenes with sodium periodate catalyzed by reusable manganese(III) salophen supported on multi-wall carbon nanotubes, *Appl. Catal.*, A, 381 (2010) 233-241.
- [29] P. Campitelli, M. Aschi, C. Di Nicola, F. Marchetti, R. Pettinari, M. Crucianelli, Ionic liquids vs conventional solvents: A comparative study in the selective catalytic oxidations promoted by oxovanadium(IV) complexes, *Appl. Catal.*, A, 599 (2020) 117622.
- [30] S. Roy, Saswati, S. Lima, S. Dhaka, M.R. Maurya, R. Acharyya, C. Eagle, R. Dinda, Synthesis, structural studies and catalytic activity of a series of dioxidomolybdenum(VI)-thiosemicarbazone complexes, *Inorg. Chim. Acta*, 474 (2018) 134-143.
- [31] M. Karman, M. Wera, G. Romanowski, Chiral cis-dioxidomolybdenum(VI) complexes with Schiff bases possessing two alkoxide groups: Synthesis, structure, spectroscopic studies and their catalytic activity in sulfoxidation and epoxidation, *Polyhedron*, 187 (2020) 114653.
- [32] H. Zakeri, S. Rayati, G. Zarei, A. Parsa, F. Adhami, Mn(II)-Schiff base complex immobilized onto MCM-41 matrix as a heterogeneous catalyst for epoxidation of alkenes, *Iran. J. Catal.*, 10 (2020) 71-78.
- [33] A. Farokhi, H. Hosseini Monfared, Highly efficient asymmetric epoxidation of olefins with a chiral manganese-porphyrin covalently bound to mesoporous SBA-15: Support effect, *J. Catal.*, 352 (2017) 229-238.
- [34] Z.H. Chohan, H. Pervez, S. Kausar, C.T. Supuran, Synthesis and Characterization of Antibacterial Co(II), Cu(II), Ni(II), AND Zn(II) Complexes of Acylhydrazine Derived Pyrrolyl Compounds, *Synth. React. Inorg. Met.-Org. Chem.*, 32 (2002) 529-543.
- [35] P. Jain, K.K. Chaturvedi, Complexes of Cu(II), Ni(II) and Co(II) with sulphamerazine salicylaldimine, *J. Inorg. Nucl. Chem.*, 39 (1977) 901-903.
- [36] P.P. Dholakiya, M.N. Patel, *Synth. React. Inorg. Met.-Org. Chem.*, 32 (2002) 753-762.
- [37] M.I. Khan, A. Khan, I. Hussain, M.A. Khan, S. Gul, M. Iqbal, R. Inayat Ur, F. Khuda, Spectral, XRD, SEM and biological properties of new mononuclear Schiff base transition metal complexes, *Inorg. Chem. Commun.*, 35 (2013) 104-109.
- [38] A.H. Kianfar, W.A.K. Mahmood, M. Dinari, M.H. Azarian, F.Z. Khafri, Novel nanohybrids of cobalt(III) Schiff base complexes and clay: Synthesis and structural determinations, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 127 (2014) 422-428.
- [39] H. Naeimi, J. Safari, A. Heidarneshad, Synthesis of Schiff base ligands derived from condensation of salicylaldehyde derivatives and synthetic diamine, *Dyes Pigm.*, 73 (2007) 251-253.
- [40] M. Fan, S. Ma, N. Ferdousi, Z. Dai, J.L. Woo, Modeling of Carbonyl/Ammonium Sulfate Aqueous Brown Carbon Chemistry via UV/Vis Spectral Decomposition, *Atmosphere*, 11 (2020) 358.
- [41] A.J. Atkin, J.M. Lynam, B.E. Moulton, P. Sawle, R. Motterlini, N.M. Boyle, M.T. Pryce, I.J.S. Fairlamb, Modification of the deoxy-myoglobin/carbonmonoxy-myoglobin UV-vis assay for reliable determination of CO-release rates from organometallic carbonyl complexes, *Dalton Trans.*, 40 (2011) 5755-5761.
- [42] M.H. Powelson, B.M. Espelien, L.N. Hawkins, M.M. Galloway, D.O. De Haan, Brown Carbon Formation by Aqueous-Phase Carbonyl Compound Reactions with Amines and Ammonium Sulfate, *Environ. Sci. Technol.*, 48 (2014) 985-993.
- [43] E. Dmitrieva, M. Rosenkranz, J.S. Danilova, E.A. Smirnova, M.P. Karushev, I.A. Chepurnaya, A.M. Timonov, Radical formation in polymeric nickel complexes with N2O2 Schiff base ligands: An in situ ESR and UV-vis-NIR spectroelectrochemical study, *Electrochim. Acta*, 283 (2018) 1742-1752.
- [44] N. Raman, J. Dhavethu Raja, A. Sakthivel, Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies, *J. Chem. Sci.*, 119 (2007) 303-310.
- [45] E. Yousif, A. Majeed, K. Al-Sammarrae, N. Salih, J. Salimon, B. Abdullah, Metal complexes of Schiff base: Preparation, characterization and antibacterial activity, *Arabian Journal of Chemistry*, 10 (2017) S1639-S1644.
- [46] N. Raman, A. Sakthivel, K. Rajasekaran, Synthesis and Spectral Characterization of Antifungal Sensitive Schiff Base Transition Metal Complexes, *Mycobiology*, 35 (2007) 150-153.
- [47] S. Haghshenas Kashani, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, Ruthenium Nanoparticles Immobilized on Nano-silica Functionalized with Thiol-Based Dendrimer: A Nanocomposite Material for Oxidation of Alcohols and Epoxidation of Alkenes, *Catal. Lett.*, 148 (2018) 1110-1123.
- [48] M. Zakeri, M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A.R. Khosropour, Multi-wall carbon nanotube supported manganese(III)tetraphenylporphyrin: efficient catalysts for epoxidation of alkenes with NaIO₄ under various reaction conditions, *J. Coord. Chem.*, 65 (2012) 1144-1157.

[49] M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, H. Kargar, N. Zeini-Isfahani, Manganese(III) porphyrin supported on multi-wall carbon nanotubes: A highly efficient and reusable biomimetic catalyst for epoxidation of alkenes with sodium periodate, *Polyhedron*, 28 (2009) 3816-3822.