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Synthesis, characterization and catalytic properties of some transition metal complexes of new phenoxy-imine ligand

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ABSTRACT

In this study a new Schiff base ligand was synthesized by the reaction of salicylaldehyde, 1,2-bis(bromomethyl)benzene and 4-nitrobenzenamine. [Cr(L)Cl₂]Cl·H₂O, [Fe(L)Cl₂]Cl·2H₂O and [Ru(L)Cl₂]Cl complexes were synthesized with this ligand and Cr(III), Fe(III) and Ru(III) chloride salts. The structures of the ligand and the obtained complexes were characterized using Elemental Analysis, FT-IR, ¹H-NMR, ¹³C-NMR, UV-Vis, Magnetic Susceptibility and thermogravimetric analysis. The synthesized phenoxy-imine ligand is a ligand of the O₂N₂ type. The resulting metal complexes are mononuclear and have octahedral geometry. Preliminary studies have also been carried out on the catalytic effects of complexes in cycloalkane oxidation and in cycloalkene epoxidation. In the general sense, the catalyst that triggers the highest product formation in the synthesized catalysts are the Ru(III) complex. It is suggested that Ru(III) complexes can be used in such catalysis reactions since they exhibit a high catalytic effect on cyclohexane oxidation.

Keywords: Phenoxy-imine ligand, metal complexes, catalyst

1. INTRODUCTION

Phenoxy-imine compounds with ethereal oxygen in their structure are obtained from the condensation of dialdehyde-structured compounds resulting from the reaction of aromatic/aliphatic halide with salicylaldehyde and its derivatives with primary amines. In recent years, the planning and synthesis of phenoxy Schiff bases and metal complexes has been an important research area because of its importance in basic and applied sciences. Schiff bases containing phenoxy groups have been widely used in coordination chemistry due to their ability

Yeni fenoksi-imin ligandının bazı geçiş metal komplekslerinin sentezi, karakterizasyonu ve katalitik özellikleri

ÖΖ

Bu çalışmada, yeni bir Schiff baz ligandı, salisilaldehit, 1,2bis (bromometil) benzen ve 4-nitrobenzenamin reaksiyonu ile sentezlenmiştir. [Cr(L)Cl₂]Cl·H₂O, [Fe(L)Cl₂]Cl·2H₂O ve [Ru(L)Cl₂]Cl kompleksleri, ligand ve Cr(III), Fe(III) ve Ru(III) klorür tuzları ile sentezlenmiştir. Ligand ve elde edilen komplekslerin yapıları Elemental Analiz, FT-IR, ¹H-NMR, ¹³C-NMR, UV-Vis, Manyetik Duyarlılık ve Termogravimetrik Analiz kullanılarak karakterize edildi. Sentezlenmiş fenoksiimin ligandı O₂N₂ tip bir liganddır. Elde edilen metal kompleksleri mononükleer ve oktahedral geometriye sahiptir. Komplekslerin sikloalkan oksidasyonundaki ve sikloalken epoksidasyondaki katalitik etkileri üzerine de ön çalışmalar yapılmıştır. Genel anlamda, sentezlenmiş katalizörler içerisinde en yüksek ürün oluşumunu tetikleyen katalizör L-Ru(III) kompleksidir. Ru(III) komplekslerinin, siklohekzan oksidasyonu üzerinde yüksek bir katalitik etki sergilediğinden, bu tür kataliz reaksiyonlarında kullanılabileceği önerilmektedir.

Anahtar Kelimeler: Fenoksi-imin ligand, metal kompleksleri, katalizör

to form stable complexes with transition metals and high catalytic effects.^{1.4} These ligands and metal complexes are of interest because of their important contributions in material science and the use of these compounds as antibacterial, antifungal, anticancer and herbicide agents has led to the intensification of scientific studies in this area.⁵⁻⁷ These compounds have been used as catalysts to convert simple organic compounds found in synthetic and marketable functional derivatives. The Schiff base metal complexes containing the phenoxy group are exciting in their catalytic effects during reactions such as oxidation, epoxidation and hydrolysis, and they are the

most commonly used catalysts in the reaction of asymmetric cyclopropane and Henry (nitroaldol).⁸⁻¹⁰

In this study, the synthesis and characterization of Schiff base compound (L) and their metal complexes are discussed with various spectroscopic methods. Metal complexes have been tested as a catalyst for the oxidation of cyclohexane and cyclohexene with hydrogen peroxide as oxidant at room temperature.

2. MATERIALS AND METHOTDS

2.1. Materials

Acetonitrile, n-butanol, diethylether, toluene, THF, EtOH, MeOH, DMF, RuCl₃ were obtained from Aldrich and Merck. All the solvents were dried and purified before use. Elemental analyses were performed on a Thermo Scientific Flash 2000 elemental analyzer. Molar conductance of the Schiff base ligands and their transition metal complexes were determined in DMF at room temperature by using Thermo Scientific electron corporation model conductivity meter. Electronic absorption spectra were recorded on a PG Instruments T80+UV/Vis spectrometer. Infrared spectra were measured in the range of 4000-400 cm⁻¹ on a Perkin-Elmer Spectrum 100 FTIR (ATR sampling accessory) spectrophotometer. The samples were dissolved in DMF and the absorption spectra were recorded in the range of 190-1100 nm. The magnetic moments of the complexes were measured by the Gouy method on a type Sherwood Scientific model Instrument. ¹H and ¹³C NMR spectra were recorded on a Bruker High Performance Digital FT-NMR (400 MHz) spectrometer with the samples dissolved in d₆-DMSO using TMS as an internal standard. Mass spectrum, EU Sciex QTRAP 3200 LC/MS/MS in the spectrophotometer were taken using electro-spray method. Thermal behaviors were examined with a SetaramLabsys TGA/DTA model thermal analyzer heated from 20-900°C under air.

2.2. Methods

Preparation of 2-((4-nitrophenylimino)methyl)phenol has been designed in keeping with the references.¹¹

2.2.1. 2(2((2((4nitrophenylimino)methyl)phenoxy)met hyl)benzyloxy)benzylidene)-4-nitrobenzenamine (L)

The synthetic route for the ligand L is shown in Scheme 1. 2-((4-nitrophenylimino)methyl)phenol (10 mmol), potassium carbonate (10 mmol) in MeCN (50 cm³) were stirred and refluxed for two hours and then 1,2-bis(bromomethyl)benzene (5 mmol) was added. The reaction mixture was stirred and refluxed for 24 h. After cooling down, the mixture was poured into water (100 cm³) and then 0.1 N 100 cm³ NaOH solution was added and extracted by CHCl₃. The CHCl₃ layer was

evaporated to dryness to give the crude product, which was recrystallized in MeCN to afford pure ligand L. Yield 80 %; color: yellow; m.p. 188°C. Mw: 586.19 g mol⁻¹. Elemental Anal. Calc. (%): C, 72.21; H, 4.63; N, 4.95. Found: C, 71.92; H, 4.46; N, 5.12% for $C_{34}H_{26}N_4O_6$. IR (cm⁻¹): 3072 (Ar- CH); 1615 (C=N); 1220 (C-O-C). ¹H NMR (400 MHz, CDCl₃): δ , ppm 5.31 (s, 4H,-OCH₂), 7.0-8.23 (m, 20H, aryl-H), 8.78 (d, 2H, N=C-H). ¹³C NMR (400 MHz, CDCl₃): δ , ppm 68.82, 121.32, 121.61, 124.26, 124.93, 128.20, 120.04, 129.55, 133.80, 134.53, 145.28, 158.07, 158.35, 158.85. UV-Vis: λ_{max} (nm) in DMF: 270 (0.923), 340 (1.848). LC/MS/MS, m/z: 587.1 [L+H]⁺.

2.2.2. Synthesis of Cr(III), Fe(III) and Ru(III) complexes

Metal (III) complexes of the Schiff bases were synthesized with the addition of $MCl_{3,n}H_2O$ (0.25 mmol) solutions in 10 ml ethanol (40°C) to the solutions of the Schiff base ligand (L) (0.25 mmol) in 30 ml CHCl₃ (40°C). The mixtures were refluxed for 6 h. After the reactions were completed, the mixtures were evaporated to dryness and obtained the crude product, which was filtered off and washed several times with petroleum ether.

[Cr(L)Cl₂]Cl⁺H₂O: Dark yellow solid, yield 26%, mp. 115-118°C. C₃₄H₂₈Cl₃CrN₄O₇ (762.96 g mol⁻¹) Elemental Anal. Calc.: C, 53.52; H, 3.70; N, 7.34. Found: C, 54.79; H, 4.27; N, 6.38 %. IR (cm⁻¹): 3073 (Ar CH); 1644 (C=N); 1240 (C-O-C), 2988 (Aliphatic CH), 532 (Cr-O); 495 (Cr-N). Meff, BM: 2.92. UV-Vis (DMF) λ_{max} (log ε): 270 (0.339), 375 (0.892), 420 (0.198) nm. Mol. Cond (S cm² mol⁻¹): 28.57. LC/MS/MS, m/z: 762.8 [[Cr(L)Cl₂]Cl·H₂O]⁺.

[Fe(L)Cl₂]Cl·2H₂O: Dark yellow solid, yield 56%, mp. 157-159°C. $C_{34}H_{30}Cl_3FeN_4O_8$ (784.83 g mol⁻¹) Elemental Anal. Calc. (%): C, 52.03; H, 3.85; N, 7.14. Found: C, 52.42; H, 3.61; N, 6.74%. IR (cm⁻¹): 3083 (Ar CH); 1645 (C=N); 1243 (C-O-C), 2988 (Aliphatic CH), 502 (Fe-O); 458 (Fe-N). Meff, BM: 7.51. UV-Vis (DMF) λ_{max} (log ε): 275 (0.559), 355 (1.182), 425 (0.113) nm. Mol. Cond (S cm² mol⁻¹): 19.36. LC/MS/MS, m/z: 784.7 [[Fe(L)Cl₂]Cl·2H₂O]⁺.

[**Ru**(**L**)**Cl**₂]**Cl**: Brown solid, yield 71%, mp. 112-116[°]C. C₃₄H₂₆Cl₃N₄O₆Ru (794.02 g mol⁻¹) Elemental Anal. Calc. (%): C, 52.43; H, 3.30; N, 7.06. Found: C, 53.54; H, 3.98; N, 7.12%. IR (cm⁻¹): 3073 (Ar CH); 1646 (C=N); 1227 (C-O-C), 2988 (Aliphatic CH), 530 (Ru-O); 493 (Ru-N). Meff, BM: 1.51. UV-Vis (DMF) λ_{max} (log ϵ): 270 (0.681), 375 (1.463), 550 (0.123) nm. Mol. Cond (S cm² mol⁻¹): 15.26. LC/MS/MS, m/z: 794.9 [[Ru(L)Cl₂]Cl]⁺.



Scheme 1. The possible reaction mechanism of the ligand.

2.2.3. General procedure for oxidation under microwave irradiation

The optimum conditions were obtained as catalyst: substrate: oxidant ratio of 1:100:250 in acetonitrile under max 300 W microwave power for 30 min. The temperature and pressure were controlled at about 100°C and max 25 bar by the instrument. A blank has been run under the similarly conditions without any catalyst.¹² The metal complexes have the octahedral geometry. The products formed by the effect of metal complexes in the catalytic oxidation of cyclohexane and cyclohexene under microwave irradiation are shown in Figures 1 and 2. The method of catalytic oxidation of cyclohexane and cyclohexene; 0.02 mmol catalyst: 2 mmol cyclohexane: 4 mmol hydrogene peroxide (1:100:250) and 5 ml acetonitrile were used for each reaction. The reaction temperature and pressure were held at around 100°C and 25 bar in closed DAP60 vessels.

3. RESULTS AND DISCUSSION

3.1. Synthesis

The Schiff base used as an intermediate (2-((4 nitrophenylimino)methyl)phenol) was synthesized from the reaction of 2 hydroxybenzaldehyde with 4-nitroaniline as described in the literature.¹¹ The new phenoxy-imine compound was synthesized from the condensation of 1,2-bis (bromomethyl)benzene and 2-((4 nitrophenylimino)methyl)phenol. Metal complexes of these ligands with metal(III) chlorine salts were obtained. The structure of ligand was characterized by using

elemental analysis, ¹H and ¹³C NMR, FT IR. The possible reaction is shown in Scheme 1. In the proposed structure, the ligand has a O2N2 core to form mononuclear metal(III) complexes. The stoichiometries of the complexes determined by mass and elemental correspond to the analysis general formula [MLCl₂]Cl.nH₂O (where M are Cr(III), Fe(III) and Ru(III). These propositions are also in accord with IR, UV-Vis data, TGA, magnetic and molar conductivity measurements. The proposed structures of the reported complexes are shown in Figure 3. The white-colored ligand and its complexes are insoluble in water and common organic solvents, but soluble in DMSO and DMF.

3.2. FT-IR analysis

The FT-IR spectra show marked changes of the ligand L. The characteristic bands of Schiff base ligand and its metal(III) complexes are given in Table 1. The IR spectra of Schiff base L showed a weak broad absorption band at 3072 cm⁻¹ assigned to the aromatic rings a stretching vibration respectively^{13,14}, absorption bands at 1615 cm⁻¹ assigned to the imin C=N stretching vibration, absorption band at 1220 cm⁻¹ assigned to the etheric oxygen C-O-C a stretching vibration, respectively. The FT-IR spectrum of the isolated L ligand shows sharp absorption band characteristic of v(C=N) stretching at 1615 cm⁻¹. In the complexes, these bands are shifted to higher about 29-31 cm⁻¹ wavenumbers indicating the participation of azomethine nitrogen in the coordination to metal ion.¹⁵⁻¹⁷ Aromatic C-H bands in ligands are shifted to upper about 4 cm⁻¹ in complexes respectively.



Figure 1. Catalytic oxidation of cyclohexane under microwave irradiation.



Figure 2. Catalytic oxidation of cyclohexene under microwave irradiation.



Figure 3. Suggested structures of Schiff base metal complexes.

A weak intensity absorption bands at 1220 cm^{-1} up to 1240 cm^{-1} in L-Cr, 1243 cm^{-1} in L-Fe and 1227 cm^{-1} in L-Ru are related to v(C-O-C) etheric oxygen stretching vibration in complexes. New bands in the complexes at $532-495 \text{ cm}^{-1}$ in L-Cr(III), $502-458 \text{ cm}^{-1}$ in L-Fe(III) and $530-493 \text{ cm}^{-1}$ in L-Ru(III) are attributed to the *v*(Ru-O) and *v*(Ru-N) vibrations.^{18,19} The IR spectra of the Schiff base ligand and a representative example of metal complexes are given in Figure 4.



Figure 4. FT-IR Spectra of L and metal complex.

3.3. NMR spectra

¹H and ¹³C NMR spectra of Schiff base ligand (L) were recorded in CDCl₃ solution. The ¹H NMR and ¹³H NMR spectrum was recorded and presented in Figure 5 and 6 for L. The ¹H NMR spectra of L showed the singlets (2H) at 8.78 ppm.²⁰⁻²² The signals of Aryl-H were assigned at δ : 7.0-8.23 (m, 20H) ppm for L

respectively. The signals of -Ph-O-C were observed at 5.31 (s, 4H) ppm for L respectively.^{2,23,24} More detailed information about the structure of Schiff base L is provided by its. ¹³C NMR spectrum in the spectrum of Schiff base was observed a new signal at 158.85 ppm for L due to imine carbon (C=N). The signal for the C_{Ar}-O carbons of the ligand was observed at 158.07 ppm, and

the peak observed at 145.28 ppm is belong to the C_{Ar}-N carbon. Ethereal oxygen of the C is considerable to correspond to δ 68.82 ppm for L. The peaks of the other aromatic ring carbons were observed at 112.62-134.53 ppm, respectively. All these observations is an evidence of formation of Schiff base.²⁵⁻²⁷

Table 1. Characteristic IR bands of the Schiff base and their metal complexes (in cm⁻¹)

Compounds	v(Ar C-H)	v(C=N)	v(C-O-C)	v(Ru-O)	v(Ru-N)	<i>v</i> (H ₂ O)
$L\left(C_{34}H_{26}N_{4}O_{6} ight)$	3072	1615	1220	-	-	-
[Cr(L)Cl ₂]Cl.H ₂ O	3073	1644	1240	532	495	3348
$[Fe(L)Cl_2]Cl \cdot 2H_2O$	3083	1645	1243	502	458	3379
[Ru(L)Cl ₂]Cl	3073	1646	1227	530	493	3355



Figure 5. ¹HNMR spectra of the ligand L.

Figure 6. ¹³CNMR spectra of the ligand L.

3.4. UV-Vis absorbance and emission studies

Ultraviolet visible spectra of phenoxy-imine ligand and metal complexes in the DMF solvent was recorded experimentally at 190-1100 nm, and the obtained spectra are shown in Figure 7.

Figure 7. UV-Vis spectra of ligand and its metal(III) complexes.

The C=N system is a weak chromophor, which absorbs ultraviolet light. Conjugation with phenyl groups shifts the absorbance to the visible region. Schiff base was observed approximately when the UV-Vis spectra gave two peaks between 210-400 nm. Transitions observed in the UV-Vis spectrum between 200 and 275 nm wavelengths are transitions originating from the aromatic rings and unshared electrons of the ligand.²⁸ The maximums are observed at 275-345 nm in L₁ related to n- π^* transitions of the imine groups. Approximately 345-275 nm in L is related to n- π^* and π - π^* transitions of the imine and etheric oxygen groups in complexes of ligand.^{29,30} The bands at 420-700 nm in L₁ show weak and intermediate transitions of d-d. Shifts of these bands to the lower and higher wavelengths indicate the complex forms of the nitrogen atoms of the imine groups and of the oxygen atoms of the phenoxy groups in coordination with the metal ion..³¹

3.5. Magnetic Moment and Molar Conductivity

The magnetic susceptibility values of the complexes obtained indicate that all the complexes are paramagnetic. The magnetic moment values of the Cr(III) complex is 2.91 B.M. which is in good agreement with the presence of three unpaired electrons.

The measured μ_{eff} value for the Fe(III) complex is 6.51 B.M. which is monomeric and high-spin at room temperature for the octahedral geometry. Magnetic moment value for the Ru(III) complex was determined to be 1.51 B.M^{31,32} which is in good agreement with the presence of one unpaired electron. From the magnetic studies, it is evident that all the metal complexes possess octahedral configuration in accordance with literature data.^{33,34}

The electrolytic conductivities of ligand Cr(III), Fe(III), and Ru(III) complexes were taken at room temperature and 10^{-3} molar concentration in DMF

solvent. The compounds have an electrolytic conductivity of 15.26-28.57µS/cm indicating their slightly polar nature due to the electrolytic behavior of chlorine. L-Cr(III), L-Fe(III), L-Ru(III) metal complexes exhibit electrolytic behavior.³⁵ The molar conductance values indicate all the complexes have 1:1 stoichiometry.

3.6. TGA

The thermal stabilities of ligand and Cr(III), Fe(III), Ru(III) complexes, thermal degradation steps of complex compounds and TGA/DTA spectra were used to determine the hydrate water in the structure. The thermal properties of the metal complexes were investigated by measuring the TGA/DTA by increasing the temperature by 10°C per minute with a continuous 2 bar nitrogen gas at 25-1000°C temperature under N₂ atmosphere. The TGA/DTA curves of the complexes are given in Figure 8.

Figure 8. The TGA/DTA/DTG curves of Ligand and its metal complexes.

As a result of this data, it is considered that the crystal water, HCl acid and phenyl group dissociate during the thermal decomposition of the complexes. When the mass losses of the complexes are considered, the TGA values and the calculated values of organic groups and crystal water which are degraded are in accordance with the literature.³⁶ The thermal stability of all the complexes increases in the order: Fe(III) < Cr(III) < Ru(III).

3.7. Cyclohexane oxidation under microwave irradiation

The reaction medium for alkane oxidation and alkene epoxidation was carried out using a Berghof MWS3+ completed, 1 μl samples were prepared from the catalyzed sample using an electronic pipette and GC-MS spectra were taken. In the alkane oxidation process, conversion %, yield % and selectivity % formation of the catalysts used (Cr(III), Fe(III) and Ru(III) complexes) and conversion percentages of cyclohexane in different catalysts are reported under microwave irradiation with cyclohexane hydrogen peroxide.³⁷ The possible reaction products are shown in Figure 9.

microwave device. After the calibration procedure was

Figure 9. Influence of the complexes in cyclohexane oxidation under microwave irridation.

According to the cyclohexane transformations and product formations in which the metal complexes are used as catalysts, the CyH conversion% is the highest 99.92% L-Ru(III), while the lowest is 58.28% L-Fe(III) complexes. Cyclohexanol (CyOH) formation is the most observed catalyst with 25.27% L-Ru(III) and the least observed is 9.75% L-Fe(III) complex. In the cyclohexanone formation, the catalyst effect was at most 15.37% L-Ru, but at least 5.09% L-Fe(III) complex is observed. In this sense, the catalyst with the most byproduct formation is L-Ru(II). Generally catalysts synthesized are the catalyst L-Ru(III) complex which triggers the highest product formation in the catalyst. The catalytic performance of mononuclear Ru(III) complexes can be compared to the catalytic activity exhibited by the different complexes reported in the literature.^{38,39}

3.8. Cyclohexene oxidation under microwave irradiation

Epoxidation reactions of cyclohexene substrates were carried out using synthesized Schiff base metal complexes. For the epoxidation, H_2O_2 was used as the initiator in the reaction medium and the reaction was carried out in microwave. As a result of the epoxidation

reaction of cyclohexene, the catalytic effects of all metal complexes appear to be high in the reaction of substrate conversion (Figure 10).

Figure 10. Influence of the complexes in cyclohexene oxidation under microwave irradiation.

However the cyclohexene conversion rates are lower. According to the instructions obtained in the epoxidation reactions, 2-cyclohexen-1-one and 2-cyclohexen-1-ol are formed. The highest cyclohexane conversion rate is epoxidation reactions using L-Ru(III) (82.64%) and L-Cr(III) (72.15%) metal complexes. The catalytic effects of iron and chrome complexes are lower. It is thought that one of the reasons for the low yield is due to the fact that the amount of H_2O_2 used as an oxidant in the reactions is lower than that in the literature.

4. CONCLUSIONS

The new Schiff base ligand containing the phenoxy group and their metal(III) complexes were synthesized and characterized by analytical and spectroscopic methods. All of the obtained results can be attributed to the fact that the Schiff base ligand functions as ONNO tetradentate chelate in mononuclear complexes. The synthesized complexes were assayed as oxidative catalysts for cyclohexane and cyclohexene oxidation products under microwave irradiation. The catalytic effect of L-Ru(III) complexes appears to be high as shown in the substrate conversion reaction. For the further work in this direction, this study indicates that the use of these kinds of complexes for catalytic purposes will possible.

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Conflict of interest

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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