



**Synthesis of Some New Carbazole-Metal Complexes and Their Thermal,
Electronic, Spectral and Catalytic Alkene Oxidation Properties**

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Abstract

Two new ligands [(*E*)-4-chloro-2-((9-ethyl-9H-carbazol-3-yl)methyleneamino)phenol, (*E*)-2-bromo-4-chloro-6-((9-ethyl-9H-carbazol-3-yl)methyleneamino)phenol] and their Cobalt (II), Manganese (II) and Nickel (II) complexes have been synthesized and characterized through various spectroscopic techniques (NMR, UV, IR, Mass etc.). Synthesized compounds have been examined for their catalytic activities in the oxidation reactions of styrene and cyclohexene. Manganese (II) complexes of both ligands showed the highest catalytic activity in alkene oxidations. Synthesized complex compounds proved that they could be used as catalysts in organic reactions requiring high temperatures. Electronic features of all the new compounds have also been reported for the first time with this paper.

Keywords: Catalysis; Complex; Schiffbase.

**Bazı Yeni Karbazol-Metal Komplekslerinin Sentezi ve Termal, Elektronik, Spektral ve
Katalitik Alken Oksidasyon Özellikleri**

Öz



İki yeni ligant [(*E*)-4-kloro-2-((9-etil-9H-karbazol-3-yl)metilenamino)fenol, (*E*)-2-bromo-4-chloro-6-((9-etil-9H-karbazol-3-yl)metilenamino)fenol] ile bunların kobalt (II), mangan (II) ve nikel(II) kompleksleri sentezlenmiş ve yapıları değişik spektroskopik yöntemlerle (NMR, UV, IR, Mass etc.) karakterize edilmişlerdir. Sentezlenen bileşiklerin katalitik aktiviteleri stiren ve siklohekzenin oksidasyon reaksiyonları üzerinde incelenmiştir. Her iki ligantın Mangan (II) kompleksleri alken oksidasyonlarında en yüksek aktiviteyi göstermiştir. Sentezlenen kompleks bileşiklerin katalizör olarak yüksek sıcaklık isteyen katalitik reaksiyonlarda kullanılabilirliği termal analizlerle kanıtlanmıştır. Bu yeni bileşiklerin elektronik özellikleri de ilk kez bu çalışma ile rapor edilmektedir.

Anahtar Kelimeler: Kataliz; Kompleks; Şifbazı.

1. Introduction

Schiff base ligands and their metal complexes have been studied and are still being studied extensively for years due to their synthetic flexibilities. They have captured many attention in the fields relating antimicrobial activity, catalytic activity especially in the reactions including alkene epoxidations [1-6], epoxide ring openings [7-9]. Among alkene epoxidation reactions, styrene and cyclohexene oxidation reactions captured quite high attention due to their versatile usage as starting materials in many synthetic organic reactions. In the literature, we have previously synthesized some carbazole derived Schiff bases and examined their catalytic activity towards the oxidation reactions of both cyclohexene and styrene [10]. Schiff base complexes were and are still being examined for their catalytic activities towards many different organic reactions [11-15]. Also, various Schiff base ligands are being examined for their biological effects like antimicrobial, anticancer and antitumour activities [16-21]. In many research carried out worldwide use carbazole moiety in the syntheses of new organic compounds and these organic compounds have been studied for their various features like thermal, electrochemical, electroluminescent features [22], as catalysts for the hydrogenation of alkenes [23], as ligands toward catalytic nitrogen fixation [24] and as photosensitizers (PS) [25]. Recently, a carbazole based Schiff base derivative was synthesized and used for detection of HSO₄⁻ ion in aqueous medium [26]. In addition above all, many different metal coordination compounds of different Schiff bases have been and are still being used in various kinds of oxidation reactions of both saturated and unsaturated hydrocarbons [27-29].

This work, first of all, deals with the synthesis and purification of 9-ethyl-3-carbazole carboxaldehyde from N-ethyl carbazole. Then it moves on to the synthesis and characterization of the two new Schiff bases and their Copper(II), Cobalt(II) and Nickel(II) complexes. All these

newly synthesized compounds have been examined for their catalytic, thermal and electronic features.

2. Experimental

9-Ethylcarbazole, Phosphorus(V) oxychloride, 2-amino-4-methylphenol, 2-aminophenol, acetate salts of Manganese(II) Cobalt(II) and Nickel(II) were purchased from Sigma Aldrich. Nuclear Magnetic Resonance spectra were recorded on a Bruker AV 400 MHz spectrometer in the solvent CDCl_3 . Infrared spectra were obtained using KBr discs on a Shimadzu 8300 FTIR spectrophotometer in the region of $400\text{-}4000\text{ cm}^{-1}$. Ultra-violet spectra were run in ethanol on a Shimadzu UV-160 A spectrophotometer. Mass spectra of the ligand were recorded on a LC/MS APCI AGILENT 1100 MSD spectrophotometer. The oxidation products were analyzed with a gaschromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column and a flame ionization detector. Elemental analyses were performed on a LECO CHNS 932 elemental analyzer and the metal analyses were carried out on an Ati Unicam 929 Model AA Spectrometer in solutions prepared by decomposing the compounds in aquaregia and subsequently digesting them in conc. HCl. Chemical composition analysis by EDAX was performed with an EDAX; Rönteckx flash detector analyzer associated to a scanning electron microscope (SEM, Leo-Evo 40xVP). The energy spectrum of characteristic X-rays is measured with Bruker energy dispersive X-ray spectroscopy (EDX) by a high resolution Si (Li) detector. Incident electron beam energies from 3 to 30 keV had been used. In all cases, the beam was at normal incidence to the sample surface and the measurement time was 100 s. All the EDAX spectra were corrected by using the ZAF correction, which takes into account the influence of the matrix material on the obtained spectra. Further, the presence of metals in the complexes was detected by an energy dispersive X-ray fluorescence (EDXRF) spectrometer and its percentage is estimated using CATXRF Program.

Thermal analyses of synthesized ligand and its metal complexes were carried out on a Perkin-Elmer Thermogravimetric Analyzer TG/DTA 6300 instrument under nitrogen atmosphere between the temperature range $30\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

2.1. Synthesis of the ligands

Formylation of 9-ethyl carbazole was done by using Vilsmeier formylating agents DMF and POCl_3 (1:1), 24h reflux at $85\text{ }^\circ\text{C}$ [10, 30, 31]. The mono aldehyde was separated by flash

chromatography with ethyl acetate/hexane (1:10) as eluent. 1 mmol N-ethylcarbazole-3-carbaldehyde was then reacted with 1 mmol 2-amino-4-chlorophenol to give (E)-4-chloro-2-((9-ethyl-9H-carbazol-3-yl)methyleneamino)phenol (L^1) and with 1 mmol 2-amino-6-bromo-4-chlorophenol to give (E)-2-bromo-4-chloro-6-((9-ethyl-9H-carbazol-3-yl)methyleneamino)phenol (L^2). Reactions were carried out in 30 mL ethanol under reflux for 9 hours. The resulting precipitates were recrystallized from methanol. Fig. 1 represents the whole reaction scheme for the synthesized compounds.

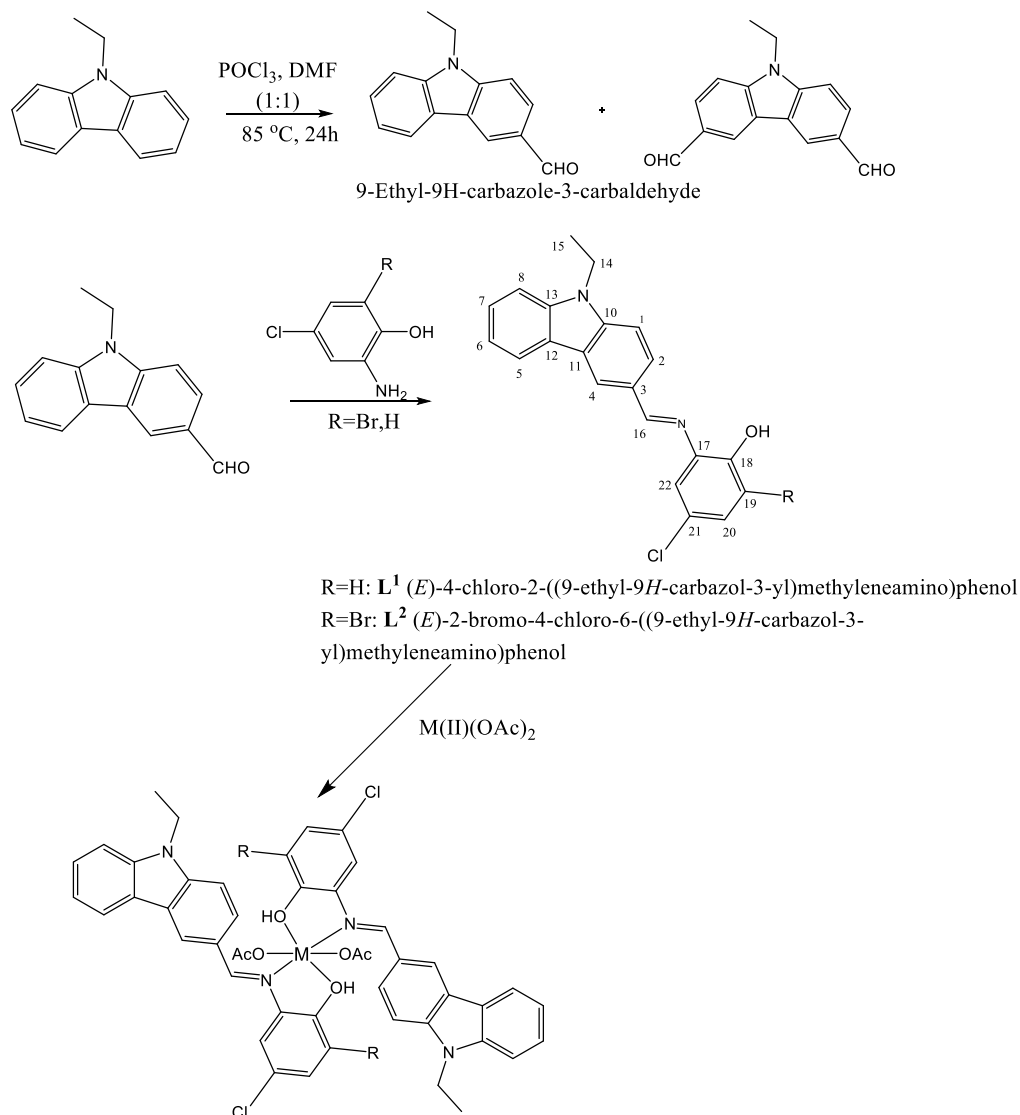


Figure 1: Synthesis scheme and the proposed structures for the synthesized compounds

2.1.1. L^1 (E)-4-chloro-2-((9-ethyl-9H-carbazol-3-yl)methyleneamino)phenol

$C_{21}H_{17}ClN_2O$. Yield: 90%, m.p.: 78-88 °C. Elemental Analysis, found % (calculated %): C 72.3(72.31) H 5.04(4.91) N 8.0(8.03), UV-Vis (ethanol) (λ_{max} , nm): 241, 292, 330. FT-IR (KBr,

cm⁻¹): 3040(C-H)_{Ar}; 2973(C-H); 1590(C=C)_{Ar}; 3380, 3312(OH); 1619(CH=N). ¹H NMR(CDCl₃): δ 8.2(H-1, d, J= 8.6 Hz); 8.06(H-2, dd, J= 8.6 & 1.4 Hz); 8.6 (H-4, d, J= 1.2 Hz); 7.5 (H-5, H-7, H-8 overlapped); 7.3 (H-6, H-22 overlapped); 4.4 (2H-14, q, J= 7.2 Hz); 1.5 (3H-15, t, J= 7.2 Hz); 8.7 (H-16, s); 6.94 (H-19, d, J= 8.6 Hz); 7.1 (H-20, dd, J= 8.6 Hz, 2.4 Hz); 10.0 (OH, s). ¹³C NMR(CDCl₃): δ 127.5 (C-1); 126.5 (C-2); 128.5 (C-3); 123.3 (C-4); 120.8 (C-5); 120.0 (C-6); 108.9 (C-7); 109.0 (C-8); 142.4 (C-10); 123 (C-11); 122.7 (C-12); 140.6 (C-13); 37.9 (C-14); 13.9 (C-15); 159.3 (C-16); 137.0 (C-17); 150.7 (C-18); 115.7 (C-19); 116.2 (C-20); 126.6 (C-22). Mass spectrum (LC/MS APCI): m/z 349.0 [M+H]⁺.

2.1.2. (L²) (E)-2-bromo-4-chloro-6-((9-ethyl-9H-carbazol-3 yl)methyleneamino) phenol

C₂₁H₁₆BrClN₂O. Yield: 84%, m.p.: 85-90°C. Elemental Analysis, found % (calculated %): C 59.3(58.97) H 4.02(3.77) N 6.3(6.55), UV-Vis (ethanol) (λ_{max}, nm): 235, 276, 293, 333. FT-IR (KBr, cm⁻¹): 3041(C-H)_{Ar}; 2850, 2918(C-H); 1587(C=C)_{Ar}; 3350, 3550(OH); 1622(CH=N). ¹H NMR(CDCl₃): δ 8.3(H-1, d, J= 8 Hz); 8.03 (H-2, dd, J= 8.6 & 1.5 Hz); 8.5 (H-4, d, J= 1.2 Hz); 7.45 (H-5, d, J= 8 Hz overlapped with H-8); 7.33 (H-6, ddd, J= 8 & 7.1 & 1.2 Hz); 7.53 (H-7, ddd, J= 8 & 7 & 1.2 Hz); 7.45 (H-8, d, J= 8 Hz overlapped with H-5); 4.4 (2H-14, q, J= 7.2 Hz); 1.5 (3H-15, t, J= 7.2 Hz); 8.7 (H-16, s); 7.4 (H-20, d, J= 2.3 Hz); 7.2 (H-22, d, J= 2.3 Hz); 10.1 (OH, s); ¹³C NMR(CDCl₃): δ 126.7 (C-1); 126.6 (C-2); 128.5 (C-3); 123.4 (C-4); 120.8 (C-5); 120.0 (C-6); 108.9 (C-7); 109.1 (C-8); 142.6 (C-10); 123.1 (C-11); 122.8 (C-12); 140.6 (C-13); 37.9 (C-14); 13.9 (C-15); 160.5 (C-16); 137.6 (C-17); 148.2 (C-18); 129.9 (C-19); 115.4 (C-20); 126.6 (C-22). Mass spectrum (LC/MS APCI): m/z 427.0 [M]⁺.

2.2. Synthesis of the complex compounds

Synthesized ligands were reacted with the acetate salts of Nickel, Cobalt and Manganese with the ratio 2:1. The ligands were first dissolved in ethanol in a round bottom flask. The appropriate metal salt which was also dissolved in ethanol were added into this solution slowly. The mixtures were refluxed for 24 hours. The resulted precipitates were recrystallized from methanol.

Co(L¹H)₂(OAc)₂

C₄₆H₄₀Cl₂CoN₄O₆. Yield: 64%, m.p.: 94-117°C. Elemental Analysis, found % (calculated %): C 63.51(63.17) H 5.01(4.61) N 6.21(6.41), Co 6.81(6.74). UV-Vis (ethanol) (λ_{max}, nm): 239, 276, 295, 334, 442. FT-IR (KBr, cm⁻¹): 3049(C-H)_{Ar}; 2975(C-H); 1591(C=C)_{Ar}; 3550, 3322(OH); 1621(CH=N). 539 (M-N); 613 (M-O)_{asym}; 584(M-O)_{sym}. Mass spectrum (LC/MS APCI): found m/z (Calculated m/z) 875.3 (874.6) [M]⁺. μ_{eff} B.M.: 4.61.

Mn(L¹H)₂(OAc)₂

C₄₆H₄₀Cl₂MnN₄O₆. Yield: 56%, m.p.: 90-110 °C. Elemental Analysis, found % (calculated %): C 63.84(63.46) H 4.77(4.63) N 6.33(6.43), Mn 6.26(6.31). UV-Vis (ethanol) (λ_{\max} , nm): 236, 275, 294, 332, 443. FT-IR (KBr, cm⁻¹): 3047(C-H)_{Ar}; 2974(C-H); 1592(C=C)_{Ar}; 3338(OH); 1620(CH=N). 538 (M-N); 613 (M-O)_{asym}; 589(M-O)_{sym}. Massspectrum (LC/MS APCI): found m/z (Calculated m/z) 870.0 (870.7) [M]⁺. μ_{eff} B.M.: 6.01.

Ni(L¹H)₂(OAc)₂

C₄₆H₄₀Cl₂NiN₄O₆. Yield: 55%, m.p.: 100-120 °C. Elemental Analysis, found % (calculated %): C 63.64(63.18) H 4.31(4.61) N 6.11(6.41), Ni 6.36(6.71) UV-Vis (ethanol) (λ_{\max} , nm): 238, 278, 294, 336, 446. FT-IR (KBr, cm⁻¹): 3044(C-H)_{Ar}; 2974(C-H); 1586(C=C)_{Ar}; 3480(OH); 1615(CH=N). 537 (M-N); 610 (M-O)_{asym}; 572(M-O)_{sym}. Massspectrum (LC/MS APCI): found m/z (Calculated m/z) 876.0 (875.4) [M+H]⁺. μ_{eff} B.M.: 3.07

Co(L²H)₂(OAc)₂

C₄₆H₃₈Br₂Cl₂CoN₄O₆. Yield: 71%, m.p.: 100-123 °C. Elemental Analysis, found % (calculated %): C 53.47(53.51) H 4.12(3.71) N 5.52(5.43), Co 5.59(5.71) UV-Vis (ethanol) (λ_{\max} , nm): 231, 277, 291, 325, 447 FT-IR (KBr, cm⁻¹): 3040(C-H)_{Ar}; 2850, 2918(C-H); 1587(C=C)_{Ar}; 3350, 3243(OH); 1622(CH=N). 538 (M-N); 613 (M-O)_{asym}; 587(M-O)_{sym}. Massspectrum (LC/MS APCI): found m/z (Calculated m/z) 1034.0 (1034.5) [M+2H]⁺. μ_{eff} B.M.: 4.60.

Mn(L²H)₂(OAc)₂

C₄₆H₃₈Br₂Cl₂MnN₄O₆. Yield: 68%, m.p.: 89-117 °C. Elemental Analysis, found % (calculated %): C 53.68(53.72) H 3.93(3.72) N 5.67(5.45), Mn 5.544(5.34) UV-Vis (ethanol) (λ_{\max} , nm): 236, 275, 294, 332, 443. FT-IR (KBr, cm⁻¹): 3047(C-H)_{Ar}; 2974(C-H); 1592(C=C)_{Ar}; 3338(OH); 1620(CH=N). 538 (M-N); 613 (M-O)_{asym}; 589(M-O)_{sym}. Massspectrum (LC/MS APCI): found m/z (Calculated m/z) 1029.0 (1029.5) [M+H]⁺. μ_{eff} B.M.: 5.88.

Ni(L²H)₂(OAc)₂

C₄₆H₃₈Br₂Cl₂NiN₄O₆. Yield: 77%, m.p.: 127-135 °C. Elemental Analysis, found % (calculated %): C 53.39(53.52) H 4.65(3.71) N 5.48(5.43), Ni 5.75(5.69) UV-Vis (ethanol) (λ_{\max} , nm): 232, 276, 292, 328, 446. FT-IR (KBr, cm⁻¹): 3040(C-H)_{Ar}; 2883(C-H); 1589(C=C)_{Ar}; 3544, 3322(OH); 1620(CH=N). 510 (M-N); 614 (M-O)_{asym}; 570(M-O)_{sym}. Massspectrum (LC/MS APCI): found m/z (Calculated m/z) 1032.0 (1032.2) [M]⁺. μ_{eff} B.M.: 3.27

3. Results and Discussion**3.1. Spectral analysis**

Both synthesized ligands L^1 and L^2 gave similar signals in their proton (Fig. 2 and Fig. 3) and carbon NMR spectra (Fig. S1 and Fig. S2). Ethyl group on the Nitrogen in the carbazole unit were seen at 4.4 ppm (2H-14) as quarted ($J = 7.2$ Hz) and at 1.5 ppm (3H-15) as triplet ($J = 7.2$ Hz). The imine protons for both ligands were seen at 8.7 ppm.

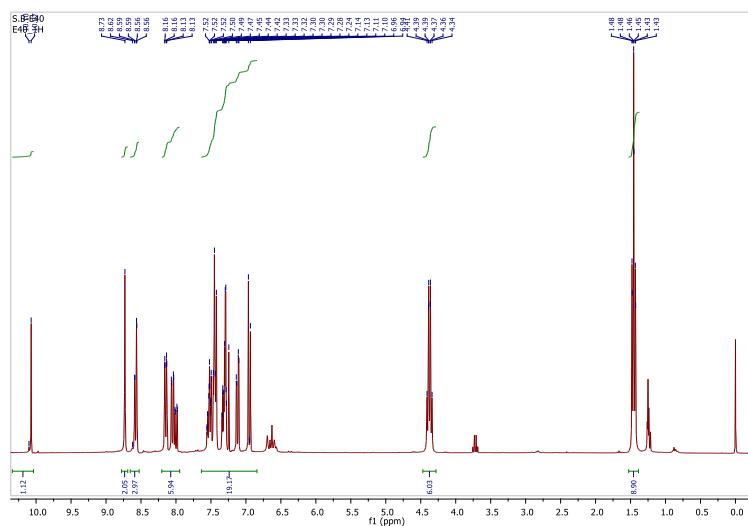


Figure 2: ^1H NMR Spectrum of L^1

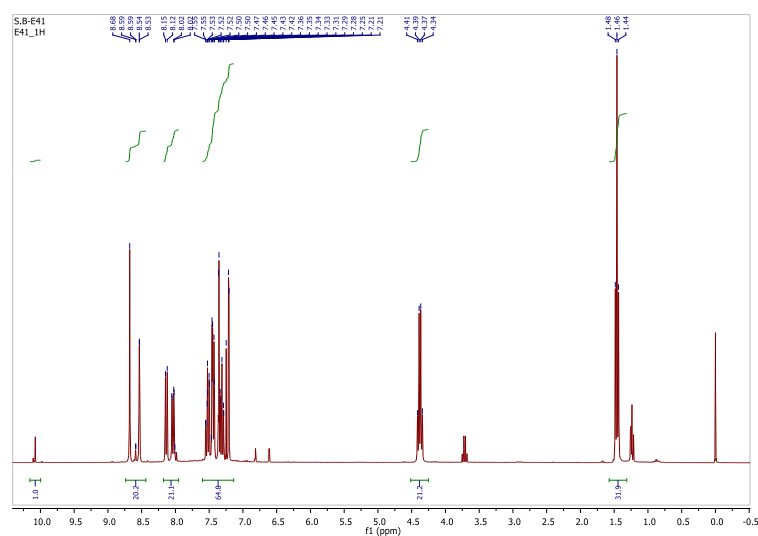


Figure 3: ^1H NMR Spectrum of L^2

Among the carbazole aromatic ring protons in ligand L^1 , next to the imine proton signal, the doublet at 8.6 ppm ($d, J = 1.2$ Hz) belongs to H-4 and the two signals appearing next to H-4 belongs to H-1 [δ 8.2 ($d, J = 8.6$ Hz)] and H-2 [δ 8.03 ($dd, J = 8.6$ & 1.4 Hz)]. We can see the rest of the aromatic protons between 6.9 ppm and 7.6 ppm for both ligands. We could clearly see the phenolic aromatic protons H-19 and H-20, belonging L^1 , at 6.94 ppm ($d, J = 8.6$ Hz) and at 7.1 ppm ($dd, J = 8.6$ & 2.4 Hz). H-22 on this ring were observed as overlapped with H-6 at 7.3. ^1H NMR spectrum of L^2 showed two sharp doublets, one at 7.4 ppm ($J = 2.3$ Hz), the other at 7.2

ppm ($J = 2.3$ Hz) belonging to H-20 and H-22 on the phenolic ring respectively. Both ligands showed the hydroxyl proton at 10.0 ppm as a weak singlet. ^{13}C NMR spectra of the ligands revealed the imine carbon signals at 159.3 ppm for L^1 and at 160.5 ppm for L^2 . The ethyl group on the carbazole unit were seen at δ 37.9 and at δ 13.9 for both ligands. The rest of the aromatic carbons were seen between 100 ppm and 154 ppm.

In the IR spectra of the ligands L^1 and L^2 , we were able to see weak signals at 1619 and 1622 cm^{-1} respectively, corresponding the imine stretching frequency. This vibration was slightly shifted in their complexes. Aromatic C-H vibrations were seen at around 3050 cm^{-1} and the aliphatic vibrations were between 2918 and 2975 cm^{-1} . The NMR spectra of the ligands gave hydroxyl signals at around 10.1 ppm and the IR spectra of the ligands showed hydroxyl stretchings between 3312 and 3380 cm^{-1} . Since all the synthesized complexes have uncoordinated two molecule of waters, their IR spectra revealed hydroxyl stretchings between 3243 cm^{-1} and 3550 cm^{-1} . For the substitution patterns of the benzene rings present in L^1 and their complexes, we could clearly see the sharp signals between 800 cm^{-1} and 808 cm^{-1} corresponding to two adjacent hydrogens on the phenolic rings. Similarly, for L^2 and its complexes, the weak signals at around 805 cm^{-1} corresponded to two isolated hydrogens in their phenolic rings. M-N stretching frequencies for all the complexes were observed between 510 cm^{-1} and 539 cm^{-1} . The IR spectra of all the complexes revealed M-O stretching frequencies both as symmetric and asymmetric in the ranges 570-589 cm^{-1} and 610-614 cm^{-1} respectively [32].

IR spectra of all the complexes gave three intense bands belonging to asymmetric and symmetric carboxylate stretchings, which proves the chelation of the carboxyls with metals. It is known that there are three possible carboxylate coordination modes: unidentate, bidentate and bridging. Also, the splitting value of carboxylate stretching bands ($\Delta = \nu_{\text{as}} - \nu_{\text{s}}$) are frequently used to attempt to distinguish between the three carboxylate coordination modes [33]. Deacon and Phillips [34] sought to correlate the difference, Δ , between the asymmetric and symmetric stretchings of carboxylates in a number of acetate and trifluoroacetate complexes. They concluded that unidentate acetate coordination is generally associated with Δ values higher than 200 cm^{-1} , bridging coordination shows lower Δ values than 150 cm^{-1} and the compounds with very low Δ values ($\ll 150$ cm^{-1}) are generally indicative of bidentate acetate chelation. In all of our synthesized complexes, these Δ values were calculated (Table 1) and they were found to be much higher than 200 cm^{-1} , which proves unidentate chelating of acetates.

Table 1: Asymmetric and symmetric IR values of carboxylate coordinations and the difference between them.

Complexes	$V_{\text{asymmetric}}$	$V_{\text{symmetric}}$	$\Delta (V_{\text{asym}} - V_{\text{sym}})$
$[\text{Co}(\text{L}^1\text{H})_2(\text{OAc})_2]2\text{H}_2\text{O}$	1679, 1573	1231	448, 342
$[\text{Mn}(\text{L}^1\text{H})_2(\text{OAc})_2]2\text{H}_2\text{O}$	1679, 1542	1233	446, 309
$[\text{Ni}(\text{L}^1\text{H})_2(\text{OAc})_2]2\text{H}_2\text{O}$	1678, 1567	1231	447, 336
$[\text{Co}(\text{L}^2\text{H})_2(\text{OAc})_2]2\text{H}_2\text{O}$	1679, 1571	1231	448, 340
$[\text{Mn}(\text{L}^2\text{H})_2(\text{OAc})_2]2\text{H}_2\text{O}$	1675, 1538	1230	445, 308
$[\text{Ni}(\text{L}^2\text{H})_2(\text{OAc})_2]2\text{H}_2\text{O}$	1660, 1532	1234	426, 298

UV-visible spectra of the ligands and the complexes showed absorption bands between 231 nm and 446 nm. The spectra of the complexes showed some bands in the high-energy region at 323-336 nm which can be assigned to charge transfer L-M bands [35, 36]. The complex compounds showed d-d transitions between 442 nm and 447 nm. The EDAX spectra of all the complexes showed characteristic K_{α} and L_{α} values for all the coordinated metals. In addition to the energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM) images of all complexes provided valuable information concerning surface morphology (Fig. S3 and Fig. S4). While the EDAX images confirms the existence of the metals and the purity of the complexes, SEM photographs display uniform and homogeneous matrixes of the synthesized complexes.

Additionally, spectrochemical analyses by EDXRF (energy dispersive X-ray fluorescence) were performed on all the complexes to detect the presence of metals in them. As it is known, this technique is based on the fact that the chemical elements emit characteristic radiation when subjected to appropriate excitation [37, 38]. The inner Shell vacancies in the atoms of elements, created by excitation, are filled by transition of electrons from outer orbitals leading to emission of characteristic X-rays [39]. The energy spectra of characteristic X-rays are measured by a high resolution Si(Li) detector. The concentration values were calculated using the net area under the K_{α} peaks of Cobalt, Manganese and Nickel. The results are given in Table 2 and they are in good agreement with the calculated values.

Table 2: Metal percentages estimated by EDXRF

Compounds	Chemical Formula	Calculated Values (%)	Experimental Values (EDXRF) (%)
$\text{Co}(\text{L}^1\text{H})_2(\text{OAc})_2$	$\text{C}_{46}\text{H}_{40}\text{Cl}_2\text{CoN}_4\text{O}_6$	6.74	7 ± 0.6
$\text{Mn}(\text{L}^1\text{H})_2(\text{OAc})_2$	$\text{C}_{46}\text{H}_{40}\text{Cl}_2\text{MnN}_4\text{O}_6$	6.31	6 ± 0.6

Ni(L ¹ H) ₂ (OAc) ₂	C ₄₆ H ₄₀ Cl ₂ NiN ₄ O ₆	6.71	7 ± 0.6
Co(L ² H) ₂ (OAc) ₂	C ₄₆ H ₃₈ Br ₂ Cl ₂ CoN ₄ O ₆	5.71	6 ± 0.6
Mn(L ² H) ₂ (OAc) ₂	C ₄₆ H ₃₈ Br ₂ Cl ₂ MnN ₄ O ₆	5.34	6 ± 0.6
Ni(L ² H) ₂ (OAc) ₂	C ₄₆ H ₃₈ Br ₂ Cl ₂ NiN ₄ O ₆	5.69	6 ± 0.6

Mass spectra of the complex compounds showed parental ion peaks. In addition, some other distinctable fragments were also observable. For example, the carbazole unit with the phenolic ring (C₂₁H₁₇ClN₂O) were seen at around 348 m/z and the phenolic ring with the imine group (C₇H₄ClNO) were observable at 154 m/z for the complexes of L¹. Same fragments (C₂₁H₁₆BrClN₂O, C₇H₃BrClNO) for L² complexes were seen at around 427 m/z and at 233 m/z. Magnetic susceptibility studies revealed the geometries of all the complexes to be octahedral. For the Manganese complexes the magnetic moments were calculated as 6.01 and 5.88 B.M. [41]. The Cobalt complexes gave these values as 4.60 B.M. and 4.61 B.M. [40]. The Nickel complexes, also revealed their characteristic magnetic moment values as 3.07 B.M. and 3.27 B.M., suggesting octahedral geometry [41].

3.2. Thermal analysis

As we all know, Thermal Analysis is a method used to examine the thermal behaviour (e.g. thermal stability and composition) of the various compounds isolated by researchers world-wide. In this work, the Thermogravimetric investigation of the isolated ligands and their complexes was carried out on Perkin-Elmer TGA 6300 instrument with nitrogen atmosphere starting at 30⁰C with a heating rate of 10 ⁰C/min. Thermal analysis studied for these new compounds revealed useful information about the decompositions of both ligands and the complexes (Fig. S5 and Fig S6). For example, examination of TG graphics of L¹ and its complexes showed well defined degradation steps that are in agreement with the proposed structures. Their decomposition starts between the temperatures 90 °C and 120 °C. Nickel (II) complex of L¹ was the most temperature resistant with a degradation temperature starting at 100 °C and its TG graphic revealed two steps of degradation, one with the loss of carbazole unit with 43.9 % (Calc. 44 %) and the other was the loss of phenolic ring with the imine group [34 % (Calc. 34.5 %)]. The residual part of this complex gave the total masses of NiO and the two coordinated acetates. Cobalt (II) and Manganese (II) complexes of L¹ showed similar degradations in their TG graphics, which can be divided in two steps. The first steps corresponded to two phenolic rings with the imine group and the second step belonged to the mass loss of two carbazoles and the two coordinated acetates. Metallic Manganese was the residual mass found for Mn(L¹H)₂(OAc)₂ and oxygenated Cobalt

was recorded as the residual part for the Cobalt complex of this ligand. The ligand L¹ itself also revealed two degradation steps consisting of the carbazole unit and the phenolic part with the imine group. Thermal analysis of the other ligand L² revealed a mass loss assigned as the residual part consisting of bromide and the ethyl group. Between 100 °C and 420 °C, the mass loss of the phenolic group without the bromide occurred with 35.7 % (Calc. 35.8 %). Above 420 °C, the mass loss of 39.3 % (Calc. 38.9 %) was attributed to the carbazole without the ethyl group. Among complexes of L², Nickel complex was the most temperature resistant with degradation temperature starting at 135 °C. Manganese and Nickel complexes showed quite similar degradation patterns in their TG graphics. For example, both revealed a mass loss belonging to the phenolic groups (2 × C₇H₄BrClNO). The second step shows mass losses of the carbazoles and the coordinated acetates mainly. Cobalt (II) complex of L², however, revealed the residual part with a mass loss of 33.8 % (Calc. 33.3 %), which corresponds to the total masses of two bromines, two acetates and Cobalt oxide. The experimental values obtained for the ligands and the complexes were all in agreement with the calculated values. All the results for the thermal analysis are listed in Table 3.

Table 3: Thermal results of synthesized compounds

Compound	M.W.	T/°C	MassLoss % Found(Calc.)	Assignment	Residual % Found(Calc.)
L ¹	348	80-450	42.7(42.6)	C ₇ H ₅ ClNO	
		450-700	56.5(56.2)	C ₁₄ H ₁₃ N	
Ni(L ¹ H) ₂ (OAc) ₂	875	100-450	34(34.5)	2(C ₇ H ₅ ClNO)	22.1(21.5) (NiO), 2(AcO)
		550-800	43.9(44)	2(C ₁₄ H ₁₂ N)	
Co(L ¹ H) ₂ (OAc) ₂	875	94-525	35(34.8)	2(C ₇ H ₅ ClNO)	8.8(8.5) (CoO)
		525-800	56.2(56.7)	2(C ₁₄ H ₁₂ N), 2(AcO)	
Mn(L ¹ H) ₂ (OAc) ₂	870	90-520	35.4(35.5)	2(C ₇ H ₅ ClNO)	6(6.3) (Mn),
		520-670	58.6(58.2)	2(C ₁₄ H ₁₂ N), 2(AcO)	
L ²	427	85-420	35.7(35.8)	C ₇ H ₄ ClNO	25(25.3) (CH ₃ CH ₂), Br
		420-800	39.3(38.9)	C ₁₂ H ₈ N	
Ni(L ² H) ₂ (OAc) ₂	1032	130-475	44.4(44.8)	2(C ₇ H ₄ BrClNO)	
		475-800	55.6(55.2)	2(C ₁₄ H ₁₂ N), 2(AcO), NiO	
Co(L ² H) ₂ (OAc) ₂	1032	100-465	28.9(29.3)	2(C ₇ H ₄ ClNO)	33.8(33.3) (CoO), 2(AcO), 2Br
		465-800	37.3(37.4)	2(C ₁₄ H ₁₂ N)	
Mn(L ² H) ₂ (OAc) ₂	1028	85-600	45.5(45.2)	2(C ₇ H ₄ BrClNO)	6.5(6.5) (MnO)
		600-800	48.0(48.3)	2(C ₁₄ H ₁₂ N), 2(AcO)	

All thermal analyses were done under nitrogen atmosphere between the temperature range 30 °C and 800 °C at a heating rate of 10 °C/min.

3.3. Cyclic voltammetry

Cyclic voltammogram studies of the title compounds were run in CH₃CN (1×10⁻³ M–0.1 M NBu₄BF₄ as supporting electrolyte at 293 K. Unless otherwise stated, all potentials quoted refer to measurements run at a scan rates (v') of 50, 100, 250, 500, 750 and 1000 mV s⁻¹ and against an internal ferrocene–ferrocenium standard. The electrochemical curves of the synthesized ligands at 50, 100, 250, 500, 750 and 1000 mV s⁻¹ scan rates are shown in the Fig. 4 and Fig. 5. As shown in Fig. 4, our ligand L¹ shows many reversible processes in all of its scan rates and a few irreversible ones. Especially at 1000 mV/s, it showed only the reversible processes. In this scan rate, both forward and reverse scans showed a total of twelve potentials, each halve shared by anodic and cathodic peaks. Examination of the complexes of L¹ revealed that the Nickel (II) and Cobalt (II) complexes showed mostly the reversible processes in all of their scan rates. Manganese (II) complex of L¹, however, showed pseudo-reversible redox processes too. In these pseudo-reversible processes, the anodic peak potentials were recorded between -0.69 V and -0.76 V and the cathodic potentials were seen between -1.17 V and -1.19 V at scan rates 250, 500, 750 and 1000 mVs⁻¹. Our second ligand L² also revealed many reversible processes, however, it showed irreversible redoxes too. For the scan rates 250, 500, 750 and 1000 mVs⁻¹ at -0.569 V, -0.621 V, -0.613 V, -0.589 V for the forward scan and at -0.388 V, -0.376 V, -0.364 V, -0.364 V peak potentials for the reverse scan revealed their anodic to cathodic ratio values were around 1.6 (I_{pa}/I_{pc}), proving their irreversible nature. Among the complexes of L², Cobalt (II) complex revealed mainly reversible processes, only for the scan rates 50 mVs⁻¹ ve 100 mVs⁻¹, it showed pseudo-reversible redoxes at -0.913 V and -0.929 V for anodic potentials and at -1.186 V and -1.322 V for cathodic potentials. Nickel (II) and Manganese (II) complexes of the same ligand revealed both reversible and pseudo-reversible processes. For all the synthesized metal complexes, one can say that the redox process occur with a simple one-electron processes [M(II)/M(I)]. For the ligands, we can draw the redox scheme in Fig. 6. The results of these experiments can be gathered in a table which can be seen in the supporting file.

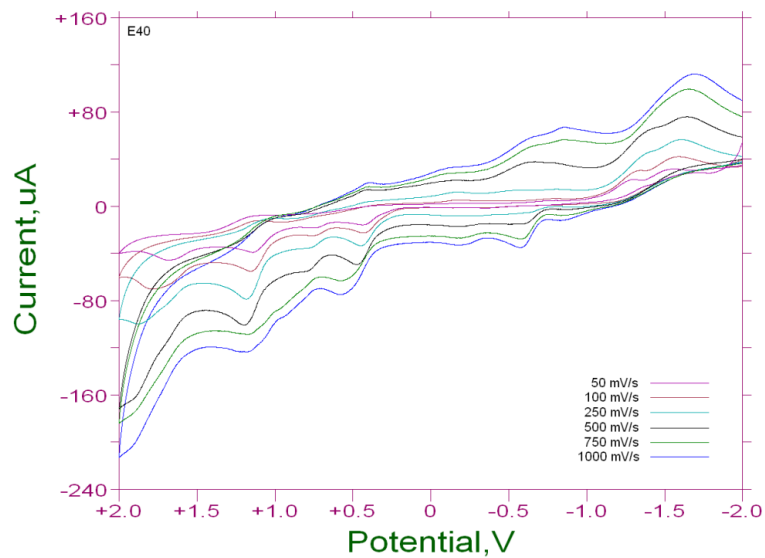


Figure 4: Cyclic Voltammogram for Ligand L¹

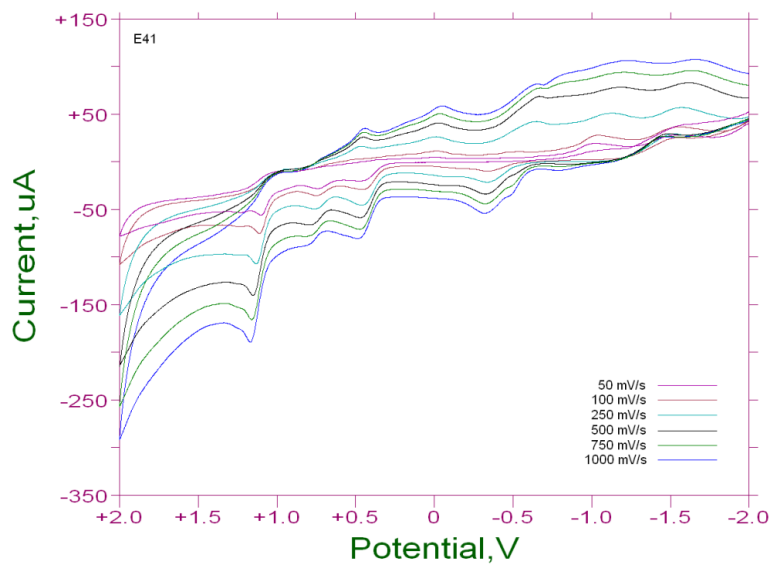


Figure 5: Cyclic Voltammogram for Ligand L²

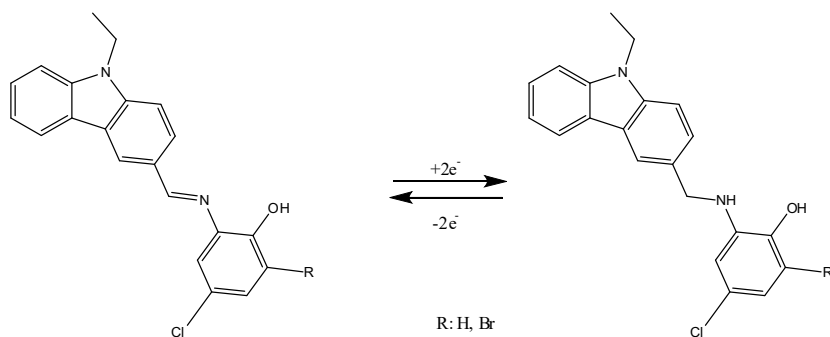


Figure 6: Redox scheme for L¹ and L²

3.4. Catalytic activity

Catalytic activities of the synthesized coordination compounds revealed high performances towards the oxidation reactions of styrene and cyclohexene (Tables 4 and 5). Among the complexes of our ligands, Manganese (II) complexes were the most effective catalysts in the alkene oxidations. In literature, although different oxidants used, Manganese complexes of similar Schiff bases revealed high styrene oxide yields as catalysts in the oxidation reactions of styrene [42]. Styrene oxide selectivities for our Manganese complexes of L¹ and L² were recorded as 58.7% and 55.2% and the same complexes gave cyclohexene oxide selectivities as 40% and 42.7% respectively. Cobalt (II) complex of the ligands showed slightly more activity than the Nickel (II) complex in the oxidation reactions of styrene. On the other hand, their catalytic activities were quite similar in cyclohexene oxidations. Compared to our previous study [43] and some other studies [44, 45], although different oxidants and conditions used, high selectivities were obtained in our studies in the oxidation reactions of both styrene and cyclohexene.

Table 4: Styreneoxidation results

	Catalyst	Styrene Conversion (%)	Selectivity (%) StyreneOxide	Benzaldehyde	BenzoicAcid	Others
1	Mn(L ¹ H) ₂ (OAc) ₂	80.9	58.7	35.0	4.2	2.1
2	Ni(L ¹ H) ₂ (OAc) ₂	67.2	38.7	41.4	9.6	10.3
3	Co(L ¹ H) ₂ (OAc) ₂	71.3	42.9	37.6	11.1	8.4
4	Mn(L ² H) ₂ (OAc) ₂	78.7	55.2	33.6	5.7	5.5
5	Ni(L ² H) ₂ (OAc) ₂	66.5	34.5	47.2	10.3	8.0
6	Co(L ² H) ₂ (OAc) ₂	70.0	40.0	35.4	13.3	11.3

Others: Phenylacetaldehyde, 1-phenylethane-1,2-diol

Reaction temperature: 70 °C (343.15 K), Solvent: Acetonitrile

Table 5: Cyclohexeneoxidation results

	Catalyst	Cyclohexene Conversion (%)	Selectivity (%) Cyclohexeneoxide	2-Cyclohexene-1-ol	Others
1	Mn(L ¹ H) ₂ (OAc) ₂	70.1	40.0	22.2	37.8
2	Ni(L ¹ H) ₂ (OAc) ₂	65.7	30.4	19.5	50.1
3	Co(L ¹ H) ₂ (OAc) ₂	62.3	33.4	21.0	45.6
4	Mn(L ² H) ₂ (OAc) ₂	73.6	42.7	26.4	30.9
5	Ni(L ² H) ₂ (OAc) ₂	61.4	31.1	18.4	50.5
6	Co(L ² H) ₂ (OAc) ₂	60.5	28.8	20.6	50.6

Others: 2-Cyclohexene-1-one, 2-cyclohexene-1-hydroperoxide

Reaction temperature: 70 °C (343.15 K), Solvent: Acetonitrile

4. Conclusion

With this work, heading from N-ethylcarbazole, two novel Schiff bases and their Cobalt (II), Nickel (II) and Manganese (II) complexes have been synthesized. All the spectral analysis supported the proposed structures of these newly synthesized compounds. All the synthesized

compounds have also been examined for their catalytic, thermal and electronic features. Good results have been obtained for the catalytic activities of the complex compounds in alkene oxidation reactions, especially Manganese (II) complex was the most effective in these reactions as catalyst.

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