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Synthesis of carbazole-derived ligands and their metal complexes: characterization, thermal, catalytic, and electrochemical features

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Abstract Heading from *N*-ethylcarbazole, two novel carbazole-derived imine compounds and their copper, cobalt, and nickel complexes have been synthesized. Their open structures have been proposed on the basis of various spectroscopic analyses. All the synthesized compounds have also been examined for their catalytic, thermal, and electronic features. Good or moderate results have been obtained for the catalytic activities of the synthesized complexes. Thermal features showed that the coordination compounds can be used in many organic reactions like oxidation reactions depending on high temperatures. Electronic features of these newly synthesized compounds have also been reported for the first time with this paper.

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Graphical abstract



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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 much attention in the fields relating antimicrobial activity and catalytic activity especially in the reactions including alkene epoxidations [1–6] and epoxide ring openings [7–9]. Epoxides are the cyclic ethers produced by oxidation reactions of alkenes. An important method for preparing epoxides is by reaction with peroxyacids. In the literature, various oxidation reagents have been used in many oxidation reactions of different alkenes. However, it is important that the reagents used are cheap and environmentally friendly and this is why hydrogen peroxide is generally preferred as oxidating agent in these kinds of reactions. Epoxidation of alkenes is also an important biochemical reaction. For example, epoxidation of an alkene group in a precursor molecule called squalene is a key step in the pathway by which our bodies synthesize cholesterol. 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 toward the oxidation reactions of both cyclohexene and styrene [10]. Schiff base complexes were and are still being examined for their catalytic activities toward many different organic reactions [11–15]. Literature survey also shows that imines and their complexes have been extensively studied for their antibacterial, antifungal, antitumor, and anticancer activities [16-19]. Many studies [20, 21] have shown the relationships between the metal ions and their metal complexes as antibacterial agents, which is a subject of great interest. This work, first of all, deals with the synthesis and purification of 9-ethyl-3-carbazolecarboxaldehyde from N-ethylcarbazole. Then, it moves on to the synthesis and characterization of the two novel Schiff bases and their copper(II), cobalt(II), and nickel(II) coordination compounds. Fully characterized new coordination compounds were used as catalysts in the epoxidation reactions of styrene and cyclohexene, which are important intermediates in the synthetic routes of different organic chemicals. In addition to their catalytic activities, thermal and electronic features of the newly synthesized compounds have also been explained for the first time.

Results and discussion

Spectral analysis

Proton NMR spectra of the synthesized ligands (Scheme 1) gave quite similar signals. For example, we can see the ethyl group attached to nitrogen on the carbazole unit at around 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 the ligands L^1 and L^2 were seen at 8.84 and 8.85 ppm, respectively. Among the carbazole aromatic ring protons in ligand L¹, next to the imine proton signal, the doublet at 8.61 ppm (d, J = 1.2 Hz) belongs to H-4 and the two signals appearing next to H-4 belongs to H-1 (8.2 ppm, d, J = 8.6 Hz) and H-2 (8.1 ppm, dd, J = 8.6 Hz, 1.5 Hz). We can see the other aromatic protons between 6.5 and 7.8 ppm for both ligands. We could clearly see the phenolic aromatic protons H-19 and H-20, belonging L^1 , at 6.97 ppm (d, J = 8.1 Hz) and at 7.04 ppm (dd, J = 7 Hz, 0.5 Hz). The broad singlet seen at 7.2 ppm belongs to H-22. The methyl protons on the phenolic ring in the same ligand (L^{1}) appeared as a sharp singlet at 2.4 ppm. As for the ligand L^2 , we could see the phenolic aromatic protons H-20 and H-21 as doublet of triplets at 6.97 and 7.22 ppm. The other two aromatic protons on the same ring gave overlapped doublet at 7.09 ppm. Both ligands showed the hydroxyl proton at 10.1 ppm as a weak singlet. ¹³C NMR spectra of the ligands revealed the imine carbon signals at 157.8 ppm for L^1 and at 158.2 ppm for L^2 . The ethyl group on the carbazole unit was seen at 37.8 and 13.8 ppm for both ligands. For ligand L^1 , the methyl group on the phenolic ring was at 20.9 ppm. The rest of the aromatic carbons were seen between 100 and 150 ppm.

In the IR spectra of the ligands L^1 and L^2 , we were able to see weak signals at 1628 and 1622 cm⁻¹, respectively, corresponding the imine stretching frequency. This vibration was red-shifted in its complexes. Aromatic C-H vibrations were seen at around 3050 cm⁻¹ and the aliphatic vibrations were between 2918 and 2973 cm⁻¹. Although the NMR spectrum of the ligands gave hydroxyl signals at 10.1 ppm, the IR spectrum of them gave weak broad peak at around 3350 and 3374 cm⁻¹; however, many sharper peaks were observed at 1262 and 1328 cm⁻¹ for O-H bendings. In all of their complexes, hydroxyl stretchings were also observed above 3200 cm⁻¹. However, this time, the hydroxyl stretchings were somewhat shifted than those of the ligands, which proves the chelation between the metals and the hydroxyls present on the phenolic rings. In the IR spectra of the ligands and their complexes, we were also able to observe some out-of-plane C-H bending vibration, which tells us about the substitution patterns of the benzene rings. In our compounds, we have three aromatic rings and the weak vibrations seen at 839 (L¹), at 901 cm⁻¹ (L¹-Co and L¹-Cu), and at 888 cm⁻¹ (L¹-Ni) correspond our two meta-substituted benzene ring containing one isolated hydrogen. The sharp signals at 745 cm⁻¹ (L¹), 747 cm⁻¹ (L¹-Co and L¹-Cu), and 746 cm⁻¹ (L¹-Ni) proves that we have one *ortho*-substituted benzene ring. Similar values were seen in the IR spectra of ligand L^2 and its complexes. IR spectra of all coordination compounds showed M-N stretching frequencies between 536 and 539 cm^{-1} . We were able to observe M–O stretching frequencies both as asymmetric and as symmetric in the ranges 611–613 and 583–589 cm^{-1} , respectively [24].

Other than the sharp peak at around 747 cm⁻¹, corresponding to the ortho-substituted benzene ring, 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. And the splitting value of carboxylate stretching bands $(\Delta = V_{as} - V_s)$ is frequently used to attempt to distinguish between the three carboxylate coordination modes [25]. Deacon and Phillips [26] 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 Scheme 1



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.

UV-Vis spectra of the ligands and the complexes showed absorption bands between 208 and 434 nm. The

spectra of the complexes showed some bands in the highenergy region at 309–332 nm which can be assigned to charge transfer L-M bands [27, 28]. The complex compounds showed d-d transitions between 423 and 434 nm.

The EDAX spectra of all the coordination compounds 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. While the EDAX images confirm the existence of the metals and the purity of the

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

Complex	$V_{\rm asymmetric}$	$V_{\rm symmetric}$	$\Delta (V_{asym} - V_{sym})$
$Co(L^1H)_2(OAc)_2$	1681, 1579	1232	449, 347
$Cu(L^1H)_2(OAc)_2$	1680, 1579	1232	448, 347
Ni(L ¹ H) ₂ (OAc) ₂	1680, 1567	1229	451, 338
$Co(L^2H)_2(OAc)_2$	1681, 1574	1234	447, 340
$Cu(L^2H)_2(OAc)_2$	1681, 1574	1232	449, 342
Ni(L ² H) ₂ (OAc) ₂	1679, 1575	1230	449, 345

complexes, SEM photographs display uniform and homogeneous matrixes of the synthesized complexes. SEM photographs and EDAX graphics of coordination compounds $Co(L^1H)_2(OAc)_2$ and $Cu(L^2H)_2(OAc)_2$ are given in Figs. 1 and 2.

Additionally, spectrochemical analyses by energy dispersive X-ray fluorescence (EDXRF) were performed on all the coordination compounds 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 [29, 30]. 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 [31]. 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, copper, and nickel. The results are given in Table 2 and they are in good agreement with the calculated values.

Mass spectra of the synthesized ligands and their complexes showed parent ion peaks as well as some other peaks belonging to different fragments suitable to the proposed structures. For example, the mass spectra of all the coordination compounds of L¹ showed a mass peak at m/z = 327corresponding to the ligand itself (C₂₂H₂₀N₂O). And since there are two of L¹ in the complexes, another peak at around m/z = 654 was also seen in the mass spectra of Co(II) and Cu(II) coordination compounds of this ligand. For all the complexes of L², the mass peaks for the two phenolic groups were clearly observed at around m/z = 186.

Magnetic susceptibility studies revealed the geometries of all the complexes to be octahedral. For the copper complexes, the magnetic moments were calculated as 2.03 and 1.91 B.M. [32]. The cobalt complexes gave these values as 5.08 and 4.98 B.M [33]. The nickel complexes also revealed their characteristic magnetic moment values as 3.4 and 4.1 B.M., suggesting octahedral geometry [33, 34]. Molar conductivities of the ligands and their coordination compounds were between 1.5 and 25.4 Ω^{-1} cm² mol⁻¹, which proves their nonelectrolite features [35].

Thermal analysis

Thermal analysis of the Schiff base ligands and their complexes was studied from ambient temperature to 800 °C in nitrogen atmosphere. Thermal analysis of the ligands gave two degradation steps, and between two Schiff bases,



Fig. 1 EDAX spectrum of complex Co(L¹H)₂(OAc)₂ and its SEM photograph



Fig. 2 EDAX spectrum of complex Cu(L²H)₂(OAc)₂ and its SEM photograph

Table 2 Metal percentages estimated by EDXRF

Compound	Chemical formula	Calculated value/%	Experimental values (EDXRF)/%
Co(L ¹ H) ₂ (OAc) ₂	C48H44CoN4O6	7.08	7 ± 0.3
Cu(L ¹ H) ₂ (OAc) ₂	$\mathrm{C}_{48}\mathrm{H}_{44}\mathrm{CuN}_{4}\mathrm{O}_{6}$	7.6	8 ± 0.3
Ni(L ¹ H) ₂ (OAc) ₂	C48H44N4NiO6	7.06	7 ± 0.3
Co(L ² H) ₂ (OAc) ₂	$\mathrm{C}_{46}\mathrm{H}_{40}\mathrm{CoN}_{4}\mathrm{O}_{6}$	7.33	7 ± 0.3
$Cu(L^2H)_2(OAc)_2$	$\mathrm{C}_{46}\mathrm{H}_{40}\mathrm{CuN}_{4}\mathrm{O}_{6}$	7.86	8 ± 0.3
Ni(L ² H) ₂ (OAc) ₂	$\mathrm{C}_{46}\mathrm{H}_{40}\mathrm{N}_4\mathrm{NiO}_6$	7.3	7 ± 0.3

L¹ was the most stable ligand with a degradation starting temperature of 200 °C. While L¹ gives the loss of phenolic group, which has the imine group attached, in the first half of the degradation, L² gives this loss in the second half of its thermal graphic. Carbazole losses were also observed as vice versa in the thermal graphics of L¹ and L². Residual part of L¹ gave the ethyl group on the carbazole unit; however, for L², the calculations for the residual part corresponded only the methyl part in the ethyl group. Overall, the degradation of the two ligands was happened in a total mass loss of 100 %.

All coordination compounds, except Ni(L¹)₂(AcO)₂, showed two degradation steps in their TG graphics. Nickel (II) complex of L¹ gave somewhat distorted three degradation steps, the first one happens between 130 and 325 °C with a mass loss of 25.4 % (calc. 25.7 %) attributed to two phenolic groups (2 × C₇H₇O). The second loss with 20.9 % (calc. 21.2 %) corresponds to the two acetates and the ethyl groups on the two carbazole units. Finally, the carbazole unit $(2 \times C_{12}H_7N)$ losses were observed between 420 and 625 °C with a total mass loss of 39.1 % (calc. 39.7 %). The residual parts of the coordination compounds of L¹ revealed the two imine groups (2 × CH=N) and the oxidized metals; however, in addition to these parts, cobalt complex of L¹ showed the two acetates as one of its residuals too. Ligand L¹ was more temperature resistant than its complexes.

TG graphics of L^2 and its complexes revealed mass losses in two degradation steps, and among the complexes of L^2 , cobalt and copper complexes were slightly more stable toward temperature than the ligand itself and nickel complex of it. The first degradation steps of nickel and copper complexes of L^2 gave mass losses of 43.9 % (calc. 44.3 %) and 51.8 % (calc. 51.2 %), respectively, corresponding to phenolic groups with imines attached, two acetates, and the ethyl groups on carbazoles. However, the mass loss for the two ethyl groups for the nickel complex of L^2 was calculated in the residual part. Generally, all the complexes of this ligand gave similar patterns in their thermal graphics, and only the cobalt complex of L^2 revealed the biggest mass loss of 69.8 % (calc. 70.6 %) attributed to two carbazoles $(2 \times C_{12}H_7N)$ and two phenolic groups with imines in the temperature range 260-600 °C. And we could see the metallic cobalt for this complex in the residual part with a percentage of 7.4 % (calc. 7.3 %). The loss of carbazole units was calculated and found around 40 % in TG graphics of all the coordination compounds and they were generally observed in the second degradation part of all the TG graphics (Figs. 3, 4).





Fig. 4 TGA graphics of L^2 and its complexes

Catalytic activity

In both styrene and cyclohexene oxidation reactions, all synthesized complexes showed good performances as catalysts. In the styrene oxidation reaction, generally we obtained high percentages for styrene conversion. The highest ones among these percentages belong to Ni(II) complex of L¹ and Co(II) complex of L², 71.2 and 68.7 %, respectively. Therefore, styrene oxide selectivities for these complexes were also slightly higher compared with the other coordination compounds. The lowest styrene oxide selectivity with 27.5 % belongs to Co(II) complex of L¹. In the cyclohexene oxidation reactions, all the coordination compounds gave moderately good selectivities for

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Table 3Styrene oxidationresults

Entry	Catalyst	Styrene conversion/%	Selectivity/%			
			Styrene oxide	Benzaldehyde	Benzoic acid	Others
1	Ni(L ¹) ₂ (OAc) ₂	71.2	43.3	46.7	6.4	3.6
2	$Cu(L^1)_2(OAc)_2$	66.4	40.1	44.6	10.3	5.0
3	$Co(L^1)_2(OAc)_2$	35.5	27.5	62.5	5.7	4.3
4	Ni(L ²) ₂ (OAc) ₂	41.4	33.9	51.1	8.9	6.1
5	$Cu(L^2)_2(OAc)_2$	56.4	36.2	46.8	11.2	5.8
6	$Co(L^2)_2(OAc)_2$	68.7	39.4	45.4	10.3	4.9

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

Reaction temperature: 80 °C (353.15 K)

Solvent: acetonitrile

Table 4 Cyclohexene oxidation results	Entry Catalyst	Catalyst	Cyclohexene conversion/%	Selectivity/%		
			Cyclohexene oxide	2-Cyclohexene-1-ol	Others	
	1	Ni(L ¹) ₂ (OAc) ₂	43.1	31.1	10.7	58.2
	2	$Cu(L^1)_2(OAc)_2$	40.8	28.4	14.3	57.3
	3	$Co(L^1)_2(OAc)_2$	32.1	25.7	19.8	54.5
	4	$Ni(L^2)_2(OAc)_2$	35.4	23.2	21.6	55.2
	5	$Cu(L^2)_2(OAc)_2$	39.7	27.7	18.5	53.8
	6	$Co(L^2)_2(OAc)_2$	38.3	28.3	20.9	50.8

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

Reaction temperature: 80 °C (353.15 K)

Solvent: acetonitrile

cyclohexene oxide. The highest cyclohexene conversions were obtained for Ni(II) and Co(II) complex of L^1 with percentages of 43.1 and 40.8, respectively. In general, Ni (II) complex of both ligands showed good catalytic activity in the oxidation reactions of both styrene and cyclohexene. The results for these reactions can be seen in Tables 3 and 4, and the oxidation reaction schemes are given in Scheme 2.

Cyclic voltammetry analysis

Cyclic voltammograms of the ligands and their complexes were run in DMF—0.1 M Bu₄NBF₄ and CH₃CN—0.1 M Bu₄NBF₄ as supporting electrolyte at 293 K. All potentials quoted refer to measurements run at a scan rates (*V*) of 100, 250, 500, 750, and 1000 mV s⁻¹ and against an internal ferrocene–ferrocenium standard, unless otherwise stated. For the scan rates 100, 250, and 500 mV s⁻¹, our ligand L¹ showed reversible redox processes, e.g., for the scan rate 100 mV s⁻¹, anodic peak potential was recorded as 0.56 V and the reverse scan gave the cathodic peak at 0.58 V. The ratio between the anodic and cathodic peak potentials was calculated as $I = I_{pa}$: $I_{pc} = 0.97$ (1), proving the reversible process. Also, for the same ligand, the scan rate 250 mV s⁻¹ gave two reversible peak potentials; -0.21 and 0.56 V for the anodic peaks and -0.17 and 0.51 V for the cathodic peaks, the value between the anodic and cathodic potentials was calculated near 1. Similar potentials were recorded for this ligand in its 500 mV s⁻¹ scan rate (Fig. 5a). For 750 and 1000 mV s⁻¹ scan rates, same ligand gave quasi-reversible processes. Cobalt complex of ligand L¹ gave both reversible and irreversible potentials in all of its scan rates. Nickel complex of the same ligand, also, gave reversible redoxes in all of its scan rates except the scan rate 100 mV s⁻¹. Figure 6a shows CV graphics for Ni (L¹H)₂(OAc)₂ at 500 and 750 mV s⁻¹ scan rates. Copper complex of the same ligand also gave well-defined reversible processes for the scan rates 100, 250, and 1000 mV s⁻¹. For this complex, irreversible processes were recorded for the other scan rates.

Electronic graphics of L^2 revealed irreversible redox processes in 100 and 1000 mV s⁻¹; however, it showed E_{pa} values at 0.56, 0.67 V and E_{pc} values at 0.59, 0.63 V for scan rates 250 and 500, respectively, whose I_{pa} : I_{pc} values equaled 1, proving their reversibility (Fig. 5b). Among the coordination compounds of ligand L^2 , only the copper and cobalt complexes revealed well-defined reversible processes in most of their scan rates, and only the scan rates 100 and 250 mV s⁻¹, for these complexes, showed irreversible or pseudo-reversible redoxes. Nickel complex of





Fig. 6 CV graphics of Ni(L^1)₂(OAc)₂ (a) and Co(L^2)₂(OAc)₂ (b) for scan rates 500 and 750 mV s⁻¹

this ligand, however, mostly revealed irreversible or semireversible redox procedures for all of its scan rates. For the cobalt complex of L^2 , the CV graphics for the scan rates 500 and 750 mV s⁻¹ are given in Fig. 6b.

Conclusion

The present work describes the synthesis and characterization of two carbazole-derived Schiff bases and their copper(II), cobalt(II), and nickel(II) coordination compounds. All spectral data and the thermal analysis supported the proposed structures of the newly synthesized compounds. Magnetic moment values strongly suggested the geometries of the coordination compounds to be octahedral. In thermal analysis, the coordination compounds of L^2 , especially the copper(II) and cobalt(II) complexes, were the most stable coordination compounds, compared with the others. However, as for the ligands, L^1 was much more temperature resistant than L^2 . As a catalyst, nickel(II) coordination compound of L¹ showed higher conversion percentages in the oxidation reactions of styrene and cyclohexene compared with the other coordination compounds that we have synthesized.

Experimental

9-Ethylcarbazole, phosphorus(V) oxychloride, 2-amino-4methylphenol, 2-aminophenol, acetate salts of copper(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 CDCl₃. Infrared spectra were obtained using KBr disks on a Shimadzu 8300 FT-IR spectrophotometer in the region of $400-4000 \text{ cm}^{-1}$. Ultraviolet spectra were run in ethanol on a Schimadzu UV-160 A spectrophotometer. Mass spectra of the ligand and the complexes were recorded on a LC/MS APCI AGILENT 1100 MSD spectrophotometer. The oxidation products were analyzed with a gas chromatograph (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 aqua regia and subsequently digesting them in conc. HCl. Chemical composition analysis by EDAX was performed with an EDAX; Rönteck xflash detector analyzer was associated with a scanning electron microscope (SEM, Leo-Evo 40xVP). The energy spectrum of characteristic X-rays is measured with Bruker energy dispersive X-ray spectroscope (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 PerkinElmer Thermogravimetric Analyzer TG/DTA 6300 instrument under nitrogen atmosphere between the temperature range 30 and 800 °C at a heating rate of 10 °C/min. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)₄] as calibrant. Molar conductances of the Schiff base ligands and their transition metal complexes were determined in MeOH (ca. 10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter.

Synthesis of the ligands

Formylation of 9-ethylcarbazole was done by using Vilsmeier formylating agent DMF and POCl₃ [10, 22, 23]. The monoaldehyde was separated by flash chromatography with ethyl acetate/hexane (1:10) as eluent. *N*-Ethylcarbazole-3-carbaldehyde (1 mmol) was then reacted with 1 mmol 2-amino-4-methylphenol to give (*E*)-2-[(9-ethyl-9*H*-carbazol-3-yl)methyleneamino]-4-methylphenol (L^1) and with 1 mmol 2-aminophenol to give (*E*)-2-[(9-ethyl-9*H*-carbazol-3-yl)methyleneamino]phenol. Reactions were carried out in 30 cm³ ethanol under reflux for 9 h. The resulting precipitates were recrystallized from methanol.

(*E*)-2-[[(9-Ethyl-9H-carbazol-3-yl)methylene]amino]-4methylphenol (L^1 , $C_{22}H_{20}N_2O$)

Yield 2.7 g (80 %); m.p.: 177 °C; ¹H NMR (400 MHz, $CDCl_3$): $\delta = 10.1$ (s, OH), 8.84 (s, H-16), 8.61 (d, J = 1.2 Hz, H-4), 8.20 (d, J = 8.6 Hz, H-1), 8.10 (dd, J = 8.6, 1.5 Hz, H-2, 7.55 (ddd, J = 8.0, 7.0, 1.2 Hz, H-7), 7.45 (d, J = 7.4 Hz, H-5 overlapped with H-8), 7.45 (d, J = 8 Hz, H-8 overlapped with H-5), 7.34 (ddd, J = 7.6, 7.1, 1.2 Hz, H-6), 7.20 (brs, H-22), 7.04 (dd, J = 7.0, 0.5 Hz, H-20), 6.97 (d, J = 8.1 Hz, H-19), 4.42 (q, J = 7.2 Hz, 2H-14), 2.40 (s, 3H-23), 1.50 (t, J = 7.2 Hz, 3H-15) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.8$ (C-16), 149.8 (C-18), 142.0 (C-10), 140.5 (C-13), 135.9 (C-17), 129.3 (C-22), 128.5 (C-3), 127.4 (C-1), 126.4 (C-2), 123.3 (C-4), 123 (C-11), 122.3 (C-12), 120.7 (C-5), 119.8 (C-6), 116.4 (C-20), 114.4 (C-19), 108.8 (C-7), 108.9 (C-8), 37.8 (C-14), 20.9 (C-23), 13.8 (C-15) ppm; FT-IR (KBr): $\overline{v} = 3350$ (OH), 3047 (C–H_{Ar}), 2973, 2920 (C–H), 1628 (CH=N), 1596 (C=CAr), 1328, 1262 (OH bending) cm⁻¹; UV–Vis (ethanol): $\lambda_{max} = 231, 274, 300, 331$ nm; MS: $m/z = 328.2 \text{ (M}^+\text{)}; \Lambda_M = 1.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

(E)-2-[[(9-Ethyl-9H-carbazol-3-yl)methylene]amino]phenol (L², C₂₁H₁₈N₂O)

Yield 2.1 g (76 %); m.p.: 191.2 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 10.1$ (s, OH), 8.85 (s, H-16), 8.62 (d, J = 1.3 Hz, H-4), 8.20 (d, J = 8.0 Hz, H-1), 8.12 (dd, J = 8.5, 1.4 Hz, H-2), 7.55 (dt, J = 8.2, 1.2 Hz, H-7), 7.46 (d, J = 8.5 Hz, H-5 overlapped with H-8), 7.46 (d,J = 8.5 Hz, H-8 overlapped with H-5), 7.35 (dt, J = 7.5, 1.1 Hz, H-6), 7.22 (dt, J = 8.0, 1.4 Hz, H-21), 7.09 (d, J = 8.0, 1.2 Hz, H-19 overlapped with H-22), 7.09 (dd, J = 8.0, 1.2 Hz, H-22), 6.97 (dt, J = 7.4, 1.4 Hz, H-20), 4.41 (q, J = 7.2 Hz, 2H-14), 1.50 (t, J = 7.3 Hz, 3H-15) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$ (C-16), 152.1 (C-18), 142.2 (C-10), 140.6 (C-13), 136.3 (C-17), 128.0 (C-3), 127.2 (C-1), 126.4 (C-2), 123.3 (C-4), 123.1 (C-11), 122.4 (C-12), 120.8 (C-5), 120.1 (C-21), 120.1 (C-22), 119.9 (C-6), 115.9 (C-20), 114.8 (C-19), 109.0 (C-8), 108.8 (C-7), 37.8 (C-14), 13.8 (C-15) ppm; FT-IR (KBr): $\overline{v} = 3374$ (OH), 3047 (C–H_{Ar}), 2970, 2918 (C–H), 1622 (CH=N), 1583 (C = C_{Ar}), 1323, 1282 (OH bending) cm⁻¹; UV–Vis (ethanol): $\lambda_{max} = 209$, 234, 292, 331 nm; MS: $m/z = 314.1 \text{ (M}^+); \Lambda_M = 1.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$

Synthesis of the complexes

The ligand L^1 or L^2 (2 mmol) was taken into a 100-cm³ round-bottomed flask and dissolved in 20 cm³ ethanol. Over this solution, 1 mmol of the acetate salt of the desired metal dissolved in 25 cm³ ethanol was poured. The mixture was left stirring under reflux for 24 h. The resulted precipitates were then recrystallised from methanol/ethanol (1:1) mixture.

Di[(E)-2-[[(9-ethyl-9H-carbazol-3-yl)methylene]amino]-4methylphenol]cobalt(II) acetate (C₄₈H₄₆CoN₄O₆)

Yield 1.6 g (70 %); m.p.: 201 °C; IR (KBr): $\bar{\nu} = 3320$ (OH), 3051 (C–H_{Ar}), 2973, 2920 (C–H), 1621 (CH=N), 1588 (C=C_{Ar}), 1681, 1579 (ν_{as} , COO⁻), 1232 (ν_{s} , COO⁻), 613 (ν_{as} , M–O), 589 (ν_{s} , M–O), 538 (M–N) cm⁻¹; UV–Vis (ethanol): $\lambda_{max} = 234$, 274, 290, 331, 430 nm; MS: m/z = 832.0 ([M-H]⁺); $\Lambda_{M} = 23.1 \ \Omega^{-1} \ cm^{2} \ mol^{-1}$; $\mu_{eff} = 5.08 \ B.M.$

Di[(E)-2-[[(9-ethyl-9H-carbazol-3-yl)methylene]amino]-4methylphenol]copper(II) acetate (C₄₈H₄₆CuN₄O₆)

Yield 1.67 g (73 %); m.p.: 210 °C; IR (KBr): $\bar{\nu}$ = 3318 (OH), 3053 (C–H_{Ar}), 2918, 2850 (C–H), 1620 (CH=N), 1588 (C=C_{Ar}), 1680, 1579 (*v*_{as}, COO⁻), 1232 (*v*_s, COO⁻), 613 (*v*_{as}, M–O), 589 (*v*_s, M–O), 538 (M–N) cm⁻¹; UV–Vis (ethanol): λ_{max} = 234, 274, 291, 331, 429 nm; MS: *m/z* = 837.2 (M⁺); Λ_{M} = 15.6 Ω⁻¹ cm² mol⁻¹; μ_{eff} = 2.03 B.M.

Di[(E)-2-[[(9-ethyl-9H-carbazol-3-yl)methylene]amino]-4-methylphenol]nickel(II) acetate (C₄₈H₄₆N₄NiO₆)

Yield 1.55 g (68 %); m.p.: 205 °C; IR (KBr): $\overline{\nu} = 3321$ (OH), 3047 (C–H_{Ar}), 2971, 2919 (C–H), 1618 (CH=N), 1587 (C=C_{Ar}), 1680, 1567 (ν_{as} , COO⁻), 1229 (ν_{s} , COO⁻),

613 (*v*_{as}, M–O), 587 (*v*_s, M–O), 539 (M–N) cm⁻¹; UV–Vis (ethanol): *λ*_{max} = 234, 276, 290, 332, 423 nm; MS (70 eV): $m/z = 833.0 (M^+)$; $A_M = 17.1 \Omega^{-1} cm^2 mol^{-1}$; $\mu_{eff} = 3.4 B$. M.

Di[(E)-2-[[(9-ethyl-9H-carbazol-3-yl)methylene]amino]phenol]cobalt(II) acetate (C₄₆H₄₂CoN₄O₆)

Yield 1.65 g (72 %); m.p.: 208.5 °C; IR (KBr): $\bar{\nu}$ = 3323 (OH), 3051 (C–H_{Ar}), 2918, 2850 (C–H), 1620 (CH=N), 1584 (C=C_{Ar}), 1681, 1574 (ν_{as} , COO⁻), 1234 (ν_{s} , COO⁻), 613 (ν_{as} , M–O), 583 (ν_{s} , M–O), 538 (M–N) cm⁻¹; UV–Vis (ethanol): λ_{max} = 235, 276, 291, 332, 434 nm; MS (70 eV): m/z = 803.1 ([M-2H]⁺); Λ_{M} = 25.4 Ω⁻¹ cm² mol⁻¹; μ_{eff} = 4.98 B.M.

Di[(E)-2-[[(9-ethyl-9H-carbazol-3-yl)methylene]amino]phenol]copper(II) acetate (C₄₆H₄₂CuN₄O₆)

Yield 1.44 g (62 %); m.p.: 222.2 °C; IR (KBr): $\bar{\nu} = 3327$ (OH), 3051 (C–H_{Ar}), 2919, 2853 (C–H), 1618 (CH=N), 1585 (C=C_{Ar}), 1681, 1574 (ν_{as} , COO⁻), 1232 (ν_{s} , COO⁻), 612 (ν_{as} , M–O), 583 (ν_{s} , M–O), 536 (M–N) cm⁻¹; UV–Vis (ethanol): $\lambda_{max} = 235$, 277, 291, 331, 433 nm; MS: m/z = 811.8 ([M + H]⁺); $\Lambda_{M} = 20.3 \ \Omega^{-1} \ cm^{2} \ mol^{-1}$; $\mu_{eff} = 1.91 \ B.M.$

Di[(E)-2-[[(9-ethyl-9H-carbazol-3-yl)methylene]amino]phenol]nickel(II) acetate (C₄₆H₄₂N₄NiO₆)

Yield 1.2 g (65 %); m.p.: 211.0 °C; IR (KBr): $\bar{\nu} = 3324$ (OH), 3050 (C–H_{Ar}), 2974, 2919 (C–H), 1618 (CH=N), 1586 (C=C_{Ar}), 1679, 1575 (ν_{as} , COO⁻), 1230 (ν_{s} , COO⁻), 611 (ν_{as} , M–O), 583 (ν_{s} , M–O), 538 (M–N) cm⁻¹; UV–Vis (ethanol): $\lambda_{max} = 208$, 238, 276, 332, 434 nm; MS: m/z = 803.0 ([M-2H]⁺); $\Lambda_{M} = 16.1 \Omega^{-1} \text{ cm}^{2} \text{ mol}^{-1}$; $\mu_{eff-} = 4.1 \text{ B.M.}$

Oxidation procedure

A mixture of 1×10^{-3} mol catalyst, 20 cm³ solvent (CH₃CN), and 10 mmol cyclohexene/styrene was stirred under nitrogen atmosphere in a 50-cm³ round-bottomed flask. Then, 20 mmol of hydrogen peroxide (30 % in water) was added dropwise. The resulting mixture was vigorously stirred for 8 h at 80 °C. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis. The yields were recorded as the GC yield based on the starting styrene or cyclohexene. The identity of the oxidation products was confirmed by GC–MS.

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