

# Synthesis and characterization of copper(II), cobalt(II), nickel(II), and iron(III) complexes with two diamine Schiff bases and catalytic reactivity of a chiral diamine cobalt(II) complex

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**Abstract** New transition metal complexes of Co(II), Cu(II), Ni(II), and Fe(III) of the ligands 6,6'-(1E,1'E)-(4,5-dimethyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(7-hydroxy-5-methoxy-2-methyl-4H-chromen-4-one)  $H_2L^1$  and 6,6'-(1E,1'E)-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(7-hydroxy-5-methoxy-2-methyl-4H-chromen-4-one)  $H_2L^2$  have been prepared and characterized using physio-chemical and spectroscopic methods. The results obtained for the complexes indicated that the geometries of the metal centres are either square planar or octahedral. Cyclopropanation reactions of unactivated olefins by ethyldiazoacetate (EDA) in the presence of  $[L^1Cu] \cdot H_2O$ ,  $[L^2Cu] \cdot 2H_2O$  and  $[L^{2*}Co] \cdot 2H_2O$  as catalysts were examined. The results showed that only  $[L^{2*}Co] \cdot 2H_2O$  can act as a catalyst for the cyclopropanation reaction of unactivated olefins with very high selectivity (up to 99% based on EDA).

## Introduction

In the last decade, Schiff bases have received much attention, mainly because of their extensive application in the field of synthesis and catalysis [1, 2]. Their complexes have also been amongst the most widely studied coordination compounds in the past few years [3–5]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal-centered electronic

factors, and enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [6, 7]. They are also becoming increasingly important as biochemical, analytical, and antimicrobial reagents [8]. These ligands are readily available, versatile, and depending on the nature of the starting materials (primary amines and carbonyl precursors), they exhibit various functionalities. Moreover, the number, the nature, and the relative position of the donor atoms of Schiff base allow a good control over the stereochemistry of the metallic centers, as well as over the number of the metal ions within homo- and heteropolynuclear complexes [9, 10]. Several complexes coordinated through the Schiff base ONNO donors have been studied as oxygen carriers and they are useful models for bioinorganic processes [11]. The cobalt(II) and manganese(II) complexes with tetradentate Schiff bases which coordinate through  $N_2O_2$  donor atoms have been extensively studied as oxygen carriers and also as catalysts for water-splitting systems [12]. Further, significant advances have also been achieved in the field of straightforward preparation of new chiral ligands such as chiral diamines and complexes for asymmetric catalysis [13]. For example, complexes based on chiral diamines have been employed for chiral hydrogenations and transfer hydrogenations [14]. Both homogeneous and heterogeneous diamine complexes have proved highly effective in enantioselective catalysis [15, 16].

Chiral metal-catalyzed reactions are potent tools for the synthesis of useful chiral compounds. Thus, various chiral metal complexes have been synthesized and used as asymmetric catalysts [17]. Some of them show high asymmetric induction and can be applied to a wide range of asymmetric reactions. Chiral complexes of the well-known Schiff base salen constitute one such class of complexes: a wide variety of these complexes have been synthesized and

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successfully used as catalysts for a range of asymmetric reactions, such as epoxidation, aziridination, cyclopropanation, and so on [18, 19]. Although high enantioselectivity has been achieved in these transformations, some of the reactions are still unsatisfactory in terms of atom efficiency and environmental considerations, improvement of which is a key issue to realize a sustainable society from the synthetic viewpoint.

In view of the versatile importance of Schiff bases, their complexes and their use in homogeneous and heterogeneous catalysis [20] and in continuation of our recent research [21–23] on synthesis and characterization of new Schiff base complexes and their use as catalysts for cyclopropanation of olefins, we describe herein the synthesis and characterization of the tetradentate Schiff bases 6, 6'-(1E,1'E)-(4,5-dimethyl-1,2-phenylene)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(7-hydroxy-5-methoxy-2-methyl-4H-chromen-4-one)  $H_2L^1$  and 6,6'-(1E,1'E)-cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(7-hydroxy-5-methoxy-2-methyl-4H-chromen-4-one)  $H_2L^2$  and their Co(II), Cu(II), Ni(II), and Fe(III) complexes. The coordination behavior of these Schiff bases toward transition metals was investigated via the IR, molar conductance, and magnetic moment measurements.  $^{13}C$  NMR spectra were also obtained to determine the structures of the ligands and some of their complexes. The catalytic activity of complexes  $[L^1Cu].H_2O$  (**3**),  $[L^2Cu].2H_2O$  (**6**) and  $[L^{2*}Co].2H_2O$  (**9**) toward the decomposition of ethyl diazoacetate (EDA) in the presence of olefins to yield cyclopropane products has also been investigated. Although various methodologies are available today, the cycloaddition of carbenoids to C=C double bonds is practically the most important one to construct this class of compounds. Stereochemical control of these reactions, such as differentiation of the enantiotopic faces of the double bond or *cis-trans* selectivity imposed on the cyclopropanation reaction by

the presence of a substituent at the carbenoid carbon are the main issues [24, 25].

## Experimental

### Materials

All the reagents employed for the preparation of the ligands and their complexes were of the best grade available and used without further purification. 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde used for the synthesis of the ligands was prepared by oxidation of visnagin according to the reported method [26]. Unless otherwise stated, all catalytic tests were carried out under an atmosphere of purified dinitrogen using modified Schlenk techniques. Solvents were dried and distilled before use by standard methods. Benzene, cyclohexene, and 1-octene were distilled over sodium; styrene and  $\alpha$ -methyl styrene were distilled over calcium hydride and stored under dinitrogen.

### Physical measurements

The ligands and their metal complexes were analyzed for C, H, N, and M contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. Analytical and physical data of the ligands  $H_2L^1$  and  $H_2L^2$  and their metal complexes are reported in (Table 1). The metal ion contents of the complexes were also determined [27–29] by the previously reported methods [30, 31]. IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400–4,000  $cm^{-1}$  and in the 500–100  $cm^{-1}$  region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer.  $^1H$  and  $^{13}C$  NMR spectra were obtained

**Table 1** Analytical and physical data of the ligands  $H_2L^1$ ,  $H_2L^2$  and their metal complexes

No.	Ligand/complexes	Color	FW	Yield (%)	Analysis (%) / found (calcd)				Molar conductance $\Lambda_m$ ( $\Omega^{-1}cm^2mol^{-1}$ )
					C	H	N	M	
1	$H_2L^1$	Beige	568.6	72	67.3 (67.6)	5.1 (5.0)	4.9 (4.9)	–	–
2	$[L^1Ni].3H_2O$	Orange	679.3	78	57.0 (56.6)	4.7 (4.8)	4.0 (4.1)	8.5 (8.6)	13
3	$[L^1Cu].H_2O$	Violet	648.1	81	59.2 (59.3)	4.5 (4.4)	4.4 (4.3)	9.7 (9.8)	9
4	$H_2L^2$	Yellow	546.6	70	65.6 (65.9)	5.6 (5.5)	5.1 (5.1)	–	–
5	$[L^2Co(H_2O)_2].2H_2O$	Brown	675.6	64	53.1 (53.3)	5.3 (5.4)	4.1 (4.2)	8.7 (8.7)	11
6	$[L^2Cu].2H_2O$	Violet	644.1	80	56.8 (55.9)	5.0 (5.0)	4.3 (4.4)	9.8 (9.9)	10
7	$L^2Fe(H_2O)Cl$	Beige	653.9	72	55.0 (55.1)	4.7 (4.6)	4.3 (4.3)	8.4 (8.5)	9
8	$[L^2Ni].H_2O$	Orange	621.3	79	57.9 (58.0)	5.0 (4.9)	5.6 (4.5)	9.4 (9.5)	9
9	$[L^{2*}Co].2H_2O$	Orange	639.5	75	56.2 (56.3)	5.2 (5.0)	4.5 (4.4)	9.1 (9.2)	12

on Bruker Avance 300-DRX or Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. The mass spectra were run at 70 eV with HP MODEL: MS. 5988A and/or GCMS. Cap 1000 EX Shimadzu spectrometer using electron impact technique. The electronic spectra of the ligands and their complexes were obtained in Nujol mulls and in saturated DMSO solutions using a Shimadzu UV–240 UV–Visible recording spectrophotometer. Molar conductivities of the metal complexes in DMSO ( $10^{-3}$  M) were measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in Ohms and the molar conductivities were calculated according to the equation:  $\Lambda = V \times K \times M / w/g \times \Omega$ , where  $\Lambda$  is the molar conductivity ( $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ),  $V$  is the volume of the complex solution (mL),  $K$  is the cell constant  $0.92 \text{ cm}^{-1}$ ,  $Mw$  is the molecular weight of the complex,  $g$  is the weight of the complex, and  $\Omega$  is the resistance measured in Ohms. Magnetic moments at 298 K were determined using the Gouy method with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. The solid ESR spectra of the complexes were recorded with an ELEXSYS E500 Bruker spectrometer in 3-mm Pyrex tubes at 298 K. Diphenylpicrylhydrazide (DPPH) was used as a g-marker for the calibration of the spectra. Mass spectra of the solid ligand were recorded using a JEUL JMS-AX-500 mass spectrometer.

### Synthesis of the Schiff bases

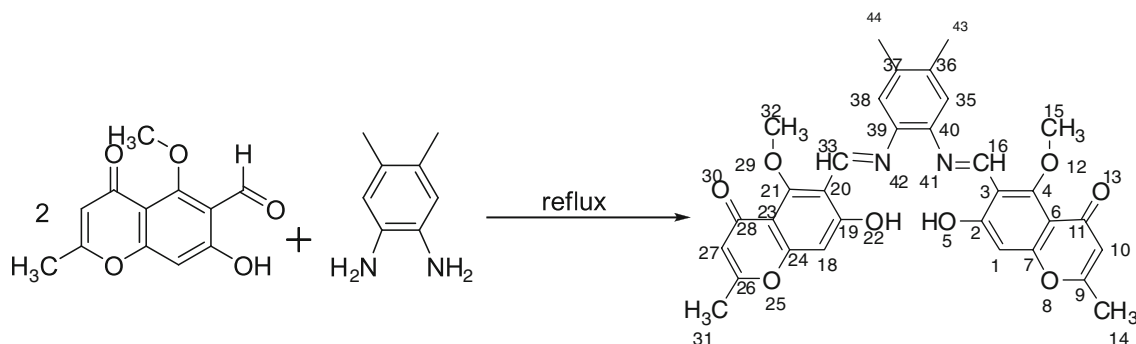
#### Synthesis of $\text{H}_2\text{L}^1$

A solution of 4,5-dimethylbenzene-1,2-diamine (0.15 g, 1.1 mmol) in ethanol (10 mL) was added dropwise to a hot ( $75^\circ\text{C}$ ) solution of 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde (0.5 g, 2.1 mmol) in ethanol (15 mL) and refluxed for 2 h. The reaction mixture was condensed to (10 mL) and the brown precipitate was then filtered off, washed with cold methanol, and dried under

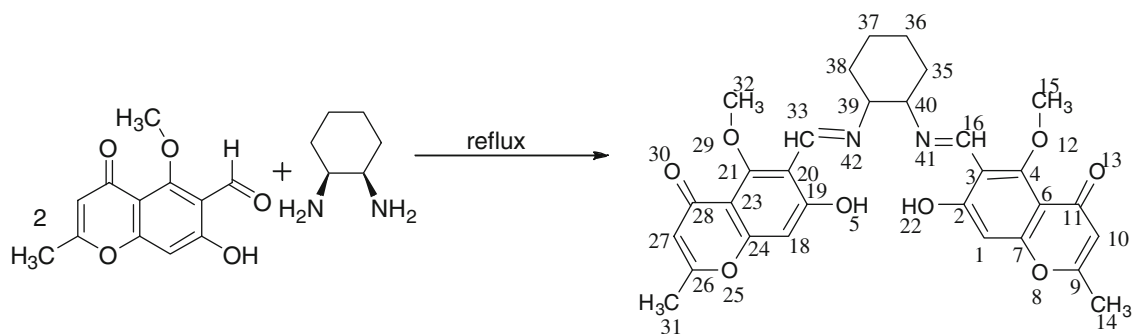
vacuum over anhydrous  $\text{CaCl}_2$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.74$  ppm [s, 2H, H(5) and H(22)], 9.11 ppm [s, 2H, H(16) and H(33)], 7.10 ppm [s, 2H, H(35) and H(38)], 6.74 ppm [s, 2H, H(1) and H(18)], 6.00 ppm [s, 2H, H(10) and H(27)], 4.01 ppm [s, 6H,  $-\text{OCH}_3$  (15) and  $-\text{OCH}_3$  (32)], 2.39 ppm [s, 6H,  $\text{CH}_3$  (43) and  $\text{CH}_3$  (44)], 2.33 ppm [s, 2H,  $\text{CH}_3$  (14) and  $\text{CH}_3$  (31)].  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ , 300 K): C(2) and C(19) 166.2, C(11) and C(28) 164.2, C(36) and C(37) 159.1, C(16) and C(33) 158.9, C(4) and C(21) 140.0, C(6) and C(23) 137.7, C(35) and C(38) 121.2, C(10) and C(27) 111.8, C(1) and C(18) 101.4, C(15) and C(32) 64.7, C(9) and C(26) 58.9, C(14), C(31), C(43), and C(44) 19.9 and 20.5 (Scheme 1).

#### Synthesis of $\text{H}_2\text{L}^2$

A solution of ( $\pm$ )-trans-1,2-diaminocyclohexane (in case of ligand ( $\pm$ ) $\text{H}_2\text{L}^2$ ) or (1R,2S)-cyclohexane-diamine (in case of ligand  $\text{H}_2\text{L}^{2*}$ ) (0.24 g, 2.1 mmol) in ethanol (5 ml) was added dropwise to a hot ( $75^\circ\text{C}$ ) solution of 7-hydroxy-5-methoxy-2-methyl-4-oxo-4H-chromene-6-carbaldehyde (1.00 g, 4.3 mmol) in ethanol (20 ml) and refluxed for 2 h. The yellow precipitate was then filtered off, washed with cold methanol, and dried under vacuum over anhydrous  $\text{CaCl}_2$ .  $^1\text{H}$ NMR (300 MHz, DMSO):  $\delta = 15.21$  [s, broad, H(5) and H(22)], 8.72 [s, 2H, H(16) and H(33)], 6.50 [m, 2H, H(1) and H(18)], 5.92 [s, 2H, H(10) and H(27)], 3.69 [s, 6H,  $-\text{OCH}_3$ (15) and  $-\text{OCH}_3$ (32)], 3.69 [s, 2H, H(39) and H(40)], 2.23 [s, 2H,  $\text{CH}_3$ (14) and  $\text{CH}_3$ (31)], 1.75 [s, 6H, H cyclohexyl].  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.94$  ppm [s, broad, H(5) and H(22)], 8.66 ppm [s, 2H, H(16) and H(33)], 6.59 ppm [m, 2H, H(1) and H(18)], 5.91 ppm [s, 2H, H(10) and H(27)], 3.76 ppm [s, 6H,  $-\text{OCH}_3$ (15) and  $-\text{OCH}_3$ (32)], 3.46 ppm [t, 2H,  $J = 7.6$ , H(39) and H(40)], 2.25 ppm [s, 2H,  $\text{CH}_3$ (14) and  $\text{CH}_3$ (31)], 1.85 ppm [s, 6H, H cyclohexyl].  $^{13}\text{C}$  NMR (300 MHz, DMSO, 300 K): C(2) and C(19) 168.1, C(11) and C(28) 164.4, C(16) and C(33) 162.7, C(4) and C(21)



**Scheme 1** Schematic representation for the formation of the Schiff base ligand  $\text{H}_2\text{L}^1$  and the numbering scheme for ligand  $\text{H}_2\text{L}^1$



**Scheme 2** Schematic representation for the formation of the Schiff base ligand  $H_2L^2$  and the numbering scheme for ligand  $H_2L^2$

145.4, C(6) and C(23) 142.6, C(10) and C(27) 110.9, C(1) and C(18) 101.4, C(39) and C(40) 69.8, C(15) and C(32) 63.7, C(35), C(38), C(36) and C(37) 24.2 and 32.3, C(14) and C(31) 20.2.  $\alpha D = +169.9$  (Scheme 2).

#### Synthesis of the metal complexes

The metal complexes of the ligands were prepared by mixing a hot (60 °C) methanolic solution of the metal salt with the required amount of a hot (75 °C) ethanolic solution of the ligand to form 1:1 (metal/ligand) complexes, as shown in (Table 2). The two cobalt complexes **5** and **9** were prepared and filtered off under dinitrogen atmosphere, since their solutions are sensitive to air but stable when they become dry. The reaction mixture was then refluxed for a time depending on the transition metal salt used. The precipitates formed were filtered off, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous  $CaCl_2$ .

#### Typical procedure for the catalytic cyclopropanation of olefins

EDA (see captions of Tables 5, 6 for quantities for  $[L^2*Co]$ .  $2H_2O$  (**9**)) was added to a suspension of the complex **3**, **6**,

or **9**, the olefin and 1-methylimidazol (NMI) in dichloroethane (10 mL) (only in case of complex **9**). The resulting pale violet or pale orange solution was heated at the required temperature under stirring. The reaction was followed until total consumption of the EDA (IR absorbance,  $\nu_{max} = 2114\text{ cm}^{-1}$ ,  $<0.025$ ) was observed. The final solution was analyzed by GC–MS after the addition of 2,4-dinitrotoluene as internal standard.

#### Results and discussion

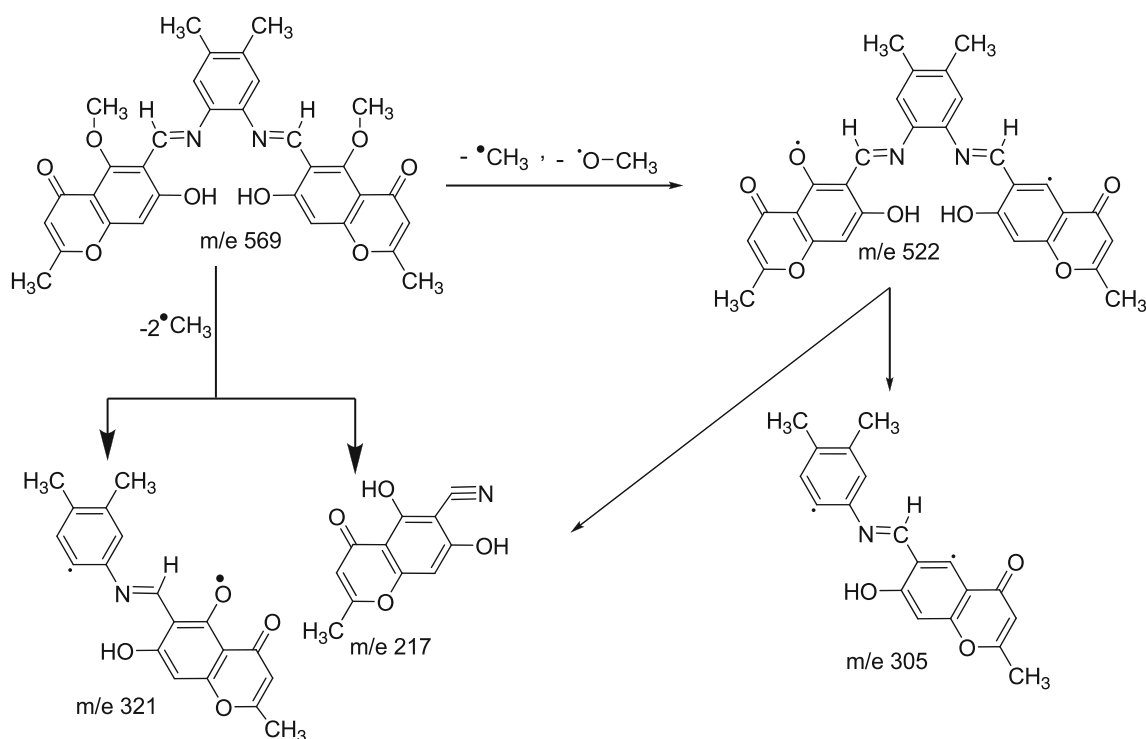
The elemental and physical data of the ligands  $H_2L^1$  and  $H_2L^2$  and their complexes (Table 1) showed that the stoichiometry of the complexes obtained is 1:1 (metal:ligand).

#### Mass spectra of the ligands

The mass spectra of the Schiff bases  $H_2L^1$  and  $H_2L^2$  revealed the molecular ion peaks at  $m/e$  569 and 547, which are coincident with the formulae weights (568.6) and (546.6), respectively, for these ligands and support the identity of their structures. The fragmentation pathway pattern of the mass spectrum of the ligands is depicted in Schemes 3 and 4.

**Table 2** Amounts of the reactants used in the formation of the metal complexes

No.	Complexes	Metal salt used	Metal chloride, in 10–20 mL methanol		Ligand in 10–25 mL ethanol	
			Mass (g) $\times 10^{-2}$	mmol $\times 10^{-2}$	Mass (g) $\times 10^{-2}$	mmol $\times 10^{-2}$
1	$H_2L^1$ complexes					
2	$[L^1Ni] \cdot 3H_2O$	$Ni(OAc)_2 \cdot 4H_2O$	13.1	52.7	30.0	52.7
3	$[L^1Cu] \cdot H_2O$	$Cu(CH_3COO)_2 \cdot H_2O$	10.5	52.7	30.0	52.7
4	$H_2L^2$ complexes					
5	$[L^2Co(H_2O)_2] \cdot 2H_2O$	$CoCl_2 \cdot 6H_2O$	23.7	64.0	35.0	64.0
6	$[L^2Cu] \cdot 2H_2O$	$Cu(CH_3COO)_2 \cdot H_2O$	18.1	64.0	35.0	64.0
7	$L^2Fe(H_2O)Cl$	$FeCl_3 \cdot 6H_2O$	27.0	64.0	35.0	64.0
8	$[L^2Ni] \cdot H_2O$	$Ni(OAc)_2 \cdot 4H_2O$	24.8	64.0	35.0	64.0
9	$[L^2*Co] \cdot 2H_2O$	$Co(OAc)_2 \cdot 4H_2O$	24.9	64.0	35.0	64.0



**Scheme 3** The pathway fragmentation pattern of the mass spectrum of  $H_2L^1$

### Optical activity

Ligand  $H_2L^2$  was prepared either from the racemic mixture of the aldehyde ( $\pm$ )-trans-1,2-diaminocyclohexane to give the racemic mixture ( $\pm$ ) $H_2L^2$  or from (1R,2S)-1,2-diaminocyclohexane to give the optically active  $H_2L^{2*}$ , which showed optical rotation of  $\alpha_D = +169.9$ .

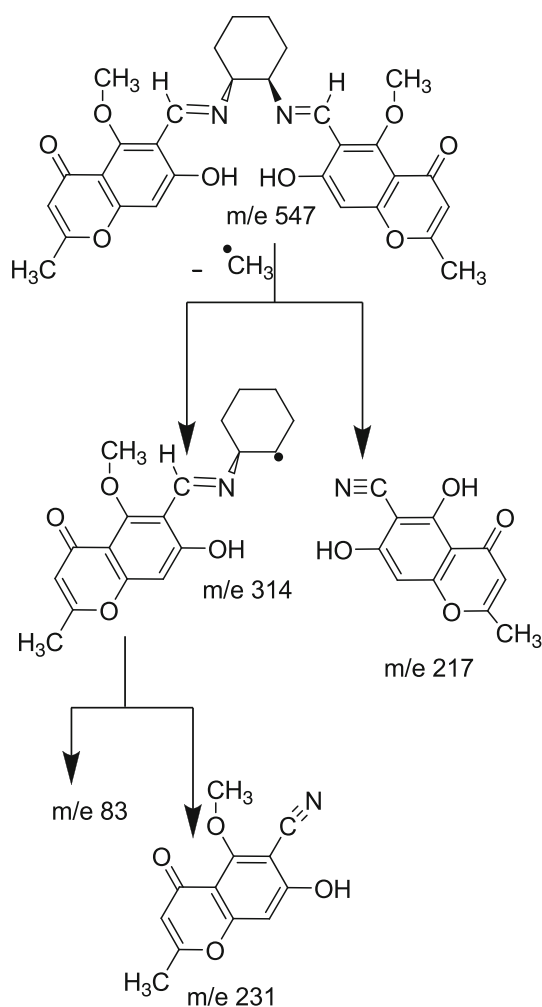
### Infrared spectra

The IR data for the Schiff bases  $H_2L^1$  and  $H_2L^2$  and their complexes are listed in (Table 3). The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation. The IR spectra of the free ligands showed a strong band in the region  $1,642$ – $1,662$   $cm^{-1}$ , which is characteristic of the azomethine group. Coordination of the Schiff bases to the metal through the nitrogen atom is expected to reduce the electron density and so the azomethine frequency. The band due to azomethine nitrogen  $\nu(C=N)$  shows a modest decrease in the stretching frequency for the complexes, being shifted to around  $1,614$ – $1,630$   $cm^{-1}$ , which indicates the coordination of the azomethine nitrogen [32, 33]. The bands at  $1,218$  and  $1,226$   $cm^{-1}$  for [ $H_2L^1$ ],  $1,222$   $cm^{-1}$  for [ $H_2L^2$ ] are ascribed to the phenolic C–O stretching vibrations. These bands are shifted upward due to O–metal coordination [34]. This assignment is further supported by the disappearance of the

$\nu(OH)$  band in the range  $3,246$ – $3,250$   $cm^{-1}$  for all the complexes, indicating the subsequent deprotonation of the phenolic proton prior to coordination [35]. The bands in the  $510$ – $540$  and  $460$ – $475$   $cm^{-1}$  regions are ascribed to the formation of M–O and M–N bonds, respectively [36, 37], which further supports the coordination of the azomethine nitrogen and the phenolic oxygen. The presence of coordinated water in the complexes [38] is indicated by a broad band in the region  $3,420$ – $3,445$   $cm^{-1}$ .

### NMR studies of diamagnetic Ni(II) complexes

Comparison of  $^1H$ NMR spectral data of the diamagnetic Ni(II) complexes, [ $L^1Ni$ ]. $3H_2O$  and [ $L^2Ni$ ]. $H_2O$  further supplements the conclusion drawn from IR data. The  $^1H$  NMR spectra of the Schiff bases revealed signals from azomethine hydrogen at 9.11 and 8.72 ppm for  $H_2L^1$  and  $H_2L^2$ , respectively, and singlets at 14.74 ppm (s, 2H) for  $H_2L^1$  and 15.21 ppm (s, 2H) for  $H_2L^2$  from OH resonances, which is clearly connected with the intramolecular hydrogen bonds system in  $H_2L^1$  and  $H_2L^2$ . Upon coordination, in the  $^1H$  NMR spectra of  $H_2L^1$  and  $H_2L^2$  signals from OH, in the range 14.74–15.21 for the free ligands were absent, indicating deprotonation of the hydroxyl group due to Ni–O bond formation. For [ $L^2Ni$ ]. $H_2O$  complex, the multiplet from H(55) and H(56) in the cyclohexyl ring is centered at 2.19 ppm. This signal is thus shifted toward lower frequencies, giving a coordination shift  $\Delta_{coord}$ :  $-1.5$  ppm,



**Scheme 4** The pathway fragmentation pattern of the mass spectrum of  $H_2L^2$

which is in favor of linkage via  $N=CH$  [39, 40]. The chemical shifts of H(17) and H(34) were found at 8.70 and 8.07 ppm for complexes:  $[L^1Ni] \cdot 3H_2O$  and  $[L^2Ni] \cdot H_2O$ , respectively. These protons exhibited large coordination shifts, because they are located three bonds from the central ion and charge distortion on these hydrogens is most

noticeable [41]. The mode of bonding suggested above has also been confirmed by the  $^{13}C$  NMR spectroscopic data. The comparison of the  $^{13}C$  NMR spectra of the complexes and ligands lead to a similar conclusion and indicate changes in the charge redistribution in the whole molecule induced by the complexation. The azomethine ( $C=N$ ) carbon signal occurring as singlet at  $\delta$  158.9–162.7 ppm in the ligands moves upfield, to  $\delta$  150.4–154.4, upon complexation, which provides further support for the coordination of the ligand through the azomethine nitrogens to metal ions. Also, the occurrence of the  $C=N$  carbon as one singlet indicates the equivalence of the two  $C=N$  carbon atoms both in the Schiff bases and their complexes.

#### Electronic and magnetic susceptibility data

The two bands observed at 270–320 and 360–490 nm in the free ligands are reasonably assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions for the phenolic-OH and azomethine moieties, respectively. The blue or red shifts of these bands with respect to the ligand depend on the type of metal ions coordinated to the ligand and indicate coordination of phenolic-OH and azomethine moieties to the metal ions.

The electronic spectrum of the Co(II) complex  $[L^2Co(H_2O)_2] \cdot 2H_2O$  (**5**) gives three bands, two of them at 800 and 531 nm. [40] These are assigned to the transitions  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ , respectively, suggesting that there is an octahedral geometry around Co(II) ion [40]. The third one at 396 nm refers to the charge transfer band. The magnetic susceptibility measurements lie at 4.80 B.M. (normal range for octahedral Co(II) complexes is 4.3–5.2 B.M.), indicative of octahedral geometry [42]. The cobalt(II) complex  $[L^{2*}Co] \cdot 2H_2O$  (**9**) exhibits absorption bands at 1,285 and 735 nm which can be assigned to  ${}^2B_{2g} \leftarrow {}^2E_g$  and  ${}^2A_{1g} \leftarrow {}^2E_g$  transitions, respectively [43, 44], in a square planar field. This cobalt complex displayed a magnetic moment of 2.68 B.M. which corresponds to a low spin square planar geometry [28].

**Table 3** IR frequencies of the bands ( $cm^{-1}$ ) of the ligands  $H_2L^1$ ,  $H_2L^2$ , and their metal complexes and their assignments

No.	Compound	$\nu(H_2O)$	$\nu(OH)$	$\nu(C=O)$	$\nu(C-O)$	$\nu(C=N)$
1	$H_2L^1$	3,445br	3,246m	1,663s and 661s	1,218 and 1,226	1,642s
2	$[L^1Ni] \cdot 3H_2O$	3,435br	–	1,658s	1,239	1,630m
3	$[L^1Cu] \cdot H_2O$	3,440br	–	1,658s	1,220	1,628m
4	$H_2L^2$	3,427br	3,250m	1,662vs	1,222	1,622vw
5	$[L^2Co(H_2O)_2] \cdot 2H_2O$	3,440br	–	1,660vs	1,226	–
6	$[L^2Cu] \cdot 2H_2O$	3,422br	–	1,660vs	1,227	1,617m
7	$L^2Fe(H_2O)Cl$	3,440br	–	1,660vs	1,225	1,614m
8	$[L^2Ni] \cdot H_2O$	3,443br	–	1,660vs	1,230	1,615m
9	$[L^{2*}Co] \cdot 2H_2O$	3,420br	–	1,660vs	1,229	–



**Table 4** The electronic absorption spectral bands (nm) and magnetic moment (B.M) for the ligands  $H_2L^1$ ,  $H_2L^2$  and their Metal complexes

No.	Ligand/complex	$\pi-\pi^*$ , $n-\pi^*$ , and CT bands	d-d bands	$\mu_{\text{eff}}$ in BM
1	$H_2L^1$	270, 360		
2	$[L^1Ni]\cdot 3H_2O$	256, 303, 361, 442sh	539sh	dia
3	$[L^1Cu]\cdot H_2O$	244, 300, 377	546	1.8
4	$(\pm)H_2L^2$ and $H_2L^{2*}$	261, 290, 320, 412, 490		
5	$[L^2Co(H_2O)_2]\cdot 2H_2O$	243, 332, 362, 396	531, 800	4.8
6	$[L^2Cu]\cdot 2H_2O$	242, 295, 376, 485	546	1.9
7	$L^2Fe(H_2O)Cl$	272, 300, 390	470, 1182	5.75
8	$[L^2Ni]\cdot H_2O$	250, 296, 355, 358, 408, 440	542	dia
9	$[L^{2*}Co]\cdot 2H_2O$	243, 296, 361, 390, 502	735, 1285	2.68

The Cu(II) complexes register a broad band at 546 nm due to  ${}^2B_{1g} \rightarrow {}^2E_g$  transition of a square planar Cu(II) structure [44]. The magnetic moment of these Cu(II) complexes is 1.8–1.9 B.M. indicating the presence of one unpaired electron. The electronic spectral results clearly indicated square planar geometry for the Cu(II) system, which should contain one unpaired electron, where  $\mu_{\text{eff}}$  value would be in the range 1.8–2.1 B.M. [45].

The nickel(II) complexes  $[L^1Ni]\cdot 3H_2O$  and  $[L^2Ni]\cdot H_2O$  show two shoulders in the ranges 539–542 nm and 440–442 nm, which are characteristic of square planar diamagnetic Ni(II) complexes [31], and resemble the absorption bands observed in the spectrum of an analogous Ni(II) complex reported by Bouwman [46]. A third band which is expected to appear at a higher energy is apparently hidden under the charge transfer band.

The electronic spectrum of the Fe(III) complex showed broad bands at 1,182 and 470 nm. The former band may be due to the spin forbidden transition  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ , which may gain intensity as a result of the vibronic mechanism in the octahedral field around ferric ion. The second band may be attributed to  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$  transitions. In addition, a third absorption band with high intensity observed at 470 nm can be assigned to a charge transfer transition. The observed magnetic moment of the Fe(III) complex is 5.75 B.M. Thus, these complexes have octahedral geometry [47] (Table 4).

#### Molar conductivities of the complexes

The molar conductivities  $\Lambda_m$  of the metal complexes dissolved in DMF or DMSO at  $10^{-3}$  M were found to be in the range 8–15  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ . These low values indicate that all these complexes are non-electrolytes due to the absence of any counter ions in their structures [48, 49] and that the  $[H_2L^1]$  and  $[H_2L^2]$  Schiff bases are coordinated to the metal ions as doubly negatively charged anions. Therefore, it seems that the two phenolic-OH have been deprotonated and bonded to the metal ions as oxygen anions [50].

#### Catalytic activity

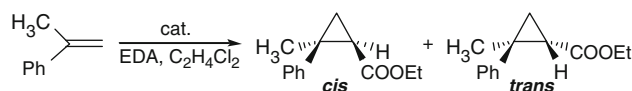
The catalytic activity of the complexes  $[L^1Cu]\cdot H_2O$  (**3**),  $[L^2Cu]\cdot 2H_2O$  (**6**) and  $[L^{2*}Co]\cdot 2H_2O$  (**9**) in cyclopropanation reactions has been investigated. As a model reaction we chose the cyclopropanation of  $\alpha$ -methyl styrene by EDA (EDA = ethyl diazoacetate) (Scheme 5). Catalytic reactions were run by adding the EDA to a stirred solution containing the olefin and the metal complex in dichloroethane under dinitrogen.

Both copper complexes **3** and **6** have low catalytic activity as cyclopropanation catalysts and at 75 °C in 1,2-dichloroethane at a [Cu]/EDA/olefin ratio of 1:20:150 we observed a conversion of less than 1.5% based on EDA after 8 h [21–23, 51–53].

The cobalt complex  $[L^{2*}Co]\cdot 2H_2O$  (**9**) showed a very high selectivity as cyclopropanation catalyst and at 75 °C in dichloroethane at a [Co]/EDA/NMI/olefin ratio of 1:20:0:150 we observed a conversion of 99% based on EDA after 110 min. To evaluate the catalytic activity of  $[L^{2*}Co]\cdot 2H_2O$  (**9**), we used this complex as a catalyst in our model reaction. Conditions of the catalytic reaction were examined by varying the temperature and the relative ratios of [Co]/EDA/NMI/olefin. The results are summarized in Table 5.

The cobalt complex  $[L^{2*}Co]\cdot 2H_2O$  (**9**) exhibited an excellent capability toward the decomposition of ethyl diazoacetate and the subsequent transfer of the carbene moiety to the C=C double bond with a very low tendency to form by-products.

According to the results shown in Table 5, it can be seen that  $[L^{2*}Co]\cdot 2H_2O$  (**9**) can act as a catalyst for the cyclopropanation reaction of unactivated olefins with a very high

**Scheme 5** Schematic representation of the model reaction

**Table 5** Cyclopropanation of  $\alpha$ -methyl styrene with EDA catalyzed by  $[L^{2*}Co] \cdot 2H_2O$  (**9**)<sup>a</sup>

Entry	Complex <b>9</b> /EDA/NMI/Olefin	Temperature (°C)	Time (min)	Conversion (%) <sup>a</sup>	Yield (%) <sup>b</sup>	<i>cis:trans</i>
1	1/20/0/150	Room	26 h	55	54	42:58
2	1/20/0/150	75	110	>99	99	45:55
3	1/30/0/200	75	197	87	86	46:54
4	1/20/1/150	Room	360	5	5	25:75
5	1/20/5/150	Room	150	25	24	36:64
6	1/30/1/200	Room	240	2	2	37:63
7	1/30/5/200	Room	240	10	10	26:74
8	1/30/5/200	75	360	50	50	33:67

Experimental conditions: EDA was added to a solution of  $[L^{2*}Co](H_2O)_2$  (**9**) (30.0 mg,  $4.7 \times 10^{-2}$  mmol), olefin and NMI in dichloroethane (10 mL)

<sup>a</sup> Conversion of the starting EDA

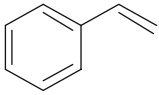
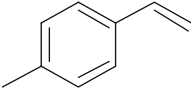
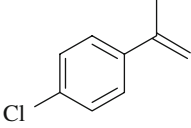
<sup>b</sup> Determined by GC–MS (yield based on EDA)

selectivity. The maximum level of diastereoselectivity reached, however, is not very satisfactory (maximum ratio *trans:cis* = 74:26) if compared to the results reported some years ago by the group of Katsuki, using Co(II) Schiff bases complexes [54, 55]. That is the reason why we did not try to investigate further the optimization of the catalyst loading; our [Co]/EDA ratio of 1:30 is still far from the one reported [Co]/EDA ratio of 1:200 [56–59] by employing chiral Co(II)-porphyrin complexes. The catalyst showed a very low tendency to form the well-known coupling by-products (maleate and fumarate) normally obtained in cyclopropanation reactions (Table 5). The temperature

played an important role in these reactions: the catalytic rate of the catalyst increases very much with increasing the temperature (compare: entry 2 with entry 1 and entry 7 with entry 8 in Table 5). The best result in terms of cyclopropane yield (99% based on EDA) was obtained at 75 °C at a complex (**9**)/EDA/olefin ratio of 1:20:150 (entry 2, Table 5). The presence of NMI improved the *cis:trans* ratio but with a decrease in the yield depending on the concentration of NMI (compare: entry 1 with entry 4, entry 1 with entry 5, and entry 3 with entry 8 Table 5).

To examine the generality of the complex  $[L^{2*}Co] \cdot 2H_2O$  (**9**) as cyclopropanation catalyst some other alkenes

**Table 6** Cyclopropanation of olefins with EDA catalyzed by  $[L^{2*}Co] \cdot 2H_2O$  (**9**)

Entry	Olefin	Time (min)	Conversion (%) <sup>a</sup>	Yield (%) <sup>b</sup>	<i>cis:trans</i>
1		5 h 10 min	76	75	36:64
2		2 h 6 min	>99	99	40:60
3		7 h	72	72	34:66

Experimental conditions: EDA was added to a solution of  $[L^{2*}Co] \cdot 2H_2O$  (**9**) (30.0 mg,  $4.7 \times 10^{-2}$  mmol) and olefin in dichloroethane (10 mL)

<sup>a</sup> Conversion of the starting EDA

<sup>b</sup> Determined by GC–MS (yield based on EDA)

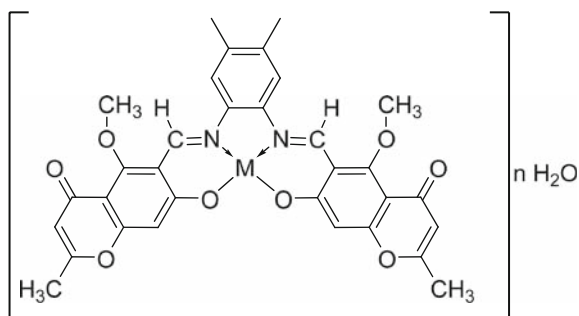


were employed to determine the substrate scope of the complex  $[L^2Co] \cdot 2H_2O^*$  (**9**). At a complex **9**/EDA/olefin ratio of 1:20:150 at 75 °C, the complex catalyzed the cyclopropanation of a range of substrates. The results are summarized in Table 6.

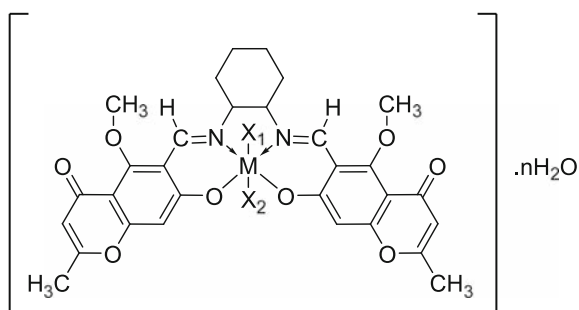
When styrene was employed as substrate, we observed a slight decrease in the quantitative conversion of the starting EDA to what observed in the case of  $\alpha$ -methyl styrene with a decrease in the conversion rate (compare entry 1 in Table 6 and entry 2 in Table 5). However in this case, the diastereoselectivity is improved (*cis:trans* = 36:64). Similar yields in cyclopropane products, but with slightly longer reaction times, are obtained when electron-donating substituents are present in the para position of the aromatic ring (entry 2 in Table 6). If 4-chloro- $\alpha$ -methylstyrene is employed as substrate both the catalytic rate and the yield decrease.

## Conclusions

We report here a study of the coordination capability of two new potentially tetradentate (ONNO) Schiff bases



**Chart 1** The proposed structures of metal complexes of the ligand  $H_2L^1$ . Complex **2**:  $[L^1Ni] \cdot 3H_2O$ : M = Ni,  $n = 3$ , and Complex **3**:  $[L^1Cu]H_2O$ : M = Cu,  $n = 1$



**Chart 2** The proposed structures of metal complexes of the ligand  $H_2L^1$ . Complex **5**,  $[L^2Co(H_2O)_2] \cdot 2H_2O$ : M = Co,  $X_1 = X_2 = H_2O$ ,  $n = 2$ , Complex **6**,  $[L^2Cu] \cdot 2H_2O$ : M = Cu,  $X_1 = X_2 = \text{none}$ ,  $n = 2$ , Complex **7**,  $L^2Fe(H_2O)Cl$ : M = Fe,  $X_1 = H_2O$ ,  $X_2 = Cl$ ,  $n = \text{none}$ , Complex **8**,  $[L^2Ni]H_2O$ : M = Ni,  $X_1 = X_2 = \text{none}$ ,  $n = 1$ , and Complex **9**,  $[L^{2*}Co] \cdot 2H_2O$ : M = Co,  $X_1 = X_2 = \text{none}$ ,  $n = 2$

diamine ligands  $[H_2L^1]$  and  $[H_2L^2]$  toward Co(II), Cu(II), Ni(II), and Fe(III). Conductivity measurements show that both Schiff bases are coordinated to the metal ions, from two phenolic oxygen atoms and two azomethine nitrogen atoms, as doubly negatively charged anions. Therefore, it seems two phenolic-OH have been deprotonated and bonded to the metal ions as oxygen anions. The proposed structures of the complexes are shown in Chart 1 and 2.

It is to be noted that the complex  $[L^{2*}Co] \cdot 2H_2O$  (**9**) acted as a catalyst in cyclopropanation reactions of unactivated olefins by ethyldiazoacetate with very high selectivity (up to 99%), although Co(II) complexes have seldom been used as catalysts for cyclopropanation reactions. Further investigations by changing the ligand skeleton will be made in the future to improve the diastereo and enantioselectivities reported in this article.

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