

Synthesis, And Characterization Of Six New Metal Transition Complexes Derived From The Schiff Base Ligand Bis(2-Hydroxybenzylidene)Oxalohydrazide (H₄L)

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Abstract

Metals transition complexes of a new Schiff base bis(2-hydroxybenzylidene)oxalohydrazide (H₄L) have been prepared and characterized by elemental analysis, infrared and ultraviolet-visible spectroscopies, room temperature magnetic moment measurement and conductivity measurement. H₄L is a potentially tetradentate ligand and its reactions with acetate or chloride salts of Mn²⁺, Ni²⁺, Co²⁺ and Cu²⁺ ions yield dinuclear neutral complex in which each metal ion is hexacoordinated. The ligand acts in its dideprotonated form (H₂L²⁻). The elemental analysis, conductance measurements and the room temperature measurement allow to formulate the complexes as neutral dinuclear : [M₂(H₂L)(OAc)₂(H₂O)₂] (M = Mn, Ni, Cu) with M situated in NO₅ inner and [M₂(H₂L)(Cl)₂(H₂O)₂] (M = Mn, Co, Cu) with M situated in NO₄Cl site. In all the complexes the environmental around the metal ion is best described as octahedral geometry according to the UV-visible data.

Keywords: Oxalylhydrazide, Salicylaldehyde, Schiff base, complex, FTIR, UV-visible, Magnetism.

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I. Introduction

For several decades, Schiff bases prepared from salicylaldehyde have been the subject of intense attention by coordination chemists for the development of compounds with important physical and biological properties [1–3]. By using salicylaldehyde with functionalized amines, ligands can be obtained that have both hard and soft donor sites. These types of Schiff bases used as ligands in coordination chemistry have allowed the generation of transition metal complexes with original structures [4–6]. When these ligands are used in the presence of co-ligands with versatile behavior such as acetates, fascinating structures can be obtained. Indeed, acetates have several coordination modes that can intervene in the structure of the complex and induce particular properties [7–9]. These properties can be improved or reduced after complexation with various metal ions [10–12]. Thus, the synthesis of new Schiff base complexes and the study of the structure-activity relationship have become a major challenge in coordination chemistry. Controlling the size of the ligand cavities and the soft or hard nature of the donor sites makes them specific. The properties of these complexes can vary depending on the substitution on the salicylaldehyde used as a keto-precursor. Indeed, the type of substituent used and the position of the substitution on the aromatic ring have particularly important effects on the properties of the molecule [13,14]. Some complexes obtained from Schiff bases generated with salicylaldehyde or one of its derivatives are used as anticancer agents [15], antimicrobial agents [16], catalysts [17], or genotoxic agents [18]. It is in this context that we report the synthesis, spectroscopic characterization of six complexes with the new tetradentate Schiff base bis(2-hydroxybenzylidene)oxalohydrazide (H₄L).

II. Material And Methods

Starting materials and Instrumentations

Salicylaldehyde, oxalylhydrazide, manganese acetate tetrahydrate, nickel acetate tetrahydrate, copper acetate dihydrate, cobalt chloride hexahydrate, manganese chloride hexahydrate and copper chloride dihydrate were commercial products (from Aldrich) and were used without further purifications. The solvents were reagent grade and were purified by usual methods. Elemental analyses were carried out using a VxRio EL Instrument. The FTIR spectra were recorded on a FTIR Spectrum Two of Perkin Elmer (4000–400 cm⁻¹). The UV–Vis spectra were run on a Perkin-Elmer UV/Visible spectrophotometer Lambda 365 (1000–200 nm). The ¹H and ¹³C NMR spectra of the Schiff base were recorded in DMSO-*d*₆ on a BRUKER 500 MHz spectrometer at room temperature

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using TMS as an internal reference. The molar conductance of 10^{-3} M solutions of the metal complexes in DMF were measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Magnetic measurements for complexes were performed at room temperature by using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: Hg[Co(SCN)₄]).

Synthesis of the ligand bis(2-hydroxybenzylidene)oxalohydrazide (H₄L)

In a flask containing 100 mL of a mixture of water and methanol (25/75), oxalyldihydrazide (5 g, 42.34 mmol) was introduced. Salicylaldehyde (10.33 g, 84.68 mmol) was added. A white precipitate appears. The suspension is heated to reflux for three hours. After cooling, the solid obtained is recovered by filtration, washed with distilled water (2 x 50 mL) and diethyl ether (2 x 50 mL). The white product is recrystallized in 100 mL of a CHCl₃/MeOH mixture (50/50) and is then dried in a desiccator under P₄O₁₀. Yield: 89%. M.p. > 300 °C. The product is soluble in DMSO. NMR ¹H (DMSO-d₆, δ(ppm)): 6.93-6.95 (m, 4H, =CH_{Ar}); 7.31-7.34 (m, 2H, =CH_{Ar}); 7.55-7.57 (m, 2H, =CH_{Ar}); 8.82 (s, 2H, HC=N); 11.01 (s, 2H, HN); 12.66 (s, 2H, -OH). NMR ¹³C (DMSO-d₆, δ(ppm)): 166.88 (-C=O); 157.55 (C_{Ar}-OH); 155.82 (C-CH=N); 150.94 (HC=N); 132.00 (CH_{Ar}); 131.63 (CH_{Ar}); 131.46 (CH_{Ar}); 129.28 (CH_{Ar}); 128.61(CH_{Ar}); 119.44 (CH_{Ar}); 118.59 (CH_{Ar}); 116.44 (CH_{Ar}). NMR ¹³C {DEPT135} (DMSO-D₆, δ/ppm) 150.94 (HC=N); 131.63 (CH_{Ar}); 131.46 (CH_{Ar}); 129.28 (CH_{Ar}); 128.61 (CH_{Ar}); 119.44 (CH_{Ar}); 116.44 (CH_{Ar}).

Synthesis of the transition metal complexes from the H₄L ligand

The preparation of transition metal complexes from the H₄L ligand consists of suspending one millimole of this ligand in ethanol, then successively adding two millimoles of LiOH·H₂O and two millimoles of the transition metal salt (Mn(OAc)₂·4H₂O, Ni(OAc)₂·4H₂O, Cu(OAc)₂·2H₂O, MnCl₂·6H₂O, CoCl₂·6H₂O and CuCl₂·2H₂O). The mixture is stirred at room temperature for three hours before filtering the suspension formed. The solid recovered was washed with cold ethanol.

[Mn₂(H₂L)(OAc)₂(H₂O)₂] (1). Yield: 78 %. Red orange solid. IR (cm⁻¹): 3432, 3022, 1743,1606, 1544, 1469, 1436, 1417, 1285, 1200, 1153, 1034, 975, 874. Λ (Ω⁻¹·cm²·mol⁻¹): 43. UV (λ (nm)): 298, 325, 343, 380, 580 nm. μ_{eff} = 11.90 μ_B.

[Ni₂(H₂L)(OAc)₂(H₂O)₂] (2). Yield: 89 %. Brown solid. IR (cm⁻¹): 3456, 3016, 1747, 1605, 1532, 1438, 1367, 1228, 1216, 1110, 1092, 899. Λ (Ω⁻¹·cm²·mol⁻¹): 14. UV (λ (nm)): 295, 355, 340, 380, 548, 872. μ_{eff} = 5.86 μ_B.

[Cu₂(H₂L)(OAc)₂(H₂O)₂] (3). Yield: 83 %. Green solid. IR (cm⁻¹): 3533, 3037, 1716, 1605, 1532, 1467, 1448, 1382, 1311, 1200, 1154, 1074, 895, 753. Λ (Ω⁻¹·cm²·mol⁻¹): 43. UV (λ (nm)): : 294, 328, 341, 390, 977. μ_{eff} = 3.90 μ_B.

[Mn₂(H₂L)(Cl)₂(H₂O)₄] (4). Yield: 63 %. Brown solid. IR (cm⁻¹): 3460, 3020, 1749, 1603, 1440, 1370, 1228, 1214, 1120, 1092, 900, 771. Λ (Ω⁻¹·cm²·mol⁻¹): 60. UV (λ (nm)): 300, 325, 341, 390, 455, 580. μ_{eff} = 11.86 μ_B.

[Co₂(H₂L)(Cl)₂(H₂O)₄] (5). Yield 59 % . Reddish solid. IR (cm⁻¹): 3456, 3016, 1739, 1600, 1538, 1436, 1366, 1228, 1216, 1110, 1092, 900, 771. Λ (Ω⁻¹·cm²·mol⁻¹): 64. UV (λ (nm)): 303, 335, 348, 445, 470, 905 nm. μ_{eff} = 10.20 μ_B.

[Cu₂(H₂L)(Cl)₂(H₂O)₄] (6). Yield 53 %. Green solid. IR (cm⁻¹): 3456, 3016, 1740, 1606, 1454, 1366, 1229, 1217, 1093, 897, 770. Λ (Ω⁻¹·cm²·mol⁻¹): 24. UV (λ (nm)): 290, 330, 340, 395, 979. μ_{eff} = 3.86 μ_B.

Table 1. Analytical data, room temperature magnetic moments and conductance of complexes 1-6.

Compound	%C		%H		%N		%Cl		μ _{eff} (μ _B)	Λ (Ω ⁻¹ ·cm ² ·mol ⁻¹)
	Calc.	Found	Calc	Found	Calc.	Found	Calc	Found		
H ₄ L	58.89	58.87	4.32	4.29	17.17	17.19	-	-	-	-
(1)	40.69	40.66	4.10	4.07	9.49	9.51	-	-	11.90	43
(2)	40.18	40.15	4.05	4.01	9.37	9.38	-	-	5.86	14
(3)	39.54	39.49	3.98	3.95	9.22	9.20	-	-	3.90	43
(4)	33.30	33.25	3.49	3.49	9.71	9.75	12.2 9	12.31	11.86	60
(5)	32.84	32.81	3.45	3.42	9.58	9.54	12.1 2	12.10	10.20	64

(6)	32.33	32.30	3.39	3.38	9.43	9.41	11.9 3	11.90	3.86	24
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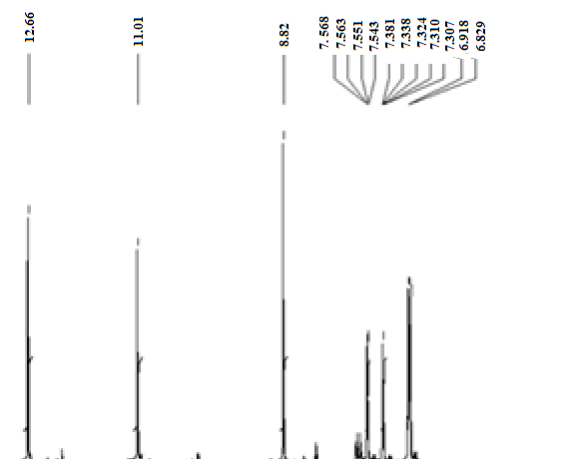
Table 2. Main FTIR and UV-visible bands for H_4L and complexes 1-6.

Compound	$\nu(O-H)$	$\nu(N-H)$	$\nu(C=O)$	$\nu(C=N)$	$\nu_s(N-N)$	$\nu_s(OAc)$	$\nu_{as}(OAc)$	$\Delta\nu$	$\lambda(nm)$
H_4L	3277	3149	1703	1633	961	-	-	-	292, 324
(1)	3432	3022	1743	1606	1034	1544	1436	108	298, 325, 343, 380, 580
(2)	3456	3016	1747	1605	1092	1532	1438	94	295, 355, 340, 380, 548, 872
(3)	3533	3037	1716	1605	1074	1552	1448	104	294, 328, 345, 390, 977
(4)	3460	3020	1749	1603	1092	-	-	-	300, 325, 341, 390, 455, 580
(5)	3456	3016	1739	1600	1092	-	-	-	303, 335, 348, 445, 470, 905
(6)	3456	3016	1740	1606	1093	-	-	-	290, 330, 340, 395, 979

III. Results And Discussion

General study

In this manuscript, we have discussed a simple procedure to synthesize the ligand H_4L and its metal transition complexes. All the compounds are characterized by elemental analysis and various spectroscopic methods. The synthesis of H_4L was achieved in one step procedure by the condensation reaction between salicylaldehyde and oxalyldihydrazide in quantitative yield (Scheme 1). The complexes are synthesized with good yield at room temperature using the ratio 1/2/2 ($H_4L/LiOH/Metal$). The elemental analysis of the ligand and the complexes allowed to formulate all compounds (Table 1). On the IR spectrum (Table 2) of the ligand, an intense band appears at 1703 cm^{-1} which is characteristic of the stretching vibration of the carbonyl group ($\nu_{C=O}$). The band which appears at 1633 cm^{-1} corresponds to the stretching vibration of the azomethine moiety ($\nu_{C=N}$) [19]. This last band shows the success of the condensation reaction, and the presence of amide function and the absence of iminol group in the solid state. The band at 1262 cm^{-1} is attributed to the ν_{C-O} vibration. The bands due to the aromatic groups are pointed between 1550 and 1450 cm^{-1} . Towards high frequencies the bands due to ν_{O-H} and ν_{N-H} are located, respectively, at 3277 cm^{-1} and 3149 cm^{-1} [20]. The 1H NMR spectrum of the ligand H_4L (Figure 1), recorded in $DMSO-d_6$, reveals a singlet signal at 12.6 ppm attributed to the phenolic protons. The signal at 11.01 ppm is assigned to the protons resulting from the iminisation of the $H-N-C=O \rightleftharpoons H-O-C=N$ function. The signal at 8.82 ppm is attributed to the protons of the azomethine $HC=N$ groups, while the signals appearing in the range [6.93-7.57 ppm] in multiplet form are attributed to the protons of the aromatic ring. The NMR spectrum of carbon ^{13}C (Figure 2) and $^{13}C\{DEPT\ 135\}$ allow to be attribute the different signals. On the ^{13}C NMR spectrum, there are more signals than expected carbon atoms and this is explained by the equilibrium of the iminisation of the compound. The signal at 166.88 ppm is attributed to the carbon atom of the carbonyl group ($C=O$). The signal at 157.55 ppm is attributed to the $C_{ipso-OH}$ carbon atom of the phenol ring. The signals at 155.82 and 150.94 ppm are, respectively, attributed to the carbon atoms $C=N$ of azomethine moiety and the carbon resulting from the iminisation. The signals of the other carbon atoms are pointed between 128.61 ppm and 132 ppm.


Figure 1. 1H NMR of the ligand in DMSO solution.

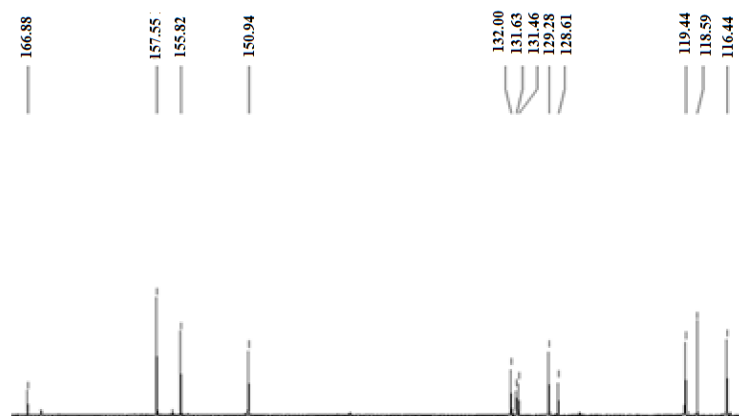


Figure 2. ^{13}C NMR of the ligand in DMSO solution.

On the basis of elemental analysis, the ligand and the complexes were found to have the composition presented in Table 1. Molar conductivity measurements of the complexes were taken in freshly prepared DMF (Table 1). Complexes (2) and (6) gave the lowest molar conductivity values of 14 and 24 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively. Complexes (1) and (3) gave an intermediate value of 43 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ while complexes (4) and (5) gave the higher molar conductivity values of 60 and 64 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively. Two weeks later, these values remained quite constant, indicating good stability of the complexes in DMF. These values are indicative of a non-electrolytic nature for the complexes 1-6 as indicated in the literature [21]. On the IR spectrum of the ligand, the medium intensity band located at 3277 cm^{-1} which was attributed to the valence vibration of the phenolic OH group disappears, after the coordination on the FTIR spectra of all the complexes (Table 2). This indicates that the phenolic groups are deprotonated, and that the ligand acts in its H_2L^{2-} form. The phenolate oxygen atom is coordinated to the metal ion in the complexes. The band due to $\nu_{\text{C}=\text{N}}$, pointed on the spectrum of the free ligand at 1633 cm^{-1} , shifts towards low frequencies for all the complexes and appears in the interval [1600 cm^{-1} -1606 cm^{-1}]. This is indicative of the involvement of the nitrogen atom of azomethine in the coordination [19]. The vibration frequency of the carbonyl group [1716 cm^{-1} -1749 cm^{-1}] in the FTIR spectra of the complexes increases considerably compared to that of the free ligand which was pointed at 1703 cm^{-1} . This fact indicates the participation of the carbonyl groups in the coordination of the metal. The presence of the $\nu_{\text{N-H}}$ band is also observed for all the complexes which indicates that the ligand has reacted in its amide form. The presence of the coordination water molecules is attested by the $\nu_{\text{O-H}}$ bands which are between 3456 cm^{-1} and 3533 cm^{-1} [20]. The band between 1532 cm^{-1} and 1552 cm^{-1} and the band in the range [1448 cm^{-1} -1436 cm^{-1}] are due to the $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ vibrations, respectively, of the coordinated acetate anion in (1), (2) and (3). The separation $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ values of the acetate asymmetrical and symmetrical stretching has been used as a criterion to distinguish the different modes of coordination of the acetate group. Generally, the following order is proposed for divalent metal carboxylates Δ (bidentate chelating) < Δ (bridging) < Δ (ionic) < Δ (monodentate) [22–24]. The magnitude of this separation $\Delta\nu$ values of 108 cm^{-1} , 94 cm^{-1} or 104 cm^{-1} for (1), (2) and (3), respectively, is indicative of bidentate chelating coordination of the acetate ion in the complexes.

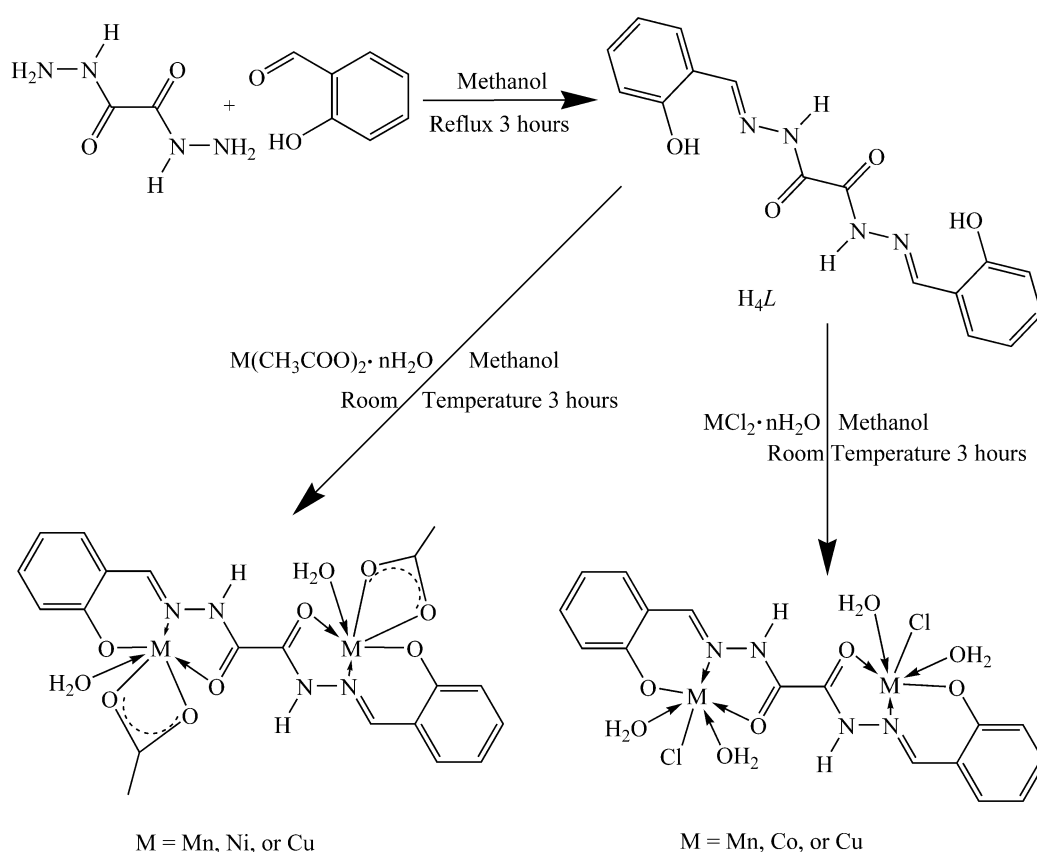
Electronic spectra

The UV-Vis absorption spectra of H_4L and its complexes 1-6 were measured in DMF solutions ($10^{-5} \text{ mol}\cdot\text{L}^{-1}$) at room temperature (Table 2). Two absorption bands are pointed at 292 nm and 324 nm in the UV-Vis spectrum of H_4L . These absorption are due to the $\pi-\pi^*$ transitions of the phenyl rings and the $\text{C}=\text{N}$ bonds of intra-ligand [25], respectively. Upon complexation, the absorption peaks of the $\pi-\pi^*$ transition of the phenyl rings are bathochromically shifted in all the complexes (Table 2). This fact is due to the coordination of the ligand to the metal ions atoms [26]. For complexes 1-6, new absorption peaks are pointed. The band near 340 nm is attributed to $\pi\rightarrow\pi^*$ of $\text{C}=\text{N}$ azomethine [27]. For complexes (1) and (4) the additional bands at 380 nm and 390 nm, respectively, belong to the ligand to metal charge transfer (LMCT). The band pointed at 580 nm in the UV-visible spectra of both compounds (1) and (4) is attributable to a $d\rightarrow d$ transition of a Mn(II) ion in an octahedral environment [28]. The similarity of the two spectra suggests a resemblance of the structures of (1) and (4) in solution. The spectrum of complex (2) shows a 380 nm band attributed to the LMCT. Two $d\rightarrow d$ bands at 548 and 872 nm are assigned respectively to the ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}$ and ${}^3\text{A}_{2g}\rightarrow{}^2\text{T}_{2g}$ transitions which are characteristic of a Ni(II) in an octahedral environment [28]. The spectra of complexes (3) and (6) are similar and show a band at ~ 392 nm that is attributed to the LMCT and a band at ~ 978 nm that assignable to a $d\rightarrow d$ transition of a Cu(II) ion in an octahedral environment [29]. The spectrum of

complex (5) shows two peaks at 470 nm and 905 nm attributed to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions, respectively. These two peaks are characteristic of high-spin octahedral cobalt(II) complexes [30].

Magnetism

Effective room temperature magnetic moment values are presented in Table 1. The magnetic moment of complexes (1) and (4) are, respectively, $11.90 \mu_B$ and $11.86 \mu_B$. These values agree with the presence of two uncoupled Mn^{2+} high-spin d^5 in octahedral environment [31]. The binuclear Ni(II) complex (2) has a magnetic moment value of $5.86 \mu_B$, characteristic of two discrete Ni(II) in an octahedral environment [32]. The room temperature magnetic moment for complexes (3) and (6) $3.90 \mu_B$ and $3.86 \mu_B$, respectively, is close to the normal value for an uncoupled two copper(II) system, and might suggests the absence of spin exchange [33]. Complex (5) show a room temperature moment values of $10.20 \mu_B$ which is consistence with the presence of two uncoupled Co^{2+} high-spin in octahedral environment [34]. Combining the results of the elemental analysis and the non-electrolytic behavior of the complexes, and the room temperature magnetic moment, the complexes are formulated as follows: $[M_2(H_2L)(OAc)_2(H_2O)_2]$ ($M = Mn, Ni, Cu$) or $[M_2(H_2L)(Cl)_2(H_2O)_4]$ ($M = Mn, Co, Cu$) (Scheme 1).



Scheme 1. Synthetic scheme for the ligand and its metal transition complexes preparation.

IV. Conclusion

In the present work, we report the synthesis and characterization of six new complexes of manganese, cobalt, nickel and copper prepared from the tetradentate ligand bis(2-hydroxybenzylidene)oxalohydrazide (H_4L). The compounds were characterized by NMR, IR, UV, conductance measurement and room temperature magnetic moment determination. All the complexes are dinuclear. The IR spectral data showed that the ligand is coordinated with the metal center through the imino nitrogen atoms, the phenolate oxygen atoms and the carbonyl oxygen atoms. The electronic spectra show bands due to the ligand and the MLCT for all complexes. The d-d bands for 1-6 complexes are in accordance with octahedral structure. Room temperature magnetic susceptibility measurement indicated that the complexes 1-6 are diamagnetic and present two uncoupled metal ions. Conductance measurement shows that the complexes 1-6 are non-electrolyte in nature. The structures of the three complexes from the acetate metal salt are isomorphous and formulated as $[Mn_2(H_2L)(OAc)_2(H_2O)_2]$ (1), $[Ni_2(H_2L)(OAc)_2(H_2O)_2]$ (2) and $[Cu_2(H_2L)(OAc)_2(H_2O)_2]$ (3) and the complexes from the chloride metal salts are similar and formulated as $[Mn_2(H_2L)(Cl)_2(H_2O)_4]$ (4) $[Co_2(H_2L)(Cl)_2(H_2O)_4]$ (5) and $[Cu_2(H_2L)(Cl)_2(H_2O)_4]$ (6).

(6). In the case of the acetate complexes, each metal center is coordinated to one imino nitrogen atom, one phenolate oxygen atom, one carbonyl oxygen atom from the ligand, two oxygen atoms from the bidentate chelating acetate group and one oxygen atom of coordinated water molecule, yielding an octahedral geometry of type NO_5 . In the case of the chloride complexes, each metal center is coordinated to one imino nitrogen atom, one phenolate oxygen atom, one carbonyl oxygen from the ligand, one coordinated chloride anion and two oxygen atoms of coordinated water molecules, yielding an octahedral geometry of type $NCIO_4$. In the complexes the symmetrical ligand acts as bridge between two metal ions.

In Memoriam

Cheikh Halidou KANE 1963–2021. The death of Dr. KANE has deeply shocked us. Dr. KANE was a very talented chemist who was deeply involved in research and supervision of doctoral students. His contribution is greatly missed by our team. This article is dedicated to his memory.