

Synthesis and Structural Features of New Schiff Base Complexes of Mononuclear Mn^{IV}, Dinuclear Co^{II}Co^{III}, and Tetranuclear Cu^{II}

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Abstract. 2-(((2-Hydroxy-3-methoxyphenyl)methylene)amino)-2(hydroxymethyl)-1,3-propanediol (LH₄, as abbreviation) reacts with $MnCl_2$ ·4H₂O, $CoCl_2$ ·6H₂O, and $Cu(ClO_4)_2$ ·6H₂O to give the new complexes [Mn(LH₂)₂] (1), [Co₂Cl(H₂O)(LH₂)₂]·4H₂O (2), and [Cu₄(LH₂)₄(H₂O)₄] (3). Complex 1 is formed by the assembly of two

1 Introduction

Polynuclear complexes of transition metals of the first row have attracted much attention because of their interesting structural variety and remarkable properties as catalysts and bioinorganic agents. One of the various successful strategies used to prepare polynuclear transition metal complexes involves the exploration of different polydentate Schiff bases as starting materials.

Schiff bases have been used extensively as ligands in the coordination chemistry.^[1,2] In addition, these compounds can show suitable applications regarding its antitumor activity,^[3] photochromism,^[4] and thermochromism^[5] by proton displacement between the hydroxyl oxygen atom and the imine nitrogen atom.

Literature search reveals that salicylaldehyde reacts with an amino group, leading to the formation of Schiff bases.^[6,7] Because of that, salicylaldehyde is a key precursor for a variety of chelate ligands. *o*-Vanillin, as substituted derivative of salicylaldehyde, besides their own biological activity,^[8,9] and tris (hydroxymethyl) aminomethane – as an amine, which enables more than one coordination site,^[10] – are good precursors for the synthesis of polydentate Schiff bases. These Schiff base ligands allow the formation of both monomers^[11] and polynuclear transition metal complexes.^[7,12]

Specifically 2-hydroxy Schiff base ligands are of interest, mainly due to the existence of O–H···N and N–H···O hydrogen bonds as models for the study of keto-enol tautomerism.^[13–15] Structurally, Schiff bases derived from salicylaldehyde gen-

 [a] Departamento de Química - LMI Universidade Federal de Santa Maria 97105–900, Santa Maria – RS, Brazil molecules of the ligand with one manganese(IV) ion. In the mixed-valence cobalt complex 2 there is an asymmetry between the coordination spheres of cobalt(II) and cobalt(III). In the tetramer 3 four copper(II) ions attain a distorted tetrahedral configuration surrounded by four molecules of the ligand.

erally exist in the phenol-imine form, $^{[16,17]}$ and sometimes enamine or keto tautomer, and a zwitterionic structure with a longer N⁺–H bond. $^{[18]}$

Many groups are involved in the utilization of the multisite Schiff-base ligand 2-(((2-hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propanediol (as abbreviation LH₄),^[19] to prepare 4f clusters, 3d-4f mixed metal compounds, and a small number of first row polynuclear transition metal complexes.^[20–24] With the aim to provide new complexes obtained from LH₄, we report the synthesis and the structural characterization of $[Mn(LH_2)_2]$ (1), $[Co_2Cl(LH_2)_2(H_2O)]$ ·4H₂O (2), and $[Cu_4(LH_2)_4(H_2O)_4]$ (3).

2 Experimental Section

2.1 General

All manipulations were conducted by use of standard Schlenk flasks. Elemental analyses for C, H, and N were performed at a Shimadzu EA 112 microanalysis instrument. IR spectra were recorded with a Tensor 27 Bruker spectrometer with KBr pellets in the 4000– 400 cm^{-1} region.

2.2 Preparations

2.2.1 Ligand 2-(((2-Hydroxy-3-methoxyphenyl)methylene)amino)-2(hydroxymethyl)-1,3-propanediol (LH_4)

In accordance with the procedures found in the literature^[23,25,26] LH₄was synthesized by condensation of *o*-vanillin (0.152 g, 1 mmol) and 2-amino-2-hydroxymethylpropane-1,3-diol (0.121 g, 1 mmol) in anhydrous methanol (25 mL). The mixture was heated in an oil bath at 65 °C and stirred for 4 h in a nitrogen atmosphere. After a week yellow crystals were obtained in the solution. Approx. yield: 43.2%. Melting point (decomp.): 181 °C. Calcd. C 56.47; H 6.66; N 5.49%; found: C, 56.47; H, 6.50; N, 5.67%. **IR** (KBr): 3343 [s, v(O–H)_{phenol}]; 3194 [m, v(O–H)_{alcohols}]; 2948[w, v(C–H)_{sp3})]; 1643 [s, v(C=N)_{imine}];

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1501 [vs, v(C=C)_{ring}]; 1227[s, v(C–O)_{methoxy}]; 1023 [m, v(C–O)_{alcohols}] cm⁻¹ (vs. = very strong; s = strong; m = middle; w = weak).

$2.2.2 \ [Mn(LH_2)_2] \ (1)$

MnCl₂·4H₂O (0.019 g, 0.1 mmol) was added to a solution of LH₄ (0.024 g, 0.1 mmol) in methanol (10 mL). After heating at 65 °C for 0.5 h triethylamine (0.013 mL, 0.129 mmol) was added to the brown solution. The mixture was stirred and heated for 3.5 h and was finally filtered. The crystallization occurred after 5 d. Approx. yield: 22.7 %. Brown crystals. Melting point (decomp.): 213.9 °C. $C_{24}H_{30}MnN_2O_{10}$: calcd. C 51.2; H 5.34; N 4.98%; found: C 51.15; H 5.45; N 4.81%. **IR** (KBr): 3419 [m, v(O–H)_{alcohols}]; 1617 [s, v(C=N)_{imine}]; 1441 [s, v(C=C)_{rine}]; 1171 [m,v(C–O)_{metnox}]; 1037 [s, v(C–O)_{alcohols}] cm⁻¹.

$2.2.3 \ [Co_2Cl(LH_2)_2(H_2O)] \cdot 4H_2O$ (2)

To a solution of LH₄ (0.024 g, 0.1 mmol) in methanol (20 mL), CoCl₂·6H₂O (0,023 g, 0.1 mmol) was added. After heating for 65 °C and stirring for 4 h, the green solution was filtered. The green solution turned brown after 1 d on ambient conditions and after 2 weeks orange crystals formed in the solution. Approx. yield: 31.3 % Melting point (decomp.): 225.6 °C. $C_{24}H_{40}ClCo_2N_2O_{15}$: calcd. C 38.4; H 5.33; N 3.73; found: C, 38.15; H, 5.44; N, 3.55 %. **IR** (KBr): 3332 [m, v(O–H)_{alcohols}]; 3142 [m, v(O–H)_{alcohols}]; 2934[w, v(C–H)_{sp3})]; 1632 [s, v(C=N)_{imine}]; 1440 [s, v(C=C)_{ring}]; 1219 [s, v(C–O)_{methoxy}]; 1076 [m, v(C–O)_{alcohols}] cm⁻¹.

2.2.4 $[Cu_4(LH_2)_4(H_2O)_4]$ (3)

To a solution of LH₄ (0.024g, 0.1 mmol) in methanol (20 mL), Cu(ClO₄)₂·6H₂O (0.037g, 0.1 mmol) was added. After heating at 70 °C for 0.5 h, triethylamine (0.013 mL, 0.129 mmol) was added to the green solution. The mixture was stirred and heated for 3.5 h and finally filtered. The crystallization occurred after 10 d. Approx. yield: 28.7%. Deep green crystals. Melting point (decomp.): over 260 °C. C₁₂H₁₇CuNO₆: calcd. C 43.0; H 5.07; N 4.18%; found: C 43.15; H 5.12; N 4.29%. **IR** (KBr): 3452 [m, v(O–H)_{alcohols}]; 3237 [m, v(O–H)_{alcohols}]; 2908 [w, v(C–H)_{sp3})]; 1627 [s, v(C=N)_{imine}]; 1470 [s, v(C=C)_{ring}]; 1219 [s, v(C–O)_{methoxy}]; 1057 [m, v(C–O)_{alcohols}] cm⁻¹.

2.2.5 X-ray Diffraction

A Bruker CCD X8 APEX II diffractometer was used for the X-ray structure analyses. The equipment was operated using graphite monochromator and Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The structures were refined with full-matrix least-squares on F^2 using all data (SHELX crystal structure solution software). The structures were solved with SHELXS^[27] by direct methods. All non-hydrogen atoms were refined with anisotropic displacement parameters with SHELXL.^[27] The hydrogen atoms were calculated in the idealized positions. More detailed information about the structures determinations of **1–3** are given in Table 1.

Table 1. Crystal data and structure refinement for 1	-3 .
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	1	2	3
Empirical formula	$C_{24}H_{30}MnN_2O_{10}$	C ₂₄ H ₄₀ ClCo ₂ N ₂ O ₁₅	C ₁₂ H ₁₇ CuNO ₆
Formula weight	561.44	749.89	334.81
<i>Т /</i> К	293(2)	100(2)	293(2)
Radiation, $\lambda / \text{Å}$	$Mo-K_a$, 0.71073	Mo- K_{a} , 0.71073	$M-K_{a}$, 0.71073
Crystal system, space group	tetragonal, $P4_12_12$	monoclinic, Cc	tetragonal, $I4_1/a$
Unit cell dimensions	0 11		
a /Å	8.1620(2)	11.6492(3)	18.7960(9)
b /Å	8.1620(2)	13.2349(3)	18.7960(9)
c /Å	37.4557(11)	19.6786(6)	15.507(2)
$a /^{\circ}$	90	90	90
β /°	90	105.9760(10)	90
y /°	90	90	90
$V/Å^3$	2495.23(11)	2916.79(13)	5478.6(8)
Z, calculated density $/g \cdot cm^{-3}$	4,1.495	4, 1.708	16, 1.624
Absorption coefficient /mm ⁻¹	0.590	1.306	1.619
F(000)	1172	1556	2768
Crystal size /mm	$0.48 \times 0.34 \times 0.22$	$0.30 \times 0.29 \times 0.21$	$0.62 \times 0.44 \times 0.40$
θ range /°	2.17-27.09	2.15-27.13	1.70-27.09
Index ranges	$-10 \le h \le 10,$	$-14 \le h \le 14,$	$-24 \le h \le 19,$
C C	$-9 \le k \le 10,$	$-16 \le k \le 16,$	$-6 \le k \le 24,$
	$-47 \le l \le 47$	$-24 \le l \le 25$	$-19 \le l \le 13$
Reflections collected	20345	21403	4501
Reflections unique	2760 $[R_{int} = 0.0423]$	$6240 [R_{int} = 0.0355]$	$2982[R_{int} = 0.0471]$
Completeness to theta max.	99.9%	99.6%	105.5%
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	0.8588 and 0.7089	0.761 and 0.683	0.522 and 0.432
Refinement method	full-matrix	full-matrix	full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2
Data / restraints / parameters	2760 / 0 / 168	6240 / 9 / 399	2982 / 0 / 177
Goodness-of-fit on F^2	1.222	1.008	0.886
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0467,$	$R_1 = 0.0320,$	$R_1 = 0.0624,$
	$wR_2 = 0.1323$	$wR_2 = 0.0715$	$wR_2 = 0.1509$
R indices (all data)	$R_1 = 0.0536$	$R_1 = 0.0380,$	$R_1 = 0.0929,$
	$wR_2 = 0.1408$	$wR_2 = 0.0742$	$wR_2 = 0.1615$
Largest diff. peak and hole /e·Å ⁻³	1.173 and -0.723	0.359 and -0.506	0.533 and -0.356

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1027788, CCDC-1027789, and CCDC-1027819 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk)

Instrumentation

UV/Vis Analysis: UV/Vis spectra were recorded with a Perkin-Elmer Lambda 191 spectrometer, using acetonitrile solutions.

CV Analysis: Cyclic voltamograms were recorded with a Princeton Applied Research (PAR) 273 system at room temperature in an argon atmosphere, in dry acetonitrile (CH₃CN). Electrochemical grade tetrabutyl ammonium hexafluorophosphate (TBAPF₆) was used as supporting electrolyte. A standard three-electrode system was employed to carry out these experiments: a glassy carbon working electrode; a platinum wire auxiliary electrode and a platinum wire pseudo-reference electrode. To monitor the reference electrode, the ferrocenium/ ferrocene redox couple was used as internal reference ($E_{1/2} = 0.40$ V vs. NHE).^[28]

3 Results and Discussion

3.1 Crystal Structures

The structures of complexes $[Mn(LH_2)_2]$ (1), $[Co_2Cl(LH_2)_2(H_2O)]\cdot 4H_2O$ (2), and $[Cu_4(LH_2)_4(H_2O_4)]$ (3) are shown in Figure 1, Figure 2, and Figure 3, respectively. Figure 4 displays the core of tetramer 3. Selected bond lengths and angles for the three compounds are listed in Table 2, Table 3, and Table 4. In complex 1 the manganese(IV) ion presents a distorted octahedral configuration, achieved through a pair of NO₂ donor atoms from two LH₄ ligands: the two phenoxo oxygen atoms (O1 and O1#) and the two oxygen



Figure 1. Molecular structure of $[Mn(LH_2)_2]$ (1). For clarity, the hydrogen atoms are omitted. Symmetry transformations used to generate equivalent atoms: (#1) *y*, *x*,*-z*+1.



Figure 2. Molecular structure of $[Co_2Cl(LH_2)_2(H_2O)] \cdot 4H_2O$ (2). For clarity, the hydrogen atoms and the solvate molecules are omitted.



Figure 3. Molecular structure of $[Cu_4(LH_2)_4(H_2O)_4]$ (3), with atom labelling for the asymmetric unit. For clarity, the hydrogen atoms are are omitted.

atoms of deprotonated alcohol groups (O3 and O3#) occupy the equatorial positions; two N atoms (N and N#) adopt a *trans* arrangement. The oxygen atoms O4, O4# ("2-hydroxymethyl") and O5/O5# ("propan-1-ol") retain their protons. A similar structure to compound **1** was reported by *Zhang* et al.^[29] in which does not occur deprotonation of the "1,3-propanediol" segment of LH₄, remaining the manganese ion as Mn^{II}.

The molecular structure of the mixed valence cobalt complex 2 (Figure 2) consists of a non-centrosymmetric dimer, in which two crystallographically independent cobalt ions are bridged by two deprotonated oxygen atoms of the alcohol group. Both cobalt ions are hexa-coordinate with distorted octahedral arrangements. Moreover, the coordination spheres of alloemeine Chemi

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Figure 4. Details of the core of tetramer **3**.Symmetry transformations used to generate equivalent atoms: (') -y+7/4, x-1/4, -z+7/4; ('') y+1/4, -x+7/4, -z+7/4; ('') -x+4/2, -y+3/2, z.

Table 2. Bond lengths /Å and angles /° for 1.

Bond lengths		
Mn–O3	1.849(2)	
Mn-O1	1.931(2)	
Mn–N	1.991(3)	
Bond angles		
O3–Mn–O3#1	94.87(16)	
O3-Mn-O1	171.73(11)	
O3#1-Mn-O1	90.21(10)	
O1-Mn-O1#1	85.53(13)	
O3–Mn–N	84.05(11)	
O3#1-Mn-N	88.83(11)	
O1–Mn–N	89.53(10)	
O1#1-Mn-N	98.20(11)	
N-Mn-N#1	169.49(17)	

Symmetry transformations used to generate equivalent atoms: #1 y, x, -z+1

both cobalt ions are different. The coordination environment of the trivalent Co1 is formed by a pair of NO₂ donor atoms from two LH₄ ligands: the two phenoxo oxygen atoms (O1 and O6), the two oxygen atoms of deprotonated alcohol group (O4 and O8), and the two imine nitrogen atoms (N1 and N2). The coordination sphere of divalent Co2 is occupied by two bridge-forming oxygen atoms (O1 and O6) from two LH₄ ligands, two (protonated) oxygen atoms of alcohol groups from two ligands (O5 and O10), a water molecule (O12), and one chloride ion. The oxidation states of Co1 (III) and Co2 (II) were assigned on the basis of charge balances and consideration of bond lengths (see Table 3). An analogue mixed valence complex of cobalt was already reported by *Ke*, *Xie* and co-workers.^[12]

The tetramer $[Cu(LH_2)(H_2O)]_4$ (3) crystallizes in the tetragonal space group $I4_1/a$ and the equivalent atoms can be generated from the asymmetric unit by the symmetry transformations (') -y+7/4, x-1/4, -z+7/4, ('') y+1/4, -x+7/4, -z+7/4

Bond lengths		
Co2-O8	2.057(3)	
Co2–O4	2.065(3)	
Co2–O12	2.085(3)	
Co2–O5	2.152(3)	
Co2-O10	2.168(3)	
Co2–Cl	2.3902(11)	
Co1–N2	1.881(3)	
Co1–N1	1.885(3)	
Co1-O6	1.897(2)	
Co1–O1	1.898(3)	
Co1-O8	1.901(3)	
Co1–O4	1.904(3)	
Bond angles		
O5-Co2-O10	175.07(12)	
N1-Co1-O8	90.82(12)	
O8–Co2–O4	76.72(10)	
O6-Co1-O8	176.55(12)	
O8-Co2-O12	173.49(13)	
O1-Co1-O8	92.41(12)	
O4-Co2-O12	97.19(13)	
N2-Co1-O4	91.40(12)	
O8-Co2-O5	92.54(11)	
N1-Co1-O4	85.99(13)	
O4–Co2–O5	86.35(10)	
O6-Co1-O4	92.89(12)	
O12-Co2-O5	89.34(12)	
O1-Co1-O4	176.21(12)	
O8-Co2-O10	87.27(10)	
O8-Co1-O4	84.50(11)	
O4-Co2-O10	88.81(11)	
Co1-O4-Co2	99.20(13)	
012-Co2-O10	90.32(12)	
08-02-01	96.05(8)	
04-C02-C1	172.68(8)	
012 - 002 - 01	90.07(10)	
05-02-01	92 89(8)	
010-02-01	92.04(9)	
$N_{2}^{-}C_{01}^{-}N_{1}^{1}$	175.93(14)	
N2-Co1-O6	96.54(13)	
N1-Co1-O6	86 73(12)	
$N_{2}-C_{0}1-O_{1}$	86 18(12)	
N1-Co1-O1	96 25(13)	
06-C01-01	90.28(12)	
N2_Co1_08	85.81(12)	
$C_{01} 08 C_{02}$	00 58(12)	

and (''') -x+4/2, -y+3/2, *z* (see Figure 3 and Figure 4). The copper(II) ions achieve a distorted tetrahedral configuration, without metal–metal interaction. In the crystal lattice of **3**, four oxygen from alcohol groups bridge (each) three copper atoms, performing four threefold bridges. One (per copper atom) deprotonated phenoxo oxygen, four imine nitrogen atoms, and four water molecules complete the distorted octahedral arrangement of the metal atoms. The Cu···OH₂ distances are 2.7861(1) Å, being on the frontier of a coordination bond, since the sum of the Cu/O van der Waals radii is 2.92 Å.^[30] Although the recommended bond valence parameter for the bond O–Cu²⁺ is 1.679 Å,^[31] the water molecules in **3** are oriented toward the axial ligand orbitals of the Cu²⁺ ions, so that the axial angles with 159.096(2)° are not excessively deviated from the axial symmetry.

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Bond lengths		
Cu01	1.909(4)	
Cu–O2	1.9495(6)	
Cu–N	1.959(6)	
CuO2"	1.9710(8)	
Cu-O2'''	2.5635(1)	
O2–Cu'	1.9710(8)	
Bond angles		
01–Cu–O2	171.93(14)	
O1-Cu-N	94.0(2)	
O2-Cu-N	84.45(15)	
O1-Cu-O2"	94.88(14)	
O2-Cu-O2"	88.21(3)	
N-Cu-O2"	165.92(16)	
Cu–O2–Cu'	108.87(2)	

Table 4. Bond lengths /Å and angles /° for 3.

Symmetry transformations used to generate equivalent atoms: (') -y+7/4, x-1/4, -z+7/4; ('') y+1/4, -x+7/4, -z+7/4;(''') -x+4/2, -y+3/2, z.

3.2 Electrochemical Behavior of Compounds 1-3

The electrochemical behaviors of compounds 1–3 were investigated by cyclic voltammetry with a glassy carbon electrode in a dry CH₃CN solution in the range of 1.0×10^{-3} to 2.5×10^{-3} M and 0.1 M TBAPF₆ as the supporting electrode in an argon saturated atmosphere in the potential range –1.00 V

	Table 5. Redox	potential	data	of	studied	compounds.
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Compound	$E_{1 \text{oxid}}$	$E_{2\text{oxid}}$	E_{1red}
LH_4 ligand	+1.35 V ^{a)}	_	-0.53 V ^{b)}
Co ^{II} Co ^{II} complex	+1.03 V ^{a)}	+1.30 V ^{a)}	_
Mn ^{IV} complex	+1.00 V ^{a)}	+1.30V ^{a)}	-0,46 V ^{b)}
Cu ^{II} complex	+1.01V ^{a)}	+1.24 V ^{a)}	-

a) Anodic peak. b) Cathodic peak.

to 2.20 V vs. NHE (Table 5). For all compounds, the Fc/Fc+ redox couple of ferrocene was used as the internal standard (see in instrumentation section).

The aromatic tri-hydroxyl type ligand LH₄ shows two irreversible redox processes as illustrated in Figure 5A. First, the anodic irreversible peak observed at $E_{\rm pa}$ = +1.35 V can be assigned to the one-electron oxidation of the Schiff base ligand. On the other hand, the only irreversible cathodic peak at $E_{\rm pc}$ = -0.53 V can be assigned to the monoelectronic reduction of the Schiff base.^[32]

The cyclic voltammograms of the manganese complex 1 shows three processes as shown in Figure 5C. A nearly irreversible reduction occurs at $E_{\rm pc} = -0.46$ V vs. NHE, which can be assigned to the Mn^{IV}/Mn^{III} redox couple. This rather negative and irreversible reduction wave at -0.46 V for the Mn^{IV}/Mn^{III} indicates a relatively stable Mn^{IV} complex, with the electronic nature of the ligand having hydroxyl and imine groups; this is in agreement with the X-ray structure in this work; the hydroxyl and imine groups are reported to be ef-



Figure 5. Cyclic voltammograms of (A) LH4 (B) Co complex, (C) Mn complex, and (D) Cu complex solution of dry acetonitrile, 0.1 M TBAPF₆, using glassy carbon electrode, at scan rate 25 to 200 mV s⁻¹.

ficient to stabilizing the higher oxidation Mn^{IV} state, thus causing a negative reduction potential for Mn^{IV}/Mn^{III} species.^[33,34] On the other hand, the first oxidation process at $E_{pa} = +1.00$ V can be attributed to the Mn^{IV}/Mn^{V} redox couple, following to the second oxidation wave at $E_{pa} = +1.30$ V, which can be assigned to the ligand Schiff base type oxidation.^[35]

Cobalt complex **2** reveals by cyclic voltammetry two irreversible processes at 0.5 V to 2.00 V oxidation range (Figure 5B). The first anodic peak observed at $E_{pa} = +1.03$ V can be assigned to the one-electron oxidation of the mixed-valence $Co^{II}Co^{III}$ complex to the corresponding $Co^{III}Co^{III}$ species, in which the $Co_2N_2O_4$ moiety is coordinated by a dichelated ligand containing N-imine and O-phenolate donor atoms (Co_2L) .^[12] The second oxidation process observed at $E_{pa} =$ +1.30 V can be assigned to the ligand oxidation Schiff base type.

In the case of copper complex **3**, two irreversible oxidation redox waves are observed at 0.75 V to 1.50 V potential range (Figure 5D). The anodic peak observed at $E_{pa} = +1.01$ V can be assigned to the one-electron oxidation Cu^{II}/Cu^{III} redox couple. The second anodic peak at $E_{pa} = +1.24$ V can be attributed to the Schiff base ligand oxidation. These facts can be supposed to the closed-packing central Cu atoms in the structure and the electronic nature of Schiff base ligand type in the coordination sphere (O-hydroxyl and N-imine donor atoms).^[36]

3.3 UV/Vis Spectroscopy

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The electronic spectra of the ligand LH₄ and their complexes **1–3** measured in acetonitrile solution reveal the following transitions listed in Table 6, respectively. The LH₄ ligand presents three absorption bands at 261, 329, and 420 nm. The first high-energy transition can be assigned to the intraligand $\pi \rightarrow \pi^*$ transition, following to the $n \rightarrow \pi^*$ C–N imine transition at 329 nm and in 420 nm a band like charge-transfer transition, refers to the phenolate group.^[32]

Table 6. Electronic absorption data /nm of compounds.

Compound	mol·L ⁻¹	$\lambda \ (\log \ \varepsilon)$
LH ₄ ligand	5.05×10^{-6}	261 (4.22); 329 (3.54); 420 (3.19)
Co ^{II} Co ^{II} complex	5.0×10^{-6}	312 (3.54); 398 (3.36)
Mn ¹ , complex	4.60×10^{-6}	266 (4.17); 346 (3.70); 418 (3.54)
Cu ^{II} complex	4.75×10^{-6}	279 (4.23); 375 (3.76); 621 (3.01)

For the Mn^{IV} complex **1**, the UV/Vis spectrum reveals three absorption transitions: at 266 nm, which can be attributed to the intraligand process ($\pi \rightarrow \pi^*$); two lower intensive bands are observed at 346 nm (log $\varepsilon = 3.70$), can be assigned to the C–N imine LMCT transition, following charge-transfer O_{phenolate} \rightarrow Mn^{IV} transition at 418 nm (log $\varepsilon = 3.54$), in a *quasi*-regular octahedral environment, in agreement with the X-ray structure proposed.^[32,37,38]

In the mixed-valence $Co^{II}Co^{II}$ complex 2 the band observed at 398 nm (log ε = 3.36) is best described as a charge-transfer process most probably originating from a $O_{phenolate} \rightarrow Co^{III}$ LMCT, in agreement with the resolved X-ray structure of cobalt complex **2** (Co1–O1 and Co1–O6). No intervalence transition at lower energy was observed, thus suggesting that the valences are also localized $[Co(1)^{III}; Co(2)^{II}]$ when **2** is dissolved in CH₃CN solution.^[12]

In the case of tetranuclear Cu^{II} complex **3** was observed a typical UV/Vis spectrum of a copper(II) complex. The lower energy absorptions can be assigned to d-d transitions at 621 nm (log $\varepsilon = 3.01$) and are typical of Cu^{II} complexes in a highly distorted octahedral environment, in agreement with the X-ray structure of complex **3**, which reveals that the central copper atoms are in the oxidation state 2+.^[36] The band at 375 nm (log $\varepsilon = 3.76$) can be attributed to a charge-transfer O_{phenolate} \rightarrow Cu^{II} LMCT transition while the one strong and highly-intense remaining band at 279 nm (log $\varepsilon = 4.23$) is assigned to intraligand transition. At lower energy range (700–900 nm) no intervalence transitions are observed in this copper(II) complex type.

4 Conclusions

The synthesis and the X-ray structural characterization of three Schiff base complexes of Mn^{IV} , $Co^{II}Co^{II}$, and Cu^{II} were discussed, as well as IR and C, H, N analyses of the new compounds. Experiments on cyclic voltammetry and UV/Vis spectroscopy were also described to evaluate the redox potential of the title complexes, as part of preliminary studies, which includes their use as mimics of the peroxidase in the reaction of phenol with H_2O_2 in the presence of an indicator.

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