



Novel N₂O₂ Schiff base derived from 1,2-Hydrazinedicarboximidamide and its complexes with Cu(II), Co(II), Ni(II), Mn(II) and Cr(III): Synthesis and characterization

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ABSTRACT

The synthesis of a (1,2-Hydrazinedicarboximidamide) was identified in this paper and condensing it with 2-4dihydroxybenzaldehyde to form tetradentate ligand (L). This ligand used to prepare five metal complexes as chloride salts [Cu₂(L)Cl₂](1), [Co₂(L)Cl₂](2), [Ni₂(L)Cl₂](3), [Mn₂(L)Cl₂](4) and [Cr₂(L)Cl₂](5) in an ethanolic medium. Dimethyl formamide (DMF) prepared complexes solutions to applied it as electrolytes. The structures were confirmed by several spectroscopic and analytical techniques indicating that metal complexes are more likely to have tetrahedral-coordinated geometry. Thus, these structures indicated the ligand show similar actions as tetradentate linked to metal ion by nitrogen (azomethine) and the negative charge of oxygen atoms from hydroxyl in 2-4dihydroxybenzaldehyde.

INTRODUCTION

Metal complexes of azomethine ligands have acquired more attention due to their easy synthesis, their stereo-electronic structures, and outstanding biological activities¹, catalytic activities^{2,3}. Synthesis and design of transition metal ion complexes get together. Continued interest of Schiff base ligands consideration of the possibility of earning multiple structures scientific research involving catalysts⁴, material science⁵, optic applications⁶, medical chemistry⁷. Synthetic ingenuity leading to variety in structural arrangement

in space considered as the gateway factors, which attending wide deal of benefit to azomethane ligands in coordination chemistry. Furthermore, their individual self-assembling behavior, result to the modeling of different supramolecular structural design, have assisted them to have the status of special ligand configuration⁸. Schiff bases are believed to be "privileged ligands" due to their easily synthesis by the reaction between aldehyde and primary amine. The Ligands of Schiff base are eligible to linked with several metal ions and to confirm them in many oxidation states⁹. Tetradentate Schiff bases with a (N₂O₂) donation atoms



to coordinate with several metal ions, and this has confirmed by many papers¹⁰.

Rather significant advantage was the azomethine group (C = N) in the configuration of the Schiff bases for the lone pair of electrons on a nitrogen atom sp²-hybridized orbital¹¹. They show premium benefits for several fields, such as speeding up the organic synthesis reaction as a catalyst, chemistry of transition metals, industrial, biological, pharmacological and optical sensor properties¹².

MATERIALS AND METHODS

Synthesis of (1,2-Hydrazinedicarboximidamide) (A)

It was prepared by reaction of thiourea (24.57 g, 0.3228 mol) and hydrazine hydrate (8 g, 0.16 mol) in ethanol (100 cm³) by refluxing for 3 h with stirring. The product was cooled at room temperature and filter it to get hydrazide¹³. The recommended structure for the synthesis ligand(A) was given in Fig. 1 and some physical properties were showed in Tables 1.

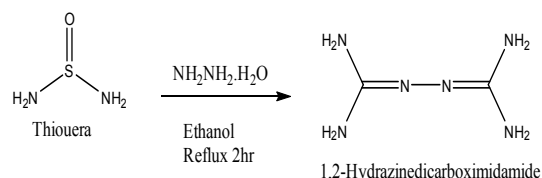
Synthesis of the Schiff base ligand (L)

L was synthesis by dissolving (0.039 mol, 5.52 g) of 2,4-dihydroxybenzaldehyde in (25 mL) of ethanol and adding about (3-2) drops of glacial acetic acid and stirred for 10 min to ensure the formation of the carbonium ion, then (0.0096 mol, 1.2 g) of compound A dissolved in (15 mL) of ethanol was slowly and step by step added while refluxing. After completing the addition process, the mixture left for (5 h) in an inert atmosphere of Akron gas. The reaction was followed up using layer chromatography¹⁴. The suggested structure for the prepared ligand(L) was showed in Fig. 2 and some physical properties were listed in Tables 1.

Synthesis of the Schiff base complexes

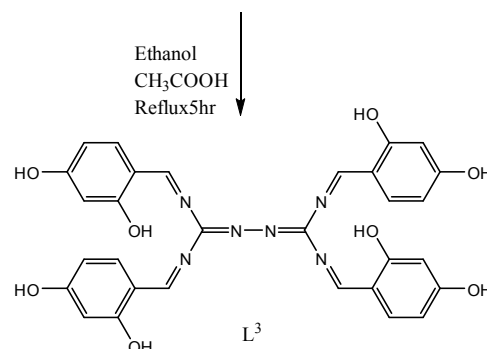
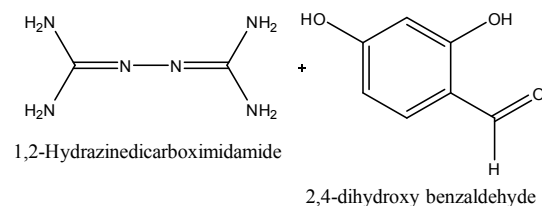
Complexes of the ions Mn (II), Co (II), Ni (II), Cu (II), Cr (III) were prepared with the Schiff bases of (L) by dissolving (0.149 g, 0.001 mol) of ligand (Dissolved L in (2: 3: 3 mL) of solvents (DMF: EtOH: MeOH)) respectively with (0.0989, 0.1189, 0.0852, 0.1188, 0.1332 g, 0.002 (mol of salts), CuCl₂·2H₂O, CoCl₂·6H₂O, MnCl₂·4H₂O (CrCl₃·6H₂O, NiCl₂·6H₂O, respectively, and the mixture still reflux for about (3 hours). With the presence of supplying of Argon gas to the reaction, a colored precipitate was observed after which the solution was filtered and the crystals were washed with diethyl ether and then the product was allowed to dry at room temperature¹⁵. The prepared

Complexes structure was suggested in Fig. 3 and some physical feature were listed in Tables 1.



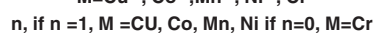
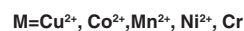
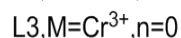
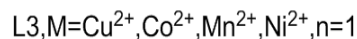
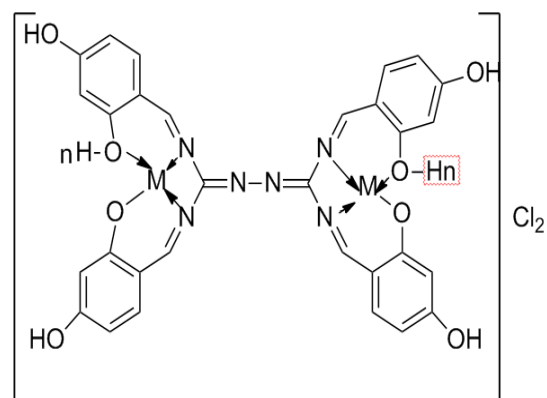
Reaction scheme of synthesis of 1,2-Hydrazinedicarboximidamide

Fig. 1. Chemical structure of the prepared compound (A)



Reaction scheme of synthesis of ligand (L)

Fig. 2. Chemical structure of the prepared Schiff base ligand



Reaction scheme of synthesis of Schiff base complexes
Fig. 3. Chemical structure of the prepared Schiff base complexes

Table 1: Some physical properties of prepared Schiff base and complexes

Symbol	Molecular formula	Molecular weight	Physical state and colour	Time of reaction(hour)	Melting point °C	Values Rf	Yield%
A	C ₂ H ₈ N ₆	116.13	White powder	3	139-140	0.25	58
L ³	C ₃ OH ₂₄ N ₆ O ₈	596.56	Orange powder	5	278-280	0.36	54
L ³ -Cu	[Cu ₂ (C ₃₀ H ₂₄ N ₆ O ₈)Cl ₂]	792.5	Brown red crystalline	3	300	-----	84
L ³ -Co	[Co ₂ (C ₃₀ H ₂₄ N ₆ O ₈)Cl ₂]	783.3	Olive powder	3	300	-----	61
L ³ -Mn	[Mn ₂ (C ₃₀ H ₂₄ N ₆ O ₈)Cl ₂]	775.3	Yellowish orange powder	3	300	-----	49
L ³ -Ni	[Ni ₂ (C ₃₀ H ₂₄ N ₆ O ₈)Cl ₂]	782.8	Yellowish red powder	3	300	----	63
L ³ -Cr	[Cr ₂ (C ₃₀ H ₂₄ N ₆ O ₈)Cl ₂]	769.4	Brown crystalline	3	300	----	54

RESULTS

Identification and characterization of synthetic Schiff base and its complexes were confirmed by many techniques like by the FTIR, UV-Vis, ¹H-NMR, ¹³C-NMR, ESI-Mass, molar conductivity and magnetic properties to prove the chemical structure of the prepared Schiff base and its complexes.

IR spectra of the ligands and complexes

The IR bands of the ligands and its complexes are given in Table 2. The most notable divergence in the IR figure of the ligand (L and

complexes (L³-Cu, L³-Co, L³-Mn, L³-Ni, L³-Cr) was the moving of C=N stretching frequencies to smaller frequencies cause to metal–ligand coordination¹⁶. The ligand (L) show vibration of azomethine at 1633 cm⁻¹ was shifted to a greater frequency in the complex (L-Cu) due to back donation and decreasing the planar specialty after complexation¹⁷ and the azomethine vibration was shifted for a less frequency in the complexes (L-Co, L-Mn, L-Ni, L-Cr) due to decreasing the double bonding property after complex¹⁸. The absorption bands in the spectra of complexes (L-Cu) (L-Co), (L-Mn), (L-Ni) and (L-Cr) at 3363 cm⁻¹, 3344 cm⁻¹, (3348-3336 cm⁻¹), 3367 cm⁻¹ and 3385 cm⁻¹ respectively were attributed to OH.

Table 2: IR bonds (cm⁻¹) of the ligands and the complexes

Symbol	νC-H (Ar.)	νC=N	νC=C (Ar.)	νOther	νN-N	νC-O	νC-N	νM-N	νM-NH	νM-O
A	-----	1643-1612	-----	δ N-H (3377-3174)	1083	-----	1473-1415	-----	-----	----
L	3039	1633	1581-1444	δ O-H 3130	1166	1230	1396	-----	-----	-----
(Cu L)	3120	1643	1537-1487	δ O-H 3363	1122	1228	1396	412	---	497
(Co L)	3205	1616	1541	δ O-H 3344	1110	1222	1435	462	----	516
(Mn L)	3215-3203	1618	1498	δ O-H 3348-3336	1162	1230	1325	499	-----	634
(Ni L)	3184	1631-1618	1585-1498	δ O-H 3367	1130	1230	1395	511	-----	634
(Cr L)	3132-3066	1618	1583-1539	δ O-H 3385	1133	1234	1429	480	-----	426

UV-Visible spectra of the ligands and complexes

The electronic spectra (UV-Vis) data of the ligands and its complexes are shown in Table 3 and The π band of the ligands L at 282 nm is assigned to phenyl of 2,4-dihydroxybenzaldehyde π→π* transition¹⁹. The azomethine group in these ligands was appeared two bands is because of the π→π* and n→π*¹⁹. These two bands were moved to higher wavelengths in the complexes. The spectra of complexes (L-Cu, L-Co, L-Mn, L-Ni, L-Cr) show new two types of bands in

higher wavelengths (visible region) are indicated to d–d transitions of the metal ion²² and ligand–metal charge transfer (LMCT) bands²⁰.

¹H-NMR, ¹³C-NMR spectra of the ligands: The ¹H-NMR spectra of the ligand L was recorded in DMSO. Using 400 MHz, and it appeared a many of characteristic signals of the ligand as shown in Table 4. The signals due to the aromatic protons were observed in the range δ = 7.53 – 6.32 ppm. The

signal observed in the $\delta = 9.90$ ppm was attributed to the azomethine protons in the molecule²¹. ¹³C-NMR spectra of the ligand was recorded in DMSO. Using 100MHZ and it showed a number of identification signals of ligand as shown in Table 5¹⁷, the signals

assigned the aromatic carbon were shown in the range $\delta = 102.19 - 132.18$ ppm. The signal observed in the $\delta 165.16$ ppm was due to azomethine carbon in the molecule and the signals observed in $\delta 163.25$ ppm was attributed to carbon guanidine group²².

Table 3: Electronic spectral data for the ligand and their complexes

Symbol compound	Wavelength and molar absorption $\pi \rightarrow \pi$	Wavelength $n \rightarrow \pi$	Wavelength and molar absorption (L-M)	Wavelength and molar absorption (d-d) nm	Transfer type (d-d)	structure
L	2,823,181, 600,011,000	3,561,630	-----	-----	-----	tetrahedral
(Cu L)	286, 1620	358, 504	440, 78	518, 37	$^3T_2 \rightarrow ^3E$	tetrahedral
(Co L)	284,320, 16,501,090	-----	376, 80	520,725,50,40	$^4F_{4/2} \rightarrow ^4P_{1/2}$ $^4F_{4/2} \rightarrow ^4T_{2/2}$	tetrahedral
(Mn L)	259,279,324, 1647,2060,1550	-----	-----	481,730,42,15	$^6A_{1g} \rightarrow ^4A_{2g}$, 4E_g $^6A_{1g(F)} \rightarrow ^4T_{2g(G)}$ $^6A_{1g(S)} \rightarrow ^4T_{2g(G)}$	tetrahedral
(Ni L)	282, 1380	321, 890	380, 112	490, 3.8	$^3F_{4/2} \rightarrow ^3P_{1/2}$ $^3F_{4/2} \rightarrow ^3A_{2/2}$ $^3F_{4/2} \rightarrow ^3T_{2/2}$	tetrahedral
(Cr L)	297,322, 740,850	328, 374	-----	460,600, 774,220,23,24	$^4F_{4/2} \rightarrow ^4P_{1/2}$ $^4F_{4/2} \rightarrow ^4T_{2/2}$	tetrahedral

Table 4: Chemical Shift of ¹H-NMR for the ligand(L3)

Symbol compound	Protons	Signal	(Chemical Shift ppm)
L	1H,HC=N	singlet	9.90
	3H,Ar-H	multiple	7.53-6.32

Table 5: Chemical Shift of ¹³C-NMR for the ligand(L³)

Carbon atoms	δ (chemical shift ppm)
	L ³
C ₁ ,(-C=N-N)	163.25
C ₂ ,(HC=N)	165.16
Ar-c	102.19-132.81

ESI-Mass spectra

ESI-Mass spectra of the synthesised compounds were carried out by using Agilent Technologies-Tehran-Iran-Trabiat Modares University. ESI-Mass spectra of the prepared ligand and complexes showed molecular ion peak (M^+) at 116, which corresponding to the molecular formula of (A), at 733 which corresponds to the molecular formula of (L). And at (723),(713),(704),(714),(701) which corresponds to molecular formula of complexes (L-Cu), (L-Co), (L-Mn), (L-Ni), (L-Cr)²³. ESI-Mass spectra of the synthesised compounds are shown in Table (6).

Molar conductivity

The measurements of Conductivity were completed at room temperature of 10^{-3} M in

DMF solvent to proven the charge order of metal complexes. The values of conductivity for the prepared metal complexes Co (II), Cu (II), Mn(II), Ni(II) and Cr(III) were found to be 82.1, 80.2, 89.5, 79.7 and 78.2 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively. So that, the suggestion for the complexes were electrolytes²⁴ due to the Chlorate ions outside the coordination sphere in solution and they were separate gradually in the DMF solvent.

Table 6: ESI-Mass spectra of prepared ligands and complexes

Compound	Molecular formula	Molecular weight	M+	Relative abundance
A	C ₂ H ₈ N ₆	116.13	M=116	83
L	C ₃₀ H ₂₄ N ₆ O ₈	596.56	M+2H=599	157
(Cu L)	C ₃₀ H ₂₄ N ₆ O ₈ (Cl ₂)Cu ₂	721.62	M+H=723	341
(Co L)	C ₃₀ H ₂₄ N ₆ O ₈ (Cl ₂)Co ₂	712.39	M+H=713	203
(Mn L)	C ₃₀ H ₂₄ N ₆ O ₈ (Cl ₂)Mn ₂	704.4	M=704	153
(Ni L)	C ₃₀ H ₂₄ N ₆ O ₈ (Cl ₂)Ni ₂	711.9	M+2H=714	143
(Cr L)	C ₃₀ H ₂₄ N ₆ O ₈ (Cl ₂)Cr ₂	698.52	M+2H=701	203

Magnetic susceptibility measurements

The calculated of magnetic moment to prepared complexes displayed that the d⁹ Cu(II) complex is 1.843.6BM reported as distorted tetrahedral geometry. The observed of magnetic moment to the d⁷ Co(II) complex is 2.531BM which is more corresponding with the SP³. The magnetic susceptibility measurement determined for the d⁵

Mn(II) complex is 5.836BM which suitable with the distorted tetrahedral geometry. The magnetic moment showed for d⁸ Ni(II) complex is 3.463BM

which is more convenient with the SP³ geometry while Cr Complex computed 3.932 BM which is more convenient with the tetrahedral geometry²⁵too.

Table 7: Conductivity of complexes

Symbol compound	Molecular formula	Cell constant A(cm ⁻¹)	Electrical conductivity Ohm ⁻¹	Molar conductivity Ohm ⁻¹ .cm ² .mol ⁻¹
(Cu L)	[Cu ₂ (C ₃₀ H ₂₂ N ₆ O ₈)]Cl ₂	1.1	82.x10 ⁻⁶	82.1
(Co L)	[Co ₂ (C ₃₀ H ₂₂ N ₆ O ₈)]Cl ₂	1.1	80.2x10 ⁻⁶	80.2
(Mn L)	[Mn ₂ (C ₃₀ H ₂₂ N ₆ O ₈)]Cl ₂	1.1	89.5x10 ⁻⁶	89.5
(Ni L)	[Ni ₂ (C ₃₀ H ₂₂ N ₆ O ₈)]Cl ₂	1.1	79.7x10 ⁻⁶	79.7
(Cr L)	[Cr ₂ (C ₃₀ H ₂₂ N ₆ O ₈)]Cl ₂	1.1	78.2x10 ⁻⁶	78.2

Table 8: Magnetic susceptibility measurements

Symbol of complex	Mass magnetic susceptibility Xg.10 ⁻⁶	Molar magnetic susceptibility Xm.10 ⁻⁶	Correct Factor D.10 ⁻⁶	Atomic Magnetic Susceptibility X _A .10 ⁻⁶	Effective magnetic moment Meff(B.M.)	Hybridization
(Cu L)	2.498	1979.66	379.3-	1600.36	1.8436	Tetrahedral
(Co L)	4.874	3817.8	380.1-	3437.7	2.531	Tetrahedral
(Mn L)	6.995	5423.22	382.5-	5040.72	5.836	Tetrahedral
(Ni L)	5.873	4600.32	371.9-	4228.42	3.463	Tetrahedral
(Cr L)	4.903	3772.36	385.6-	3386.76	3.932	Tetrahedral

DISCUSSION

The L ligand and its metal complexes of Cu(II), Co(II), Mn(II), Ni(II) and Cr(II) have been structurally proven by several techniques. The stoichiometry of metal ligand in all these complexes clarify that analytical data is 2:1. In DMF solvent appeared all these complexes are electrolytes. That ligand showed the spectral data deal as neutral and tetradentate coordinating through nitrogen atom of the azomethine and oxygen atoms of hydroxyl group of the 2-4dihydroxybenzaldehyde. Depending on all information that gotten from technique like molar

conductance, magnetic and spectral data, lead to considerable opinion that complexes wer assigned to be in tetrahedral geometry (SP³).

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Conflict of Interest

The authors declared that there is no conflict of interest regarding the publication of this paper.

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