



Synthesis and Characterization of Some Novel Metal Complexes Derived from Oxalic Acid Dihydrazide

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Abstract: Complexes of oxalic acid dihydrazide (ODH, L¹) with Co²⁺, Ni²⁺, Zn²⁺, and Pd²⁺ salts were isolated and characterized by elemental analyses, spectral (IR, UV-Vis., mass), TGA, and magnetic measurements. The complexes are of the types, [Ni₂(ODH-H)(OH)₂(CH₃OH)₂H₂O].H₂O, [Ni(ODH-H)(H₂O)₂Cl], [Co₂(ODH-2H)Cl₂H₂O)₆CH₃OH].3H₂O, [Zn₃(ODH-H)₂(OCH₃)₂(CH₃OH)₂].H₂O, [Co(ODH-H)₂(H₂O)₂], and [Pd₃(ODH-H)₂Cl₄](H₂O)₂].2CH₃OH. In the first three complexes, the ligand behaves in a bidentate manner; and is coordinated through NH and the enolized carbonyl oxygen groups with a removal of a proton from the latter group. Also, it acts as a bidentate ligand coordinated through the enolized (C=O) and (C=N) groups with the removal of a proton from the former group forming a five-membered ring around the Co²⁺ ion in the complex, [Co(ODH-H)₂(H₂O)₂]. Finally, two ligands bonded three Pd²⁺ ions in which the terminal two palladium ions are bonded through the (C=O) and the (C=N) moieties forming two five-membered rings around the Pd²⁺ ions, while the intermediate Pd²⁺ ion is coordinated to two NH and two enolized carbonyl oxygen with the removal of two protons forming two five-membered rings around the Pd²⁺ ion. The geometries of the complexes were determined depending on the spectral and magnetic measurements.

keywords: Phenylboronic, Suzuki, Cationic, DFT

1. Introduction

Acid hydrazides have been the subject of many previous papers. We reported earlier the coordination of some simple aliphatic acid hydrazides up to isobutyric acid (IBH) [1]. Also, cinnamic acid hydrazide (CAH) forms complexes with different M²⁺ cations derived from the 3d-metal ions [2]. The route of coordination with acid hydrazides for these complexes has been a matter of some discussion. Thus, some authors [3] claim to synthesize complexes with hydrazides bonded *via* the carbonyl oxygen, while other authors favor bonding through the NH₂ group and the carbonyl group or *via* the carbonyl group only [4]. Another possible mode of coordination proceeds using the NH group as reported by Ahmed and co-workers [5].

On the other hand, the complexes derived from oxalic acid dihydrazide (ODH) with some vital bivalent transition metal salts serve as models of biological systems, for example, of protein compounds with some metal ions, and

for the synthesis of pharmacological substrates. In earlier communication, we reported earlier the synthesis and characterization studies of some mono hydrazides with 3d-metal ions [6-12]. Herein we report some metal complexes of oxalic acid dihydrazide (ODH) with some metal ions. This study aimed to explore the coordination behavior of this ligand towards some divalent metal ions (Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and Pd²⁺) in the presence and/or absence of sodium acetate. Also, the structure of the ligands and new metal complexes were identified by elemental analyses, spectral (IR, UV, mass), TGA, and magnetic measurements for some selected metal complexes.

2. Experimental

The chemicals utilized were of the purest grade and purchased from Aldrich and used without further purification.

2.1. Synthesis of L^1 (ODH)

Hydrazine hydrate (6.27 mL, 0.2 mole) was added drop by drop to diethyl oxalate (13 mL, 0.1 mole) in ethanol solution (20 mL) with stirring for 15 min. L^1 (oxalic acid dihydrazide) was obtained as a white solid, then filtered and washed successively with EtOH followed by diethyl ether, and then dried in a vacuum over anhydrous $CaCl_2$ in a desiccator.

2.2. Synthesis of metal complexes

2.2.1. Synthesis of Cu^{2+} , Ni^{2+} , Co^{2+} , and Zn^{2+} complexes

L^1 (5 mmol, 0.6 mg) was dissolved in dist. H_2O (25 mL) with the heating on a hot plate and $NiCl_2 \cdot 6H_2O$ (5 mmol, 1.18 mg) was dissolved in a small quantity of methanol (20 mL). The resulting solution was boiled under reflux for 30 min. (1:1). The complex, $[Ni_2(ODH-H)(OH)_2(CH_3OH)_2H_2O] \cdot 2H_2O$, obtained as a solid was filtered; and washed with dist. $H_2O + MeOH$ followed by diethyl ether. The Co^{2+} complex with the general formula, $[Co(ODH-H)_2(H_2O)_2]$, was synthesized by dissolving $CoCl_2 \cdot 6H_2O$ (5 mmol, 1.89 g) in the least quantity of methanol (20 mL) followed by adding to the ligand (10 mmol, 1.18 g) dissolved in 25 mL of dist. H_2O . The mixture was heated under reflux for 30 min on a water bath. The solution was found to have a pH in the 5-6 range. The product was obtained by filtration, and then washed with a mixture of dist. $H_2O + MeOH$ followed by diethyl ether.

The metal salts [$NiCl_2 \cdot 6H_2O$, (2.37 g, 10 mmol), $CoCl_2 \cdot 6H_2O$ (2.37 mmol), and $ZnCl_2$ (1.36 g, 10 mmol)] were dissolved in methanol (20 mL) and then added to L^1 (5 mmol, 0.6 g) dissolved in 25 mL of dist. H_2O . The reaction mixtures were heated on a hot plate for 30 min. The complexes were adjusted at pH=3-4 for $[Ni(ODH-H)(H_2O)_2Cl]$, and at pH=4-5 for both $[Co_2(ODH-2H)Cl_2(H_2O)_6CH_3OH] \cdot 3H_2O$, and $[Pd_3(ODH-H)_2Cl_4](H_2O)_2 \cdot 2CH_3OH$. The isolated products were obtained on a sintered glass Gooch (G.4); and washed with a mixture of solvents (dist. $H_2O + MeOH$) followed by diethyl ether. On the other hand, the pH's of the two complexes with the general formulae, $[Ni_2(ODH-H)(OH)_2(CH_3OH)_2H_2O] \cdot H_2O$ and $[Co_2(ODH-2H)Cl_2(H_2O)_6CH_3OH] \cdot 3H_2O$, were obtained at pH=2-3. Sodium acetate was added

to rise the pH in which the solid complexes were separated out. A hot solution of aqueous methanol of L^1 (10 mmol, 1.18 g) was added to a solution of $PdCl_2$ (5 mmol, 0.88 g) dissolved in 100 mL of 3M Conc. HCl. The mixture was kept under reflux on a water bath for 2 h. The isolated complex was isolated in an acidic medium, where the pH was found to be 2-3. The isolated product was washed many times with hot dilute methanol; and left in an oven to dry at 120 °C for 0.5 h. All the separated compounds were kept to dry in a vacuum desiccator over anhydrous $CaCl_2$. The data obtained are depicted in **Table 1**.

2.2.2. Physical measurement

Carbon, hydrogen, and nitrogen contents were carried out at the Microanalytical Unit (Cairo University). Mattson 5000 FTIR spectrophotometer was used to record the IR spectra of the solid complexes in the 400-4000 cm^{-1} range using KBr discs. The complexes in DMSO were recorded using a UV-1601 spectrophotometer in the range of (200-900 nm). Sherwood balance was used to determine the magnetic moments at 25 °C and the balance was adjusted using $Hg[Co(NSC)_4]$ as a calibrate. The results of thermal measurements (TGA and DTG) were obtained using the Shimadzu model 50 instrument. The heating rates were 20 cm^3/min and 10 °C/min under nitrogen flow as reported earlier [13], respectively. The metal contents and the percentage of chloride ions were determined using standard methods [14].

3. Results and Discussion

The complexes are insoluble in most organic solvents but the Pd(II) complex is easily soluble in DMSO. The structures of ODH complexes derived from Co(II), Ni(II), and Pd(II) salts were suggested on the basis of the results of physical, spectral, magnetic together with the elemental analyses listed in Table 1. All the complexes have a high melting point (>300 °C) suggesting that the bond between M and L ion is very strong.

The structures of ODH and its Co(II), and Ni(II) complexes are confirmed by some physical properties and elemental analyses results as listed in Table 1. ODH shows an enormous ability to form various stereochemistry containing metal-ligand

complexes of the types (1:1; M:L) and (2:1; M:L) as in Co, and Ni complexes. Both Zn(II), and Pd(II) complexes show the ratio (3:1; M:L) as shown in **Table 1**.

Table 1: Elemental analyses of some metal complexes.

Compound*	Formula	M. Wt	Color	M.P.	Found (Calcd.) %				
					C	H	N	M	Cl
1	C ₂ H ₆ N ₄ O ₂	118.1	White	243	20.8 (20.3)	5.4 (5.1)	48.4 (47.4)	-	-
2	C ₄ H ₂₀ N ₄ Ni ₂ O ₉	369.6	Pale green	>300	13.6 (13.0)	2.4 (5.5)	15.4 (15.2)	31.2 (31.8)	-
3	C ₂ H ₉ ClN ₄ NiO ₄	248.3	Green	>300	10.7 (9.7)	3.2 (3.7)	19.3 (22.6)	23.5 (23.6)	15.1 (14.3)
4	C ₈ H ₂₆ N ₈ O ₉ Zn ₃	574.5	Cream	>300	16.6 (16.7)	2.15 (4.6)	19.1 (19.5)	33.8 (34.1)	-
5	C ₄ H ₁₄ CoN ₈ O ₆	329.2	Pale brown	>300	13.5 (14.6)	2.6 (4.3)	4.2 (34.0)	18.5 (17.9)	-
6	C ₃ H ₂₆ Cl ₂ Co ₂ N ₄ O ₁₂	499.0	Brick-red	>300	7.8 (7.2)	3.3 (5.3)	11.8 (11.2)	23.2 (23.6)	14.1 (14.2)
7	C ₆ H ₂₂ Cl ₄ N ₈ O ₈ Pd ₃	795.3	Brown	>300	8.7 (9.1)	2.2 (2.8)	15.9 (14.1)	40.4 (40.1)	17.8 (17.8)

* Compounds names are as follow:

1: ODH; 2: [Ni₂(ODH-H)(OH)₂(CH₃OH)₂H₂O].H₂O; 3: [Ni(ODH-H)(H₂O)₂Cl]; 4: [Zn₃(ODH-H)₂(OCH₃)₂(CH₃OH)₂].H₂O 5: [Co(ODH-H)₂(H₂O)₂]; 6: [Co₂(ODH-2H)Cl₂(H₂O)₆CH₃OH].3H₂O; 7: [Pd₃(ODH-H)₂Cl₄](H₂O)₂.2CH₃OH

3.1. IR spectra

The IR spectrum of oxalic acid dihydrazide (L¹, ODH) exhibits two medium bands at 3600 and 3590 cm⁻¹ attributed to ν(OH, free) and ν(OH, hydrogen-bonded), and three sharp bands at 3297, 3200 and 3183 cm⁻¹ assignable to ν(NH₂, free), ν(NH₂, hydrogen-bonded), and ν(NH) vibrations, respectively, as shown in Fig. 1. These foundations confirm that the ligand exists in tautomer (keto/enol) forms as shown in Fig. 2.

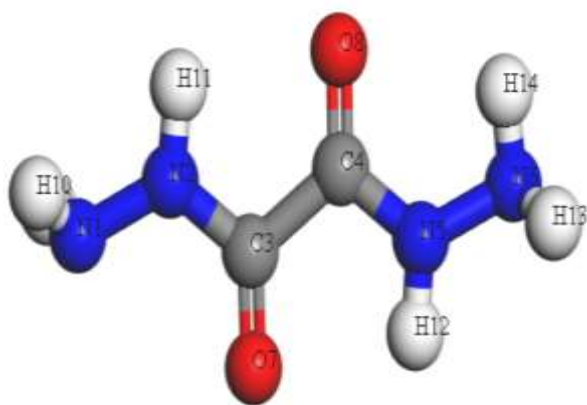


Fig. 1. Structure of L¹ (ODH).

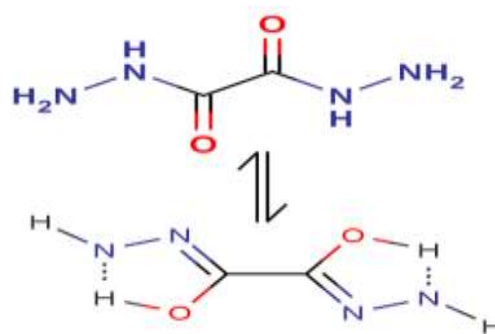


Fig. 2. Tautomeric forms of L¹ (ODH).

Finally, the presence of new three splitter bands at (1612, 1559 cm⁻¹), (1540, 1487 cm⁻¹), and (1459, 1396 cm⁻¹) which are assigned to ν(C=N, free), and ν(C=N, hydrogen-bonded), ν(CONH₂, free), and ν(CONH₂, hydrogen-bonded), and ν(C-OH, free), and ν(C-OH, hydrogen-bonded) supports the existence of a tautomer form as in Fig. 2.

Different modes of chelation were suggested for the isolated metal complexes on the basis of IR, electronic spectra, and magnetic measurements. The results suggest the presence of three categories of bonding. The six complexes with the general formulae; [Ni₂(ODH-H)(OH)₂(CH₃OH)₂H₂O].H₂O (2), [Ni(ODH-H)(H₂O)₂Cl] (3), [Co₂(ODH-2H)Cl₂(H₂O)₆CH₃OH].3H₂O (6), [Pd₃(ODH-H)₂Cl₄](H₂O)₂.2CH₃OH (7), [Co(ODH-H)₂(H₂O)₂] (5), and [Zn₃(ODH-H)₂(OCH₃)₂(CH₃OH)₂].H₂O (4) is proposed. The IR spectra of the former three complexes show that the ligand coordinates *via* the NH and the enolized carbonyl oxygen with the removal of a proton

from the enolized carbonyl oxygen (-C-OH) group forming a five-membered ring around the metal ions. The $\nu(\text{N-N})$ vibration is observed at 1101 cm^{-1} in the uncoordinated ligand (ODH). This band is shifted and observed in $1173\text{--}1208\text{ cm}^{-1}$ region indicating that the ligand coordinates *via* either the NH or NH_2 groups. Doubtless the large shifts of the $\nu(\text{N-N})$ vibration that exists in the hydrazine complexes is traced in the complexes behave in a bidentate hydrazine [15]. Both the $\beta(\text{NH}_2)$ and $\delta(\text{NH}_2)$ vibrations in the free ligand are observed at 1632 , 1321 , and 1159 cm^{-1} which are shifted in the complexes and observed in $1547\text{--}1581$, $1306\text{--}1316$, and $1173\text{--}1208\text{ cm}^{-1}$ region, respectively. All these foundations suggest that the NH group is taking part in coordination. The band at 1005 cm^{-1} is assigned to $\delta(\text{NH})$ vibration [16], however this band is not observed in the spectra of the complexes. Both the two bands at 1045 and 920 cm^{-1} , 1632 , 1321 , and 1159 cm^{-1} assigned to $\nu_{\text{as}}(-\text{C-O})$ and $\nu_{\text{s}}(-\text{C-O-})$ vibrations, respectively, are observed in the metal complexes.

3.2. Electronic spectra, and magnetic measurements

The electronic spectra of the metal chelates were executed in DMSO and some in Nujol (Ni^{2+} complexes). The Ni^{2+} complex with the general formula, $[\text{Ni}_2(\text{ODH-H})(\text{OH})_2(\text{CH}_3\text{OH})_2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$, displays three bands at 10204 , 14835 , and 21314 cm^{-1} in Nujol mull assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g} (\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g} (\text{F}) (\nu_2)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g} (\text{P}) (\nu_3)$ [17], respectively. The bands at 31603 and 25450 are attributed to $L \rightarrow M$ (LMCT). Also, the values of ν_2/ν_1 (1.49) together with the value of μ_{eff} (3.1 BM) support the presence of octahedral geometry around the Ni(II) ion as shown in Fig. 3.

On the other hand, the electronic spectrum of the second Ni(II) complex with the general formula, $[\text{Ni}(\text{ODH-H})(\text{H}_2\text{O})_2\text{Cl}]$, was carried out in Nujol mull. The three bands at 10141 , 14815 , and 25316 cm^{-1} assigned to ${}^3B_1 \rightarrow {}^3B_2$, ${}^3B_1 \rightarrow {}^3A_2$, and ${}^3B_1 \rightarrow {}^3A_2, {}^3E(\text{P})$ transitions, respectively, suggest a square-pyramidal geometry (Fig. 4) around the Ni^{2+} ion [18]. Another strong evidence for the presence of a square-pyramidal structure around the Ni(II) ion comes from the value of magnetic moment (3.54 BM).

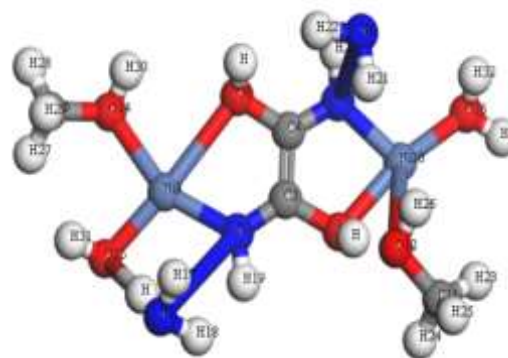


Fig. 3: Structure of $[\text{Ni}_2(\text{ODH-H})(\text{OH})_2(\text{CH}_3\text{OH})_2\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$.

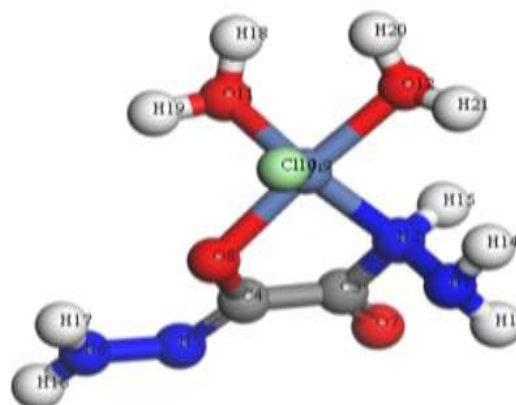


Fig. 4: Structure of $[\text{Ni}(\text{ODH-H})(\text{H}_2\text{O})_2\text{Cl}]$.

Both the spectra of the two Co^{2+} complexes, $[\text{Co}_2(\text{ODH-2H})\text{Cl}_2(\text{H}_2\text{O})_6(\text{CH}_3\text{OH})]\cdot 3\text{H}_2\text{O}$, and $[\text{Co}(\text{ODH-H})_2(\text{H}_2\text{O})_2]$, were carried out in DMSO. The first $\text{Co}(\text{II})$ complex shows two bands at 18819 and 9570 cm^{-1} which are assigned to ${}^4T_{1g} \rightarrow {}^4T_g\text{P}(\nu_3)$ transition. The ν_2 band was calculated and found to be 5560 cm^{-1} attributed to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition and hence the value of ν_3/ν_2 equals 2.69. The results of the electronic spectrum together with the magnetic moment (5.56 BM) suggest the existence of an octahedral geometry around the first $\text{Co}(\text{II})$ ions as shown in Fig. 5.

The second Co^{2+} complex, $[\text{Co}(\text{ODH-H})_2(\text{H}_2\text{O})_2]$, exhibits a band at 14970 cm^{-1} assigned to ${}^4T_{1g} \rightarrow {}^4T_g\text{P}(\nu_3)$ transition while the ν_2 was calculated and found to be 5560 cm^{-1} attributed to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition and hence the value of ν_3/ν_2 equals 1.96. The results of the magnetic moment (3.87 BM) as well as the values of the electronic spectrum suggests the presence of an octahedral geometry around the second $\text{Co}(\text{II})$ ion as shown in Fig. 6.

The low value of magnetic moment (3.87 BM) is explained on the basis of the existence of metal-metal bond.

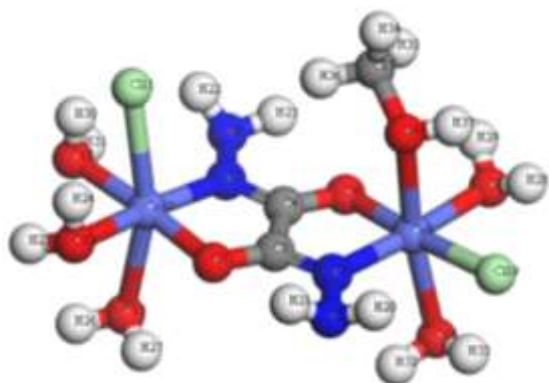


Fig. 5. Structure of $[\text{Co}_2(\text{ODH-2H})\text{Cl}_2(\text{H}_2\text{O})_6(\text{CH}_3\text{OH})].3\text{H}_2\text{O}$.

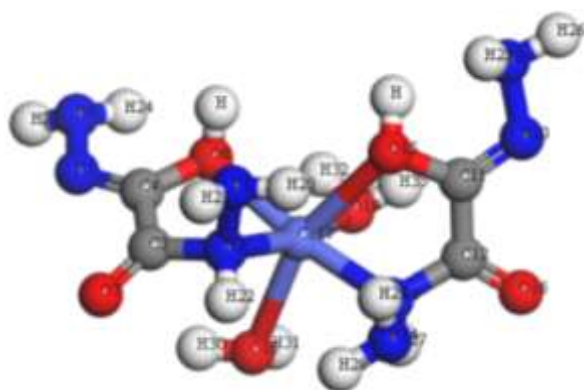


Fig. 6. Structure of $[\text{Co}(\text{ODH-H})_2(\text{H}_2\text{O})_2]$.

The spectrum of diamagnetic Pd^{2+} complex, $[\text{Pd}_3(\text{ODH-2H})\text{Cl}_4](\text{H}_2\text{O})_2].2\text{CH}_3\text{OH}$, shows

Table 2: Electronic spectra of the metal complexes.

Compound*	μ_{eff} . (BM)	Spectral bands (cm^{-1})			Dq (cm^{-1})	$\beta = \frac{B}{B_0}$	B (cm^{-1})	Transitions
		\square_1	\square_2	\square_3				
2	3.1**	10204	14835	21314	1020	0.35	369	${}^3A_{2g} \rightarrow {}^3T_{2g}(\square_1)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\square_2)$ ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\square_3)$
3	3.54	10141	14815	25316	1014	0.62	1041	${}^3B_1 \rightarrow {}^3B_2$ ${}^3B_1 \rightarrow {}^3A_2$ ${}^3B_1 \rightarrow {}^3A_2, {}^3E(P)$
5	5.56	5560	9570	18819	986.4	0.85	822	${}^4T_{1g} \rightarrow {}^4T_{2g}$ ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$
6	3.87**	5660	9745	18926	487	0.56	822	${}^4T_{1g} \rightarrow {}^4T_{2g}$ ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$
7	Diam.	-	26323	31906	-	-	-	$\pi \rightarrow \pi^*(M \rightarrow L)$ $\pi \rightarrow \pi^*(L \rightarrow M)$

* Compounds names are as follow:

2: $[\text{Ni}_2(\text{ODH-H})(\text{OH})_2(\text{CH}_3\text{OH})_2\text{H}_2\text{O}].\text{H}_2\text{O}$; **3:** $[\text{Ni}(\text{ODH-H})(\text{H}_2\text{O})_2\text{Cl}];$ **5:** $[\text{Co}(\text{ODH-H})_2(\text{H}_2\text{O})_2];$

6: $[\text{Co}_2(\text{ODH-2H})\text{Cl}_2(\text{H}_2\text{O})_6\text{CH}_3\text{OH}].3\text{H}_2\text{O};$ **7:** $[\text{Pd}_3(\text{ODH-H})_2\text{Cl}_4](\text{H}_2\text{O})_2].2\text{CH}_3\text{OH}$

** : per one metal atom

Conclusion:

Six complexes derived from **OXD** (L^1) were synthesized and characterized by chemical, spectral, and magnetic measurements. The IR spectra suggest that the ligand acts in a

two bands at 26323, and 31906 cm^{-1} assigned to $\pi \rightarrow \pi^*(M \rightarrow L)$, and $\pi \rightarrow \pi^*(L \rightarrow M)$ transitions [19, 20], respectively. The spectrum as well as the diamagnetic behavior suggests structure **Fig. 7.**

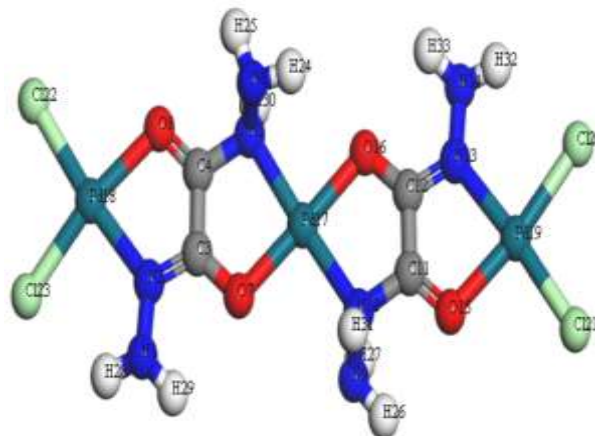


Fig.7. Structure of $[\text{Pd}_3(\text{ODH2H})\text{Cl}_4](\text{H}_2\text{O})_2].2\text{C H}_3\text{OH}$

bidentate manner through the enolized carbonyl oxygen and the NH groups with the removal of a proton from the former group. Also, it acts as a bidentate ligand coordinated *via* the azomethine ($\text{C}=\text{N}$) and the enolized carbonyl oxygen with the removal of a proton from the

latter group forming a five-membered ring around the Co^{2+} ion. Finally, two ligands bonded three Pd^{2+} ions in which the terminal two palladium ions are bonded through the carbonyl oxygen and the azomethine groups forming two five-membered rings around the Pd^{2+} ions, while the intermediate Pd^{2+} ion is coordinated to two NH and two enolized carbonyl oxygen with the removal of two protons forming two five-membered rings around the Pd^{2+} ion. The geometries of the complexes were determined depending on the spectral and magnetic measurements. The amounts of solvents either inside or outside the coordination sphere were determined using the weight loss and TGA methods.

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