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Synthesis, Characterization and Antimicrobial Activity of Some Transition Metal Complexes (Mn, Co, Zn, Ni) With L-Proline and Kojic Acid

Sangita Sharma[a]*, Jayesh Ramani[a], Jasmin Bhalodia[a], Neha Patel[a], Khushbu Thakkar[a] and Rajesh Patel[b]

[a]Department of chemistry, Hemchandracharya North Gujarat University, Patan, Gujarat, India
[b]Department of Life Science, Hemchandracharya North Gujarat University, Patan, Gujarat, India

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ABSTRACT

Four Mixed ligand complexes of the type MAL, where M = Mn(II), Co(II), Ni(II), Zn(II), A= L-Proline and L = Kojic acid have been synthesized. All complexes have been characterized by modern methods like elemental analyses, IR spectroscopy, magnetic moments, thermogravimetric analysis, UV-Visible reflectance spectra and conductivity measurements. All complexes are found to be coloured and Mn(II) complexes have been assigned octahedral geometry and tetrahedral geometry for Co(II), Ni(II), Zn(II) complexrs. The ligands and the metal complexes have been screened for antibacterial and antifungal activity.

Keywords: Synthesis, Metal Complexes, L-Proline, Kojic acid.

INTRODUCTION

Co-ordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bound. On the basis of nature of the metal as well as the type of ligand, these metal complexes have extensive applications in various fields of human interest [1,2]. Chelation or complexation observes more potent antibacterial effect against some microorganisms than the respective drug [3,4,5]. Kojic acid is known as insecticider, plant growth regulator and as an antifungal and antimicrobial agent. It is also used as a depigmenting agent (and/or skin whitening agent) as it inhibits melanin synthesis by inhibition of tyrosine’s activity. Amino acids are the building blocks of the protein which are major biomolecules of the cell. The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage and transport of transition metals in living organisms [6,7]. Synthesis of Co(II), Ni(II) and Zn(II) complexes with thiazole ring containing Schiff base ligands and their antimicrobial activities were tested against eight different microorganisms [8,9,10]. Spectral, redox and antimicrobial activity of Schiff base transition metal (II) complexes derived from 4-amino antipyrine and benzyl have been already [11]. Synthesis, characterization and antimicrobial studies of transition metal complexes have been an active field of research [12,13,14,15,16]. The coordination chemistry of manganese is dominated by stable Mn(II) and

Mn(III) centers and a mononuclear Mn^{+2} centers has been established at the active site of some enzymes that display superoxide dismutase activity [17,18].

Many metal complexes possess toxicological and pharmacological properties but the problem is that some lose their activity in vivo upon exposure to proteins and appear to have better affinities than the ligands studied for metal ions, which are deactivated once they are embedded in the proteins [19]. The present paper describes the synthesis, characterization and antimicrobial activity of mixed ligand Mn(II), Co(II), Ni(II), Zn(II) complexes formed with L-Proline and Kojic acid.

MATERIALS AND METHODS

2.1. Materials

The ligands L-Proline, Kojic acid and Sodium hydroxide were obtained from S. d. fine chemicals Ltd. India. A stock solution of Mn(II), Co(II), Ni(II) and Zn(II) salts were prepared and standardized by complexometric method [20]. Conductivity water was used introducing the experiments.

2.2. Preparation of Complexes

The complexes were prepared by three mixing metal salts, kojic acid and L-proline in proportion - 1:1:1(50ml of 0.5M metal salts, 50ml of 0.5M Kojic acid and 50ml of 0.5M L-proline). The mixture was constantly stirred for 1 hour with magnetic stirrer. The pH of mixture was raised to ~ 6.5 using 0.1N NaOH solutions. This resulted precipitation of the complexes. The obtained solution was allowed to settle down. After two days pale yellow, brown, green and colorless crystals were obtained as complexes of Mn(II), Co(II), Ni(II) and Zn(II) respectively. The complexes obtained were separated from supranant and washed with 1:1 mixture of ethanol and water, so as to remove excess of ligand and unreacted metal. All complexes were dried at room temperature and stored in desiccators.

2.3. Analysis and Physical Measurements

Elements like C, H, O and N were analyzed with a Perkin-Elmer 2400 series II elemental analyzer. The metal content was estimated with titrematry method using standardized EDTA solution after decomposing the complexes with mixture of concentrated hydrochloric acid, nitric acid, perchloric acid and sulphuric acid (aquaregia mixture) in 5:2:3:2 ratios respectively. Magnetic susceptibilities were measured at room temperature on a Gouy [21] balance using $Hg[Co(CNS)]_4$ as calibrate. The IR spectra were recorded on a Perkin-Elmer Lamda-983 spectrometer with samples prepared as KBr pellets and UV-Visible reflectance spectra were obtained on a Beckman DK-2A spectrophotometer using MgO as reference. Thermal measurements were carried out using Perkin-Elmer TGA-7DSC-PYRIS-1-DTA-7 thermal analyzer maintained at a $10^oC\ min^{-1}$ heating rate.

2.4. Bioassay

2.4a. Test Organisms:

The antimicrobial activity of ligands and synthesized metal complexes were examined against bacteria (*Escherichia coli;* MTCC 1687, *Bacillus subtilis;* MTCC 441), Yeast *Sacharomyces cerevisiae* (MTCC 170) and fungal (*Aspergillus niger;* MTCC 1344) strains collected from IMTECH, Chandigarh, India.

2.4b. Maintenance of culture:

The culture of bacteria, yeast and fungi were maintained on Nutrient agar, GYE agar and Sabourad's agar respectively and sub cultured monthly.

2.4c. Inoculum preparation:

One loopful growth of bacteria and yeast were transferred in the 25 ml of Nutrient broth and GYE broth respectively in 250 ml of Erlenmeyer flask. The cultures were incubated overnight on rotary shaker adjusted at 120 rpm, 37^0C. Similarly fungal inoculums were prepared from the spore's suspension in the Sabourad's broth.

2.4d. Antimicrobial Assay:

The experiments were designed so as to test the effect of the presence of the ligand and their metal chelates in liquid culture media. $2*10^{-3}$M of ligands and their metal chelates Mn(II), Co(II), Ni(II) and Zn(II) were supplemented in nutrient broth and glucose yeast extract broth for bacteria and yeast respectively. The flasks were inoculated with 5% (v/v) actively growing inoculums and incubated for 24 hours on rotary shaker adjusted at 120 rpm and 37^0C**.** After that incubation growth was measured spectrophotometrically at 660 nm. In case of fungal culture, similar concentrations of test compound were employed in Sabourad's broth and cultures which had been incubated for 48 hours on rotary shaker adjusted at 120 rpm and 37 ^{0}C. As the growth of the fungi was filamentous so measurement of optical density can't be used to monitor the growth therefore, gravimetric analysis was carried out to determine dry cell mass. The % growth inhibition was calculated with reference to growth in the respective medium without any inhibitory compounds.

RESULTS AND DISCUSSION

The analytical data of the complexes is presented in Table 1 indicates 1:1:1 stoichiometry. The general equation for the formation of the complexes is shown as below:

$$M^{+2} + HA + HL \longrightarrow MAL + 2H^{+}$$

Where M^{+2} = Mn(II) or Co(II) or Ni(II) or Zn(II), A = L-Proline and L = Kojic acid

All synthesized complexes are colored and possess high decomposition points. All are amorphous and stable in air. The complexes are partially soluble in methanol and insoluble in water and other organic solvents like benzene, chloroform, carbon tetrachloride. Hence it was not possible to characterize them by conventional methods like osmometry or viscosity measurements.

Table 1. Analytical Data and Some Physical Properties of the Metal Complexes

Complex	Molecular Formula	Colour	Formula Weight	Yield % (gm)	Analysis of elements (%) Found (Calculated)					Molar Conductance ohm^{-1} cm^2 mol^{-1}	D.P. (^{o}C)
					M	C	H	O	N		
[Mn.A.L.$2H_2O$]	$MnC_{11}H_{18}O_8N$	Pale yellow	346.17	70 (3.63)	17.71 (17.69)	42.60 (39.65)	4.19 (2.41)	30.95 (30.90)	4.52 (4.81)	13.27	>300
[Co.A.L]	$CoC_{11}H_{16}O_6N$	Reddish Brown	314.16	64 (3.02)	18.76 (18.72)	42.06 (41.57)	4.14 (1.78)	30.56 (30.53)	4.46 (6.4)	9.22	>300
[Ni.A.L]	$NiC_{11}H_{16}O_6N$	Green	313.92	58 (2.73)	18.70 (18.65)	42.10 (41.16)	4.14 (1.72)	30.58 (30.54)	4.46 (5.6)	12.56	>350
[Zn.A.L]	$ZnC_{11}H_{16}O_6N$	Colorless	320.62	63 (3.03)	20.40 (20.35)	41.21 (41.13)	4.05 (1.19)	29.94 (29.90)	4.37 (3.3)	8.14	>300

Note*: Where A = L-proline, L = Kojic acid and D.P. = Decomposition point*

3.1. Conductance Measurements

The conductivity of complexes was measured in 1:1 mixture of methanol and water at room temperature. All the complexes showed the molar conductance values for 10^{-3} M concentration in range 8 to 14 $ohm^{-1}cm^{2}$ mol^{-1}. It is suggesting that all complexes have non electrolyte nature [22].The molar conductance values of the complexes are listed in table 1.

3.2. Infrared Spectra

There is strong coupling among the IR bands of ternary complexes and hence quantitative interpretation of the bands in the IR spectra is not possible without normal coordinate analysis. Important IR frequencies of the complexes are listed in Table 2 along with their suggested assignments.

Table 2. Infrared Spectra of the Metal Complexes (cm^{-1})

Complex	**υ_{O-H} Phenolic / Water**	**υ_{O-H} Carboxylic**	**$\upsilon_{C=O}$ Carboxylic**	**$\upsilon_{C=O}$ unsaturated lactons**	**$\upsilon_{C-C=O-}$ adjuscent double bond**	**υ_{M-O}**	**υ_{M-O-C}**	**υ_{M-N}**	**υ_{M-OH2}**
L-Proline	-	2937 br(s)	1612 br(vs)	-	-	-	-	-	-
Kojic acid	3250 br(s)	-	-	1659(s) Sh	1659(s) Sh	-	-	-	-
[Mn·A·L·2H_2O]	3245 br(s)	-	1620 sh(s)	1630(s)	1630(s)	461 sh(m)	547 sh(s)	612 (m) 799 (s)	870 sh(m)
[Co.A.L]	3048(s)	-	1617 sh(s)	1652(s)	1653(s) 1617(s)	484 sh(m)	552 sh(m)	615 (m) 786 (s)	-
[Ni.A.L]	3046(s)	-	1623 sh(vs)	1654(s)	1653(s) 1623(s)	498 sh(m)	552 sh(m)	610 (m) 787 (s)	-
[Zn.A.L]	3050(s)	-	1630 sh(s)	1653(s)	1653(s) 1630(s)	492 sh(m)	553 sh(s)	613 (s) 785 (s)	-

A= L-Proline, L= Kojic acid, (s) = Strong, (m) = Medium, br = broad, W = Weak, (vw) = Very weak and sh = sharp

The IR spectra of all of the complexes differed from those of the ligands. A strong band ascribed to the presence of υ_{OH} of carboxylic acid appears at 2937 cm^{-1} in spectrum of L-Proline. This band disappears in spectra of all metal complexes which accounts for coordination of carboxylic – OH. The spectra of L-Proline also shows $\upsilon_{C=O}$ stretching band at 1612 cm^{-1} related to carboxylic group. The same band in IR spectra of complexes is displaced to 1620 cm^{-1} for Mn(II), 1617 cm^{-1} for Co(II), 1623 cm^{-1} for Ni(II) and 1630 cm^{-1} for Zn(II). The $\upsilon_{C=O}$ of the free ligand (L-Proline) at 1612 cm^{-1} has shifted to lower frequency by 5-25 cm^{-1} in all metal complexes. This also suggests that carboxylic group is involved in coordination to metals [23]. In case of L-Proline there is a intense peak at 3675 cm^{-1} and this peak can be attributed to υ_{N-H} bending. Similar peak appears at 3649 cm^{-1} for Mn(II), 3600 cm^{-1} for Co(II), 3660 cm^{-1} for Ni(II) and 3650 cm^{-1} for Zn(II) in all complexes. A Strong broad band due to phenolic group i.e υ_{OH} appears in the range of 3400-3200 cm^{-1}. A broad and strong band is observed in IR spectra of Kojic acid in the range of 3400-3150 cm^{-1} indicating for υ_{-OH} stretching in Kojic acid. But this band is missing in all metal complexes except in Mn(II) complex. In Mn(II) complex again strong and broad band appears in the range of 3245 cm^{-1} giving indication for presence of water molecules. The complexes also show some new bands at 460-420 cm^{-1} and 580-560 cm^{-1} which may be assigned to $\nu_{(M—O)}$ and $\nu_{(M—O—C)}$ respectively [24]. The bands at 780 cm^{-1} and 640 cm^{-1} in the complexes correspond to $\nu_{(M—N)}$ stretching [25].

3.3. Thermo gravimetric Analysis

Thermogravimetric analysis of the metal complexes was carried out in air by heating at a constant rate of 10°C per minute using a Perkin-Elmer TGA-7DSC-PYRIS-1 DTA-7 thermal analysis system. The complexes lost weight gradually during every phase of the experiment, then the samples underwent an accelerated weight loss and finally in the temperature range of about 500-600°C rate of weight loss became much more moderate. During the initial phase the gradual weight loss may be due to water of hydration which may be either crystal or coordinated water.

Thermogravimetric data of the primary ligands L-Proline, Kojic acid and the synthesized metal complexes are presented in Table 3. The cumulative weight losses of metal complexes at 150°C and 200°C are presented in table 4. The nature of the water observed in the Mn(II) complexes is coordinated water, as reported earlier [26,27]. The rate of decomposition of metal complexes is lower than that of the ligand suggested that there may be weak intermolecular hydrogen bonding. The percentage of loss observed in all complexes above 300°C is higher indicates for decomposition of complexes and formation of oxides.

Table 3. Cumulative % Weight Loss Data of the Ligand and Its Metal Chelates at Various Temperatures (°C)

Complex	**% Weight loss at temperature (°C)**											
	50	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**	**600**
L-proline	0.2	0.5	0.9	1.2	38	80	83	85	87	89	89	89
Kojic acid	0.1	0.4	0.8	40	80	82	84	86	87	88	88	88
[Mn·A·L·2H_2O]	0.1	1.01	4.50	10.40	12	28	80	82	83	84	84	84
[Co·A·L]	0.1	0.1	0.2	0.5	1	3	76	76	76	76	76	76
[Ni·A·L]	0.1	0.5	0.8	1.0	1.5	4.0	76.5	77	77	77	77	77
[Zn·A·L]	0.1	0.1	0.2	0.5	1.5	4.0	73.5	75	76	76	77	77

A= L- proline and L= Kojic acid

Table 4. Cumulative Weight Loss Data of Metal Chelates at 50°C to 200°C

Complex	**Found**									
	50°C		**100°C**		**150°C**		**200°C**		**250°C**	
	gm	**%**	**gm**	**%**	**gm**	**%**	**gm**	**%**	**Gm**	**%**
[Mn·L·2H_2O]	0.35	0.1	3.46	1.01	15.58	4.50	36.00	10.40	41.54	12
[Co·A·L]	0.31	0.1	0.31	0.1	0.63	0.2	1.57	0.5	3.14	1.0
[Ni·A·L]	0.31	0.1	1.57	0.5	2.5	0.8	3.14	1.0	3.14	1.0
[Zn·A·L]	0.31	0.1	0.32	0.1	0.64	0.2	1.6	0.5	4.81	1.5

A= L- praline and L= Kojic acid

3.4. Electronic Spectra and Magnetic Measurements

The information regarding geometry of these complexes is also obtained from their electronic data and magnetic moments which are presented in tables 5 and 6.

The Mn(II) complexes are found to be diamagnetic, as expected for six-coordinated d^5 octahedral complexes. The electronic spectra of Mn(II) d^5 complex exhibits electronic transition at 4504 cm^{-1}(υ_1), 4950 cm^{-1} (υ_2) and 5405 cm^{-1}(υ_3) and 12658 cm^{-1} and gives B = 187 cm^{-1}, β = 0.22 and β^0

= 78%. These transitions are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, $^6A_{1g} \rightarrow {}^4E_g$, $^6A_{1g} \rightarrow {}^4A_{1g}$ for Mn(II) complexes in octahedral environment due to large crystal field splitting.

Magnetic moment 3.87 B.M. value of Co(II) suggests an tetrahedral geometry. The $3d^7$ Co(II) has the ground state term 4F which splits into the $^4A_2$, $^4T_2$ and $^4T_1(F)$ states. The electronic spectrum of cobalt complex exhibits electronic transitions at 4237 cm^{-1}(υ_1), 6250 cm^{-1} (υ_2) and 13333 cm^{-1} (υ_3). These are assigned to three spin allowed transitions $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1(F)$, $^4A_2 \rightarrow {}^4T_1(P)$. The calculated values for B, β and β° are 611 cm^{-1}, 0.63 and 37% respectively. These values indicate covalent character in Co(II) complexes.

Ni(II) complexes has shown electronic transitions at 6250 cm^{-1} (υ_1), 12195 cm^{-1} (υ_2) and 18868 cm^{-1} (υ_3) and according to energy level diagram three possible transitions are $^3T_1 \rightarrow {}^3T_2$, $^3T_1 \rightarrow {}^3A_2$’ $^3T_1 \rightarrow {}^3T_1(P)$. The value 6250 cm^{-1} at which the first transitions occur is too high for a tetrahedral complex. So the transition at 12195 cm^{-1} has been taken as υ_2 and Dq as 678 cm^{-1}. The calculated values for B, β and β° are 611 cm^{-1}, 0.63 and 37% respectively.

In Zn(II) complex a well developed shoulder appears between 12500–6666cm^{-1}. This has been assign as MLCT (Metal to Ligand Charge Transfer) t2g → t1u transition [28]. Such bands arise either due to n → Л* or Л → Л* transition of the ligands or a merger of both transitions [29,30].

3.5. Antimicrobial Activity

The antimicrobial effect of metal complexes at $2*10^{-3}$ M concentration on the growth of bacteria (*Escherichia coli and Bacillus subtilis*), yeast (*Sacharomyces cerevisiae*) and fungi (*Aspergillus niger*) was investigated in liquid media. Growth inhibition pattern for free ligands, uncompleted metal salts and synthesized metal complexes are given in Table 7.

The highest activity was reported with Ni(II) complexes with 92.65%, 88.09%, 85.77% and 45.1% growth inhibition for *S. cerevisiae, E. coli, B. subtilis* and *A. niger* respectively. The second highest antimicrobial activity was exerted by cobalt complex with 80.39%, 71.38%, 70.51% and 52.62% growth inhibitory effect respectively for *B. subtilis, S. cerevisiae, E. coli,* and *A. niger.* The Ni(II) complexes exerted the highest activity amongst all test organisms under study except for *A. Niger* which was best with Zn(II) complexes. The least activity has been reported for the Mn(II) complexes. This may be due to fact that manganese is an essential trace nutrient in living cell life and a wide group of enzymes have manganese as cofactor.

All synthesized metal complexes have shown more inhibitory activity against bacteria, yeast and fungi as compared to parental ligands. Similar correlation and increase in antifungal and antibacterial activity of ligands on complexation with reference to parent ligands has been well cited [31,32,33]. Such increased activity of the metal chelates can be explained on the basis of Overtone’s concept and chelation theory. According to Overtone’s concept of cell permeability the lipid membrane that surrounds the cell favors the passage of only lipid soluble materials due to which liposolubility is an important factor that controls antimicrobial activity. On chelation, the polarity of metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π-electrons over the whole chelate ring and enhances the lipophilicity of the complex. The increased lipophilicities of complexes permit easy penetration into lipid membranes of organisms and facilitates as blockage of metal binding sites in enzymes [34].

Table 5. Electronic Spectra and Magnetic Moment Data for the Complexes

Complex	**Absorption region (cm^{-1})**	**Band assignment**	**Magnetic moment μ_{eff} (B.M.)**	**Geometry**
[Mn·A·L·2H$_2$O]	4504 cm^{-1} 4950 cm^{-1} 5405 cm^{-1} 12658 cm^{-1} Broad band	$^6A_{1g}\rightarrow{}^4T_{1g}$ $^6A_{1g}\rightarrow{}^4T_{2g}$ $^6A_{1g}\rightarrow{}^4E_g$ $^6A_{1g}\rightarrow{}^4A_{1g}$	5.92	Octahedral
[Co·A·L]	4237 cm^{-1} 6250 cm^{-1} 13333 cm^{-1}	$^4A_2\rightarrow{}^4T_2$ $^4A_2\rightarrow{}^4T_1(F)$ $^4A_2\rightarrow{}^4T_1(P)$	3.87	Tetrahedral
[Ni·A·L]	4310 cm^{-1} 12195 cm^{-1} 18868 cm^{-1}	$^3T_1\rightarrow{}^3T_2$ $^3T_1\rightarrow{}^3A_2$ $^3T_1\rightarrow{}^3T_1(P)$	2.83	Tetrahedral
[Zn·A·L]	12500 cm^{-1}----6666 cm^{-1} Broad band	$T_{2g}\rightarrow T_{1u}$	0	Tetrahedral

A= L-proline and L= Kojic Acid

Table 6. Parameters of the Electronic Spectra of Metal Complexes

Complex	**d-d transition (cm^{-1})**			**Dq (cm^{-1})**	**B (cm^{-1})**	**β= B/B°**	**β° (%)**
	υ_2	**υ_3**	**υ_4**				
[Mn·A·L·2H$_2$O]	4950	5405	12658	4504	187	0.22	78
[Co·A·L]	6250	13333	-	4237	611	0.63	37
[Ni·A·L]	12195	18868	-	6250	986	0.96	4
[Zn·A·L]	-	-	-	-	-	-	-

A= L-proline and L= Kojic Acid

Table 7. Effect of Ligand and Metal Complexes on the Growth of Bacteria and Fungi

Compound	**Bacteria**		**Yeast**	**Fungi**
	B. subtilis* *% inhibition	***E. coli* *% inhibition***	***S.cerevisiae* *% inhibition***	***A. niger* *% inhibition***
Control	0	0	0	0
L-Proline	32.78	5.8	31.38	22.68
Kojic Acid	11.45	31.65	0.36	24.57
Mn(II) comp.	46.35	5.86	25	33.61
Co(II) comp.	80.39	70.51	71.38	52.62
Ni(II) comp.	85.77	88.09	92.65	45.1
Zn(II) comp.	81.35	35.75	32.5	92.17

Figure 1. Octrahedral Geometry for Mn(II) Complex

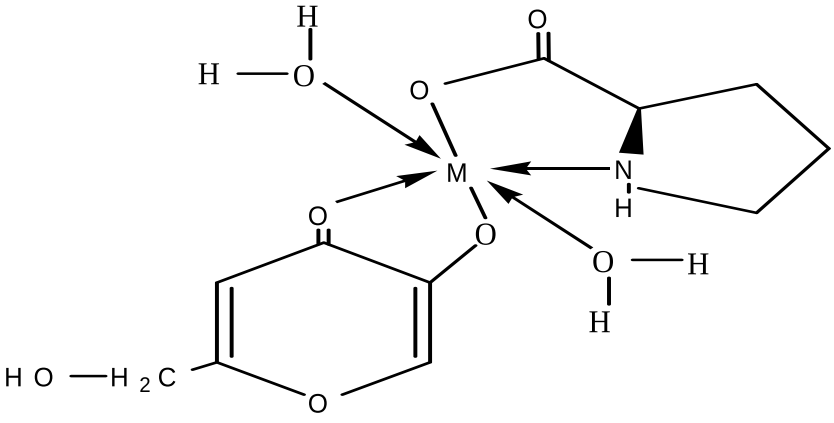
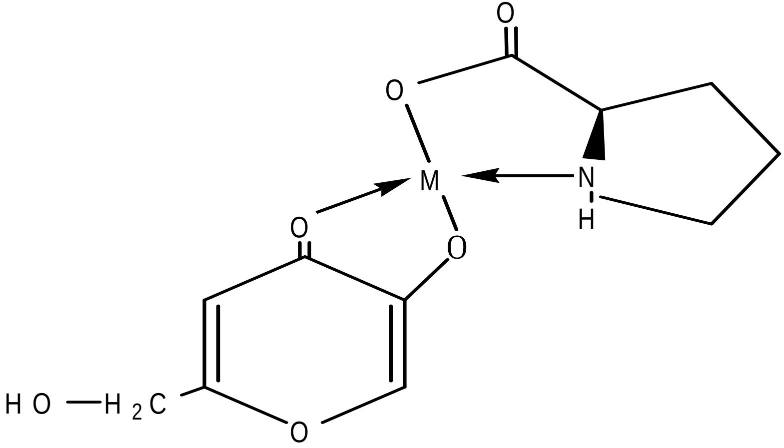


Figure 2. Tetrahedral Geometry for Co(II), Ni(II), Zn(II) Complexes



CONCLUSION

On the basis of elemental analyses, IR, thermogravimetric analyses, uv-visible reflectance spectra and magnetic properties, it is possible to assign octahedral geometry to the Mn(II) and tetrahedral geometry to the Co(II), Ni(II), Zn(II) complexes as shown in Fig.1 and Fig.2. The calculated values of β are favorable for assigned structure of accouter for covalent character of complexes.

We are optimistic that future studies on biological properties complexes of kojic acid and L-proline and there derivatives may lead to the development of a new class of specific and effective pharmaceutical agents.

Ni(II) complexes have shown promising antibacterial activity against *B. subtilis*, *E. coli*, *S. cerevisiae*, and antifungal activity against *A. niger*. Similar that is shown by Co(II) complexes. Least activity is shown for Mn(II) complexes because Mn(II) are as cofactor in many system. The antimicrobial activity is explores on the bases of overtone concept of cell permeability.

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