



# SYNTHESIS AND CHARACTERIZATION OF SOME METAL COMPLEXES WITH BIS[O,O-2,3;O,O-5,6-(N,N-DICARBOXYLIC METHYLIDENE)-N-2-METHYLENEPYRIDYL]-L-ASCORBIC

## ACID

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**Keywords:** Synthesis, bis[O,O-2,3;O,O-5,6-(N,N-dicarboxylicmethylidene)-N-2-methylene pyridyl]-L-ascorbic acid, metal complexes; analysis.

The reaction of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid with the 2-picolyamine gave new product bis[O,O-2,3;O,O-5,6-(N,N-dicarboxylicmethylidene)-N-2-methylenepyridyl]-L-ascorbic acid (LP), which was isolated and characterized by <sup>1</sup>H, <sup>13</sup>C-NMR, elemental analysis (CHN), mass spectroscopy, UV-visible and Fourier Transform infrared (FTIR) methods. The complexes of LP with metal ions, M<sup>2+</sup> (Cu, Co, Ni, Cd, Hg) and Cr<sup>3+</sup> were synthesized and characterized by FTIR, UV-Visible, molar conductance, atomic absorption, magnetic susceptibility, elemental analysis (CHN) methods. The analysis showed that the ligand coordinates with metal ions through the monodentate carboxylato and amino group resulting in six-coordinated metal ion complexes. The TLC for LP and complexes showed one spot for each, indicating the purity of these compounds.

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### Introduction

Taking into account of the activity of four hydroxyl groups ( $pK_{a1} = 4-12$ ) and their steric environments in L-ascorbic acid, studies of its alkylation, allylation, photo oxygenation, etc. under different experiment conditions have been carried out.<sup>1</sup> The reaction of L-ascorbic acid with chloro-, dichloro- and trichloroacetic acids in the presence of potassium hydroxide with different molar ratio gave (X-carboxylicmethylidene)-L-ascorbic acid derivatives (X= Cl<sub>1-4</sub>), these derivatives are easy to prepare and are significant in organic synthesis as they are more soluble in organic solvents.

Some metal ions complexes of these ligands have already been prepared and characterized.<sup>2-5</sup>

In view of this we used bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid as starting material, and reacted it with 2-picolyamine to give new a derivative of L-ascorbic acid, LP, and reacted it with some metal ions to give complexes. The properties and characterization of these new metal complexes are also presented.

### Experimental

#### Materials and Methods

All chemicals were purchased from BDH, and used without further purifications. FTIR spectra were recorded in KBr on a Shimadzu- spectrophotometer in the range of 4000-400 cm<sup>-1</sup>. Electronic spectra in distilled water were

recorded using a Shimadzu UV-visible spectrophotometer in the range of 200-1100 nm with quartz cell of (1 cm) path length. Melting points were measured with an electro thermal Stuart apparatus, model SMP30. Electrical conductivity measurements of the complexes were recorded at (25 °C) for 10<sup>-3</sup> mol L<sup>-1</sup> solution of the samples in dimethylsulfoxide (DMSO) using WTW inolap cond 720 digital conductivity meter. Mass spectra in agilent mass spectrometer 5975 quadrupole analyser, was performed at Tarbiat Modares University, Tehran, Iran. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX (500-MHz) spectrometer in DMSO and Bruner DRX (500-MHz) at Sharif Sainte University, Tehran, Iran. Chemical shifts are in ppm relative to internal Me<sub>4</sub>Si. Elemental microanalyses of the ligand and complexes were carried out by using Euro Vectro-3000A.

Metal content of the complexes were measured using atomic absorption technique by Shimadzu (AA620) atomic absorption Spectrophotometer, while Hg metal is determined using Biotech Eng. Management Co. Ltd. (UK). Magnetic susceptibility values were obtained at room temperature using the Gouy method, Johnson Matthey, model MSB-MKs Magnetic Susceptibility Balance Mode (MSB-MKI). Thin layer chromatography (TLC) was performed on aluminium plates coated with silica gel Fluke, and detection was performed using iodine.

#### Synthesis of ligand (LP)

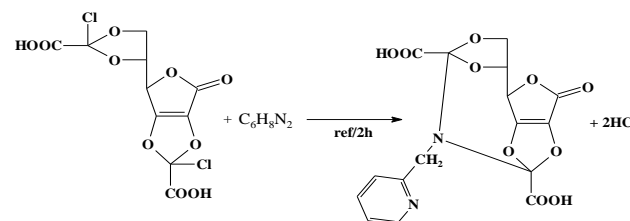
Bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid (0.375 g, 1 mmole) was dissolved in a mixture of 15 mL ethanol+5mLwater. Then 2-picolyamine (0.103 mL, 0.001 mole) was added drop wise to the solution and refluxed for 2 h, A dark brown solution was formed, this solution was left to stand at room temperature for a few days when a dark brown mass crystallized out. The resultant mass was recrystallized from ethanol when a dark brown less stiff crystalline material was formed, melting point was found to be 121 °C, yield was 81.62 %.

**Table 1.** Physical properties and analytical data for the synthesized ligand (LP) and its complexes

Empirical formula	Color	Mp °C	Yield %	Found( Calc.)(%)			
				C	H	N	M(II), Cr <sup>+3</sup>
Ligand C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub>	Dark Brown	121	81.62	48.41 (48.98)	2.97 (3.08)	6.96 (7.14)	
[Cr(C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub> )Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl·7H <sub>2</sub> O	Dark walnut	166	76.41	42.89 (43.25)	2.61 (2.72)	6.06 (6.30)	7.53 (7.68)
[Cu(C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub> )Cl(H <sub>2</sub> O) <sub>3</sub> ]Cl·2H <sub>2</sub> O	Charcoal	190	78.2	41.98 (42.15)	2.51 (2.65)	6.02 (6.14)	11.44 (11.29)
[Co(C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub> )Cl(H <sub>2</sub> O) <sub>3</sub> ]Cl·2H <sub>2</sub> O	Reddish-Brown	139	73.68	42.18 (42.59)	2.48 (2.68)	6.10 (6.20)	10.64 (10.42)
[Ni(C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub> )Cl(H <sub>2</sub> O) <sub>3</sub> ]Cl·4H <sub>2</sub> O	Pale Green	147	75.17	42.20 (42.61)	2.56 (2.68)	6.23 (6.21)	9.70 (9.88)
[Cd(C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub> )Cl(H <sub>2</sub> O) <sub>3</sub> ]Cl·3H <sub>2</sub> O	Light orangr	163	69.44	37.90 (38.07)	2.28 (2.39)	5.40 (5.55)	17.61 (17.85)
[Hg(C <sub>16</sub> H <sub>12</sub> O <sub>10</sub> N <sub>2</sub> )Cl(H <sub>2</sub> O) <sub>3</sub> ]Cl·4H <sub>2</sub> O	Dark olive	185	71.12	32.01 (32.41)	1.91 (2.04)	4.45 (4.72)	26.98 (27.26)

**Table 2.** shows the Rf for ligand (LP) and its complexes

Compound	Molecular weight	R <sub>f</sub>
Ligand (LP)	392.28	0.51
LP-Cr	712.78	0.34
LP-Cu	616.83	0.40
LP-Co	612.21	0.37
LP-Ni	647.97	0.29
LP-Cd	683.69	0.22
LP-Hg	789.87	0.16

**Scheme 1.** The reaction of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid with 2-picolylamine.

### Synthesis of Metal Complexes

To a solution of LP (0.392 g, 1 mmol) in (20 mL ethanol) a solution of 1 mmol of metal chloride (0.170 g CuCl<sub>2</sub>·2H<sub>2</sub>O, 0.237 g NiCl<sub>2</sub>·6H<sub>2</sub>O, 0.238 g CoCl<sub>2</sub>·6H<sub>2</sub>O, 0.183 g CdCl<sub>2</sub>·H<sub>2</sub>O, 0.271 g HgCl<sub>2</sub>·2H<sub>2</sub>O or 0.266 g CrCl<sub>3</sub>·6H<sub>2</sub>O) in 20 mL ethanol was added. The solutions were stirred for 1 hr and were left to evaporate slowly to precipitate the complexes. The complexes were recrystallized from ethanol. The isolated complexes are coloured solids, stable in air and insoluble in common organic solvents but completely soluble in water, ethanol, methanol, DMSO and DMF. Some physical properties of LP and its complexes are shown in Table 1.

### Thin layer chromatography (TLC)

The solution of LP and its complexes in ethanol as solvent, appeared as one spot each, confirming that all these compounds are pure and have only one isomer. Table 2 shows the R<sub>f</sub> for complexes and the ligand (LP).

### Results and discussion

LP was synthesized in a good yield by the reaction of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid with 2-picolylamine in the ratio (1:1) in ethanol as a solvent to give a new derivative of L-ascorbic acid, LP, (Scheme 1).

### FT-IR spectral analysis

The IR spectrum of bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid as starting material is compared with the spectrum of the ligand, LP. The results are summarized in Table 3.

Bis[O,O-2,3;O,O-5,6-(chloro(carboxylic)methylidene)]-L-ascorbic acid exhibits a band at 833 cm<sup>-1</sup> due to  $\nu(\text{C-Cl})$  position, this disappeared in the spectrum of the ligand, LP, with the appearance aromatic C-H stretching. Two bands assigned to aromatic absorption are of medium intensity at 3080 and 3016 cm<sup>-1</sup>. The presence a broad band is seen at 3383 cm<sup>-1</sup> and is related to carboxylic-OH band.<sup>6</sup> 1683 cm<sup>-1</sup> is due to  $\nu(\text{C=O})$  in carboxylic acid. The lactone (C-1=O) stretching vibration appeared at 1737 cm<sup>-1</sup>. The band centred at 1597, 1683 cm<sup>-1</sup> are due to  $\nu(\text{C=C})$ , (C=O) respectively.<sup>3,6,7</sup> The band at 1477 cm<sup>-1</sup> is attributed to the conjugated C=C and C=N bonds in pyridine ring. The band at 1190 cm<sup>-1</sup> is assigned to the N-C bond.<sup>8</sup>

In all the complexes, bands at 1519 and 1355 cm<sup>-1</sup> in the Cr-complex, at 1573 and 1363 cm<sup>-1</sup> in the Cu-complex, at 1562, 1350 cm<sup>-1</sup> in the Co-complex, at 1568 and 1384 cm<sup>-1</sup> in the Ni-complex, at 1572 and 1390 cm<sup>-1</sup> in the Cd-complex, and at 1593 and 1394 cm<sup>-1</sup> in the Hg-complex are due to the asymmetric and the symmetric stretching frequencies of the carboxylic group. The value of  $\Delta\nu\text{COOH}$ = 164, 210, 212, 184, 182, 199 cm<sup>-1</sup>, respectively indicated that the carboxylic group coordinate to metal ion as a monodentate ligand.<sup>9,10</sup> The pyridine-N in all complexes are shifted to lower frequencies and is attributed to coordination of pyridine-N group with the metal ion.<sup>10</sup> The absorption band in the range of 886-802 cm<sup>-1</sup> is assigned to the coordinated water in all complexes.<sup>11,12</sup> Conclusive evidence of the bonding is also shown by observation that new bands in the spectra of all metal complexes appeared in the low frequency region at 499-439 cm<sup>-1</sup> and 465-412 cm<sup>-1</sup> characteristic to M-N and M-O stretching vibration.<sup>9,10</sup> One carboxylic group is present in the spectra of all complexes confirming that one COOH is uncomplexed, whose stretching frequency is lower as compared to that of LP, this is related to the degree of hydrogen bonding.<sup>10</sup>

## NMR spectra for the ligand (LP)

$^1\text{H-NMR}$  spectrum (Figure 1) of LP in  $\text{DMSO-d}_6$  exhibited several signals, carboxylic-OH weak signal appeared at 9.75 ppm. Pyridine showed multiplet at 7.17-8.41 ppm. Peaks at 3.98, 4.16 ppm are attributed to  $\text{CH}_2$ -6, CH-5, while that at 5.56 is due to CH-4 lactone ring. 3.74 ppm attributed to pyridine- $\text{CH}_2$ .

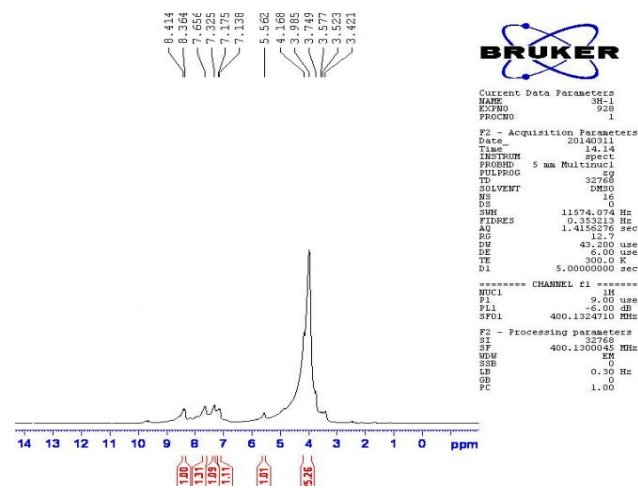


Figure 1.  $^1\text{H-NMR}$  spectrum of the ligand (LP)

$^{13}\text{C-NMR}$  spectrum (Figure 2) showed a peak at 178 ppm which is due to carboxylic acid, while the  $\text{C=O}$  carbon and pyridine  $\text{C=N}$  signals are appeared at 168 and 163 ppm. The two peaks at 127 and 136 ppm are attributed to C-2 and C-3 carbons, respectively. This may be due to the conjugated double bond from C-1 to C-3 causing up field shift of C-3 carbon signal. The signals at 73,72 and 63 ppm are assigned to C-4, C-5 and C-6 carbon atoms, whereas the signals at 123, 122 ppm are assigned to C-7, C-8 carbon atoms, the signals at 38, 161, 123, 138, 121 and 148 ppm are assigned to C-9, C-10, C-11, C-12, C-13 and C-14 carbon atoms of 2-methylpyridine.

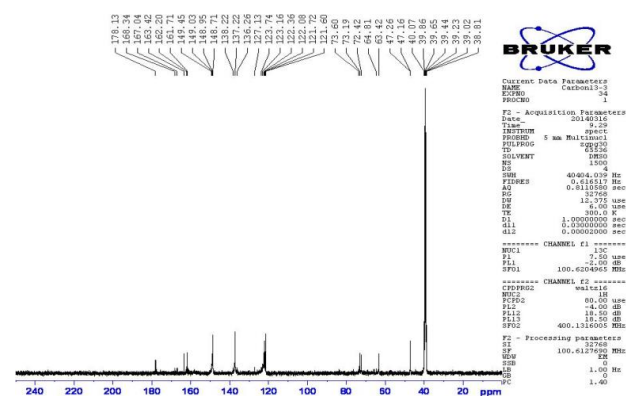


Figure 2.  $^{13}\text{C-NMR}$  spectrum of the ligand (LP)

## Mass spectrum for the ligand (LP)

The mass spectrum data for LP (Figure 3) showed a molecular ion peak at  $(m/z = 395)$ .<sup>13</sup> The molecular ion peak corresponds to  $(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2 + 3\text{H})$ . Other fragments are summarised in Table 4 and Scheme 2.

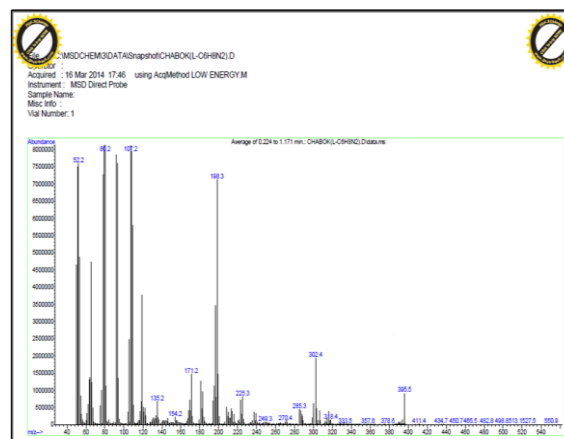
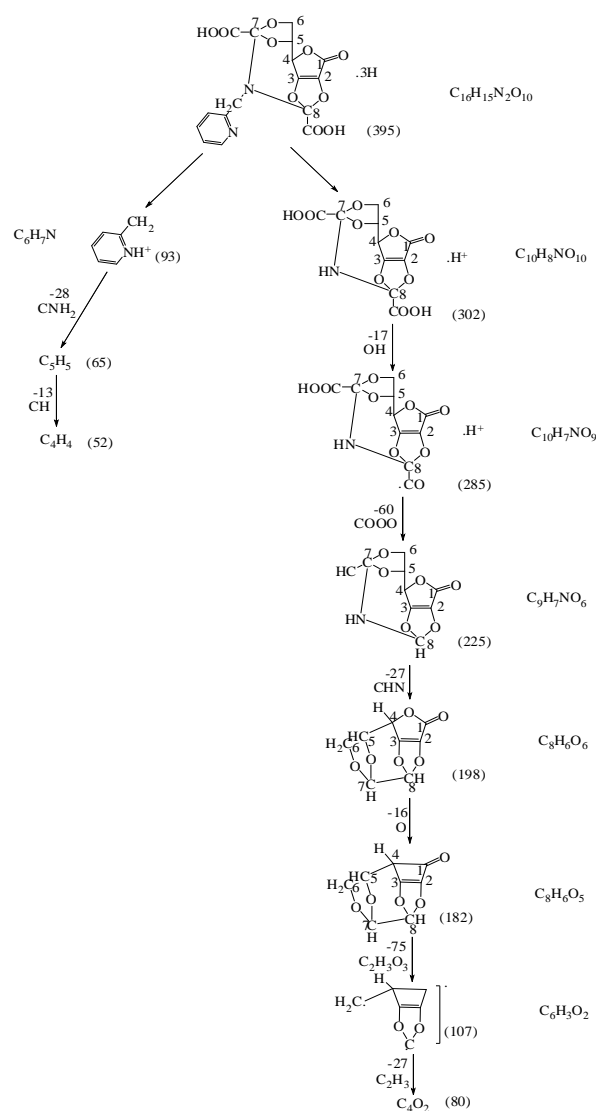


Figure 3. Mass spectrum of the ligand LP



Scheme 2. The fragmentation of the ligand (LP)

## UV-VIS Spectral studies

The electronic absorption bands as well as the magnetic moment values are summarized in Table 5. The UV-Visible spectrum of LP showed one absorption at 270 nm ( $37037 \text{ cm}^{-1}$ ), which is due to  $\pi-\pi^*$  transition.<sup>14</sup>

**Table 3.** Assignments of the IR spectral bands of starting material, LP and its complexes( $\text{cm}^{-1}$ )

Empirical formula	$\nu_{\text{OH}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	$\nu_{\text{COOH}}$		Coordinated $\text{H}_2\text{O}$	$\nu_{\text{C-Cl}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
	$\nu_{\text{COOH}}$	aromatic	$\nu_{\text{C=O}}$	$\nu_{\text{as}}$	$\nu_{\text{s}}$					
Starting material $\text{C}_{10}\text{H}_6\text{O}_{10}\text{Cl}_2$	3392,br	-	1726	1670,br	1600	1412	-	833,s	-	-
Ligand $\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2$	3383,br	3016,w	1737	1683,m	1595	1433	-	-	-	-
$[\text{Cr}(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2)\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl}\cdot 7\text{H}_2\text{O}$	3332,br	3012,w	1702	1664,m	1519	1355	802,w	-	480	443
$[\text{Cu}(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2)\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$	3373,br	3076,w	1710	1627,m	1573	1363	875,w	-	495	426
$[\text{Co}(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2)\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot 2\text{H}_2\text{O}$	3371,m	3113,w	1720	1655,m	1562	1350	879,w	-	499	463
$[\text{Ni}(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2)\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot 4\text{H}_2\text{O}$	3365,br	3062,w	1716	1645,m	1568	1384	873,w	-	488	465
$[\text{Cd}(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2)\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot 3\text{H}_2\text{O}$	3367,m	3025,w	1726	1600,m	1572	1390	856,w	-	439	412
$[\text{Hg}(\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{N}_2)\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}\cdot 4\text{H}_2\text{O}$	3383,br	3069,w	1751	1680,m	1593	1394	886,w	-	487	464

**Table 4.** Mass spectral data of ligand (LP)

Fragments	Formula weight, $\text{g mol}^{-1}$	Relative abundance %
$\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_{10} + 3\text{H}$	395	11.4
$\text{C}_{10}\text{H}_8\text{NO}_{10} + \text{H}$	302	23.68
$\text{C}_{10}\text{H}_7\text{NO}_9 + \text{H}$	285	6.14
$\text{C}_9\text{H}_7\text{NO}_6$	225	10.52
$\text{C}_8\text{H}_6\text{O}_6$	198	87.71
$\text{C}_8\text{H}_6\text{O}_5$	182	16.66
$\text{C}_6\text{H}_3\text{O}_2$	107	100
$\text{C}_4\text{O}_2$	80	99.12
$\text{C}_6\text{H}_7\text{N}$	93	93.85
$\text{C}_5\text{H}_5$	65	58.77
$\text{C}_4\text{H}_4$	52	89.47

The electronic spectrum of Cr(III) complex in ethanol solution showed three bands in the visible region at  $24509.8 \text{ cm}^{-1}$  ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ ) ( $\nu_3$ ),  $17543.85 \text{ cm}^{-1}$  ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ ) ( $\nu_2$ ) and the last one is at  $12537 \text{ cm}^{-1}$  ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ ) ( $\nu_1$ ). The ratio of  $\nu_2/\nu_1$ , (1.39) was applied on Tanaba-Sugano diagram for  $d^3$  octahedral complexes,  $B_{\text{complex}}$  and  $\beta$ ,  $10Dq(\nu_1)$  were calculated theoretically.<sup>15</sup> Spectrum of Co-complex in ethanol solution exhibited two bands appearing at  $14992.5 \text{ cm}^{-1}$  and  $17452 \text{ cm}^{-1}$ , which were assigned to the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  ( $\nu_2$ ) and  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{p})$  ( $\nu_3$ ) transitions respectively of octahedral geometry.<sup>16</sup> From the ratio of  $\nu_3/\nu_2$  (1.16) the value of  $Dq/B$  (0.98) was obtained. The value of  $B'$  (869.52) as well as the position of  $\nu_1(10Dq)$  ( $8375 \text{ cm}^{-1}$ ) were calculated by using Tanaba-Sugano diagram for  $d^7$  configuration of the octahedral configuration geometry.<sup>17</sup> The value of  $\beta$  (0.88) indicates some covalent character. The conductivity measurement indicates that the Co-complex is ionic. Spectrum of Ni(II) complex showed three bands in the visible region at  $24271.84 \text{ cm}^{-1}$ ,  $13449.89 \text{ cm}^{-1}$  and  $10385 \text{ cm}^{-1}$  which are assigned  $3\text{A}_{2g} \rightarrow 3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ),  $3\text{A}_{2g} \rightarrow 3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) and  $3\text{A}_{2g} \rightarrow 3\text{T}_{2g}$ , ( $\nu_1$ ) respectively. The ratio of  $\nu_2/\nu_1$ , (1.29) was applied on Tanaba-Sugano diagram for  $d^8$  octahedral complexes,<sup>18,19</sup>  $B_{\text{complex}}$  and  $\beta$ ,  $10Dq(\nu_1)$  were calculated theoretically. The conductivity showed that the Ni(II)-complex was electrolyte. The spectrum of Cu(II) complex showed broad band at  $12804 \text{ cm}^{-1}$  assigned to  $2\text{E}_g \rightarrow 2\text{T}_{2g}$  transition which refers to Jahn-Teller distortion of octahedral geometry.<sup>20</sup> The conductivity measurement of the complex indicates that the complex is an electrolyte. The spectra of Cd(II), Hg(II) complexes gave

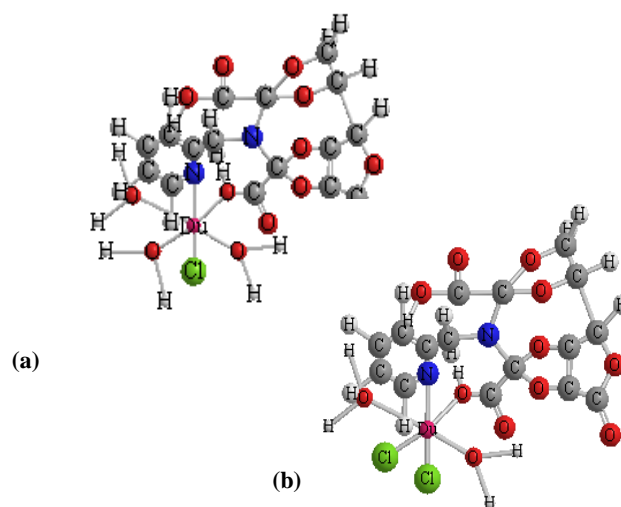
no bands in the visible region, only bands assigned to charge transfer transitions were observed at  $31446.54 \text{ cm}^{-1}$  and  $29154.5 \text{ cm}^{-1}$  Hg(II) and Cd(II) complexes, compared to free ligand which showed one band at  $37037 \text{ cm}^{-1}$  confirming the complex formation.<sup>21</sup> The conductivity measurements of the two complexes indicate that the complexes are electrolytes.

### Magnetic studies

The magnetic moment values at 294 K of the  $[\text{MLCl}_2\cdot 3\text{H}_2\text{O}]\text{Cl}\cdot \text{XH}_2\text{O}$  [ $\text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$ ] and  $[\text{CrLCl}_2\cdot 2\text{H}_2\text{O}]\text{Cl}\cdot \text{XH}_2\text{O}$  are 1.85, 4.64, 3.16 and 3.73 B.M. (Table 5) respectively which are lower than the total spin-only values indicating a high spin octahedral geometry around metal ion. The lowering of these magnetic moments indicates a dominant antiferromagnetic interaction in all complexes. This may be due to the fact that the syn-syn carboxylate provide a small metal-metal distance and results in a good overlap of the magnetic orbitals, an antiferromagnetic coupling is always induced.<sup>22</sup>

### Conclusion

The ligand, LP, coordinates with metal ions through the monodentate carboxylate and amino group resulting in six-coordinated metal ion in an octahedral geometry (Figure 5).

**Figure 5.** The proposed molecular structure of complexes, M(II) = Cu, Co, Ni, Cd, Hg (a) and Cr(III) (b).



**Table 5.** Magnetic moments and electronic spectral bands (cm<sup>-1</sup>) the complexes.

Complex	$\mu_{\text{eff}}$ , B.M.	Band position, cm <sup>-1</sup>	Assignments	$B_{\text{complex}}$	$\beta$	10Dq ( $\nu_1$ ) theoretical, cm <sup>-1</sup>	$\Lambda_m$ $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup>
L-Cr(III)	3.852	24509.80 $\nu_3$ 17543.85 $\nu_2$ 13357 $\nu_1$	4A <sub>2g</sub> →4T <sub>1g</sub> (P) 4A <sub>2g</sub> →4T <sub>1g</sub> (F) 4A <sub>2g</sub> →4T <sub>2g</sub>	895.63	0.91	9276	44.21
L-Co(II)	4.641	17452 $\nu_3$ 14992.5 $\nu_2$	4T <sub>1g</sub> →4T <sub>1g</sub> (p) 4T <sub>1g</sub> →4A <sub>2g</sub>	869.52	0.88	8375	46.03
L-Ni(II)	3.283	24271.84 $\nu_3$ 13449.89 $\nu_2$ 10385 $\nu_1$	3A <sub>2g</sub> →3T <sub>1g</sub> (P) 3A <sub>2g</sub> →3T <sub>1g</sub> (F) 3A <sub>2g</sub> →3T <sub>2g</sub>	887.44	0.85	10216	47.53
L-Cu(II)	1.869	12804	2E <sub>g</sub> →2T <sub>2g</sub>	-	-	-	46.51
L-Cd(II)	-	31446.54	ILCT	-	-	-	45.36
L-Hg(II)	-	29154.50	ILCT	-	-	-	44.52

**Table 6.** Molar ratio data for LP-complexes.

V, ml	LP-Cr ( $\lambda=408$ )	LP-Co ( $\lambda=573$ )	LP-Ni ( $\lambda=412$ )	LP-Cu ( $\lambda=781$ )	LP-Cd ( $\lambda=318$ )	LP-Hg ( $\lambda=343$ )
0.25	0.239	0.244	0.213	0.338	0.204	0.211
0.5	0.463	0.390	0.335	0.514	0.351	0.390
0.75	0.635	0.493	0.446	0.662	0.458	0.505
1	0.790	0.607	0.530	0.835	0.566	0.662
1.25	0.909	0.680	0.664	0.950	0.645	0.750
1.5	0.970	0.745	0.729	1.010	0.718	0.826
1.75	1.020	0.800	0.753	1.090	0.786	0.890
2	1.064	0.892	0.840	1.117	0.845	0.993
2.25	1.092	0.931	0.906	1.169	0.930	1.072
2.5	1.106	0.973	0.921	1.178	1.040	1.124
2.75	1.132	0.998	0.970	1.239	1.107	1.201
3	1.201	1.100	0.995	1.320	1.197	1.300

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