



Syntheses, spectral, thermal and pH-metric studies on bivalent metal ion complexes of N,N'-bis(3-carboxy-1-oxo-z-prop-2-elenyl)ethylenediamine

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A novel carboxyamide ligand has been synthesized using maleic anhydride and ethylenediamine. Co(II), Ni(II), Cu(II) and Pd(II) complexes of the ligand, i.e., N,N'-bis(3-carboxy-1-oxo-z-prop-2-elenyl)ethylenediamine [H₂L] have been prepared and characterized by elemental analyses, IR, electronic, ¹H NMR, EPR spectral and thermal studies. It is revealed by IR and ¹H NMR spectral studies that the ligand coordinated to the metal ions through deprotonated carboxylate oxygen and non-deprotonated amide nitrogen in all the complexes. It is suggested by electronic spectral and magnetic moment studies that N₂O₂ coordination is around each metal center with a strong field square planar chromophore. All the complexes have been studied by TGA and DTA studies done simultaneously. The complex formation between ligand and metal ions [Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] has also been studied pH metrically in 75% aqueous DMF solution at 298 K in 0.1 M NaClO₄. The probable structures of the complexes have also been proposed.

Keywords: Carboxyamide, potentiometric, Bivalent metal ion complex, Coordination compounds

The coordination chemistry of the metal-amide linkage [-C(O)NH-] has received much attention due to their close relationship to biological molecules and their role in biological processes^{1,2}. An amide group offers two coordinating sites, N and O, for metal coordination. The nature of ligands bound to the metal ions decides the properties of coordination compounds³⁻⁵. In the recent past, the main focus of researchers remains to design new chelating ligands and to study the subsequent electronic and/or chemical properties of the complexes^{6,7}. The amide-based ligands, in general, have been exceptionally successful in this context⁸. The coordination of the amide ligand through nitrogen and oxygen has been reported in the literature⁹⁻¹¹. The selectivity of amide moieties of metal coordination strongly depends on the ease of deprotonation of the amide group to form stable chelated compounds. Both neutral and deprotonated amides also have excellent ability to stabilize metal ions in their higher oxidation states¹². These ligands are also reported to serve as an excellent binding moiety for metal ions to form a wide variety of biomimic metal complexes that can potentially catalyze important organic transformations¹³. There are numerous examples of the *in vivo* interactions of metal ions with the amide group(s), and

their biological importance¹⁴⁻¹⁶. Recently these ligands were reported to be useful as corrosion inhibitors¹⁷. The behaviour of carboxyamide ligands has been widely investigated^{18,19} because of the lipophilic group of the aromatic ring and hydrophilic group of carboxyamide. Few studies are available on metal coordination with amide ligands having anchored carboxylic groups taking part in coordination²⁰.

In view of the diverse coordinating behaviour and biological importance of such ligands, we have synthesized Co(II), Ni(II), Cu(II) and Pd(II) complexes with a novel carboxyamide ligand [H₂L] derived from maleic anhydride and ethylenediamine. All the complexes have been analyzed by elemental analysis, IR, electronic, ¹H NMR, EPR spectral, thermal, magnetic measurement and pH metric studies to ascertain their coordinating behaviour. We have proposed the probable structures of the complexes based on the conducted studies.

Experimental Section

All reagents used in the studies were of analytical grade and were used without further purification. The elemental analysis of the ligand and complexes were carried out using a Perkin Elmer CHN analyzer. The

metal content of the complexes was determined by atomic absorption spectroscopy (Perkin-Elmer 2380). ^1H NMR spectra of ligand and palladium complex were recorded on Perkin-Elmer R-32 spectrometer in DMSO-d_6 . IR spectra were recorded in nujol mulls and KBr discs on a Perkin-Elmer FT-IR spectrophotometer. UV/visible absorption spectra were recorded in DMF on a Beckmann DU-64 spectrophotometer. Magnetic moment studies were carried out in polycrystalline state on a vibrating sample magnetometer at 5500 G field strength. X-band EPR spectra of the copper complex were recorded at room and liquid nitrogen temperature in solid state on a JEOL JES-3XG ESR spectrometer. The TG and DTA curves were simultaneously recorded for powdered samples on Rigaku 8150 thermoanalyser in static air at the heating rate of 283 K min^{-1} in a platinum crucible, with alumina as the reference material.

Synthesis of the ligand [H_2L]

Maleic anhydride (9.8 g, 0.1 mol) was dissolved in 50 mL of glacial acetic acid in an RB flask, and ethylenediamine (3.4 mL, 0.05 mol) was dropped with constant stirring while cooling in ice. The white solid separated was filtered, washed thoroughly with acetone and dried in air. The white product was dissolved in 5% Na_2CO_3 solution to recrystallize and then regenerated with dil. HCl. The recrystallized product was washed several times with water and finally with acetone. The synthesis scheme is shown in Scheme 1. (Yield: 90%; m.p.: 471 K).

Syntheses of complexes

For the synthesis of complexes, the ligand (0.02 mol) was suspended in 50 mL of water, and a calculated amount of standard Na_2CO_3 solution (0.02 mol) was added to this suspension while

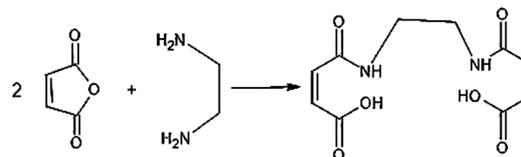
stirring. A clear solution of the ligand (Na_2L) was formed. To this solution of metal salt (0.02 mol) in water (40 mL) (chloride/nitrate of cobalt, nickel, palladium and acetate of Cu) was mixed. A coloured complex precipitated immediately, was filtered by suction, and washed with warm dil. Na_2CO_3 solution, then with warm distilled water and dried *in vacuo* over P_4O_6 . (Yield: 70-80%).

Results and Discussion

All the complexes were coloured, high melting (m.p. more than 500 K) and microcrystalline/powders, stable in free air, insoluble in water and organic solvents except DMF and DMSO. Physical and analytical data for the ligand and complexes are presented in Table 1. The analytical data are in good agreement with the formula ML ($\text{M(II)} = \text{Co, Ni, Pd}$) and $[\text{ML}]_2$ (where $\text{M} = \text{Cu}$).

Vibrational spectral studies

The vibrational spectra of the ligand and complexes recorded in nujol mulls /KBr disc and characteristic IR bands are summarized in Table 2. On comparing the IR spectra of ligand and complexes, it was observed that the ligand coordinates through the deprotonated carboxylic oxygen and nitrogen of the amide group. The IR band observed at 3300 cm^{-1} due to $\nu_{\text{N-H}}$ mode in the ligand shifts to a lower frequency by $50\text{-}70 \text{ cm}^{-1}$ in complexes indicating that the nitrogen of the amide group is coordinating²¹. The strong amide I band observed at 1620 cm^{-1} in the



Scheme 1 — Synthesis of ligand

Table 1 — Analytical data and Magnetic moments of the ligand and complexes

Ligand/ Complex	Colour	Yield (%)	Elemental analysis: found (Calcd.) %				μ_{eff} (BM)
			C	H	N	M	
H_2L	Shiny White	90	46.59 (46.68)	4.60 (4.69)	10.30 (10.34)	-	-
CoL	Light Brown	72	38.32 (38.35)	3.17 (3.19)	8.94 (8.95)	18.82 (18.83)	2.38
NiL	Pale Green	81	38.22 (38.38)	3.12 (3.20)	8.88 (8.95)	18.68 (18.77)	Diamagnetic
$[\text{CuL}]_2$	Pale Blue	78	37.80 (37.80)	3.10 (3.15)	8.62 (8.82)	19.82 (20.00)	1.49
PdL	Yellowish	74	33.26 (33.29)	2.76 (2.77)	7.74 (7.76)	29.50 (29.53)	Diamagnetic

ligand does not show any shift upon complexation, indicating the non – participation of the CO group. The IR bands due to ν_{COO^-} (asym) and ν_{COO^-} (sym) stretching frequencies of the carboxylic group observed at 1540 cm^{-1} and 1420 cm^{-1} in free ligand shows an enhancement in ν value (difference between asym and sym ν_{COO^-} frequencies) upon complexation with metal ions²². In the spectra of complexes $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ bands are observed at around 400 cm^{-1} and 520 cm^{-1} , respectively.

Electronic spectra and magnetic moments

Electronic spectra of the ligand and complexes were recorded in DMF and are presented in Table 3. The spectra of the Co(II) complex show three bands at 10380 , 22810 and 27145 cm^{-1} , which suggest the formation of a low spin four coordinate complex²³. The magnetic moments of square planar Co(II) complexes at room temperature are reported in the range of 2.2 - 2.7 B.M. ²⁴. The magnetic moment of the present complex was found to be 2.38 B.M. However, very few four coordinate square planar Co(II) complexes are reported in the literature.

The nickel complex was found to be diamagnetic, and it showed two spectral bands at 21270 and 28170 cm^{-1} . Square planar Ni(II) complexes are expected to show three d-d transition bands: ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$, ${}^1\text{A}_{2g} \leftarrow {}^1\text{A}_{1g}$, ${}^1\text{E}_g \leftarrow {}^1\text{A}_{1g}$. It was observed that usually, one or two bands are observed²³. In the present complex, the higher energy band at 28170 cm^{-1} is assigned as the charge transfer band ($\text{M} \leftarrow \text{C}$), and the d-d transition

band observed at 21270 cm^{-1} is assigned as ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$.

The two spectral bands have been observed in the copper complex at 13895 and 27700 cm^{-1} . The band I at 13895 cm^{-1} is assigned to ${}^1\text{E}_g \leftarrow {}^2\text{B}_g$ transition, and the band II observed at 27700 cm^{-1} is assigned to $\text{M} \leftarrow \text{L}$ charge transfer from oxygen atom of ligand to Cu(II). The band II is also considered as a diagnostic criterion for Cu-carboxylate dimer formation²⁵. The magnetic moment value of the Cu(II) dimer complex is observed at 1.49 B.M. , which also supports a binuclear structure.

The spectral bands for Pd(II) complex have been observed at 22350 , 26784 and 35700 cm^{-1} . The band observed at 22350 cm^{-1} is assigned to ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ and the band observed at 26784 cm^{-1} to ${}^1\text{E}_g \leftarrow {}^1\text{A}_{1g}$ transition. The third band observed at 35700 cm^{-1} is assigned to the ligand to metal charge transfer band. Magnetic moment measurement shows Pd(II) complex to be diamagnetic and supports the electronic spectral data indicating a square planar geometry of the Pd(II) complex²⁶.

Thermal analysis

All the complexes have been studied by TGA and DTA studies done simultaneously. A clear plateau was observed in all the complexes between 560 - 540 K with a simple degradation mechanism, as revealed by the appearance of a single DTA peak. Thermograms of the complexes showed stepwise decomposition of the ligand from the complexes. The final products of decomposition in all the complexes were metal

Table 2 — Characteristics IR frequencies (cm^{-1}) of the ligand and complexes

Ligand/Complexes	$\nu_{\text{N-H}}$	Amide I	Amide II	ν_{COO^-} asym	ν_{COO^-} sym	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
H ₂ L	3300	1620 s	1480 m	1540 s	1420 s	-	-
CoL	3248 m	1625 s	1460 m	1570 s	1390 s	520 w	380
NiL	3240 m	1620 s	1450 m	1560 s	1380 s	516 m	400
[CuL] ₂	3300 m	1620 s	1480 m	1575 s	1410 s	522 m	390
PdL	3230 m	1620 s	1460 m	1562 s	1385 s	540 w	400

s, strong; m, medium; w, weak

Table 3 — Ligand field parameters and thermal analysis data of the complexes

Complex	d-d band(s)	MLCT band	TG range (K)	Activation energy (E_a/kJmol^{-1})	Metallic residue
H ₂ L	-	-	505-525	-	-
CoL	10380 22810 27145	-	576-830	34.66	CoO
NiL	21270	28170	558-810	28.48	NiO
[CuL] ₂	13895	27700	522-598	23.22	CuO
PdL	22350 26784	35700	590-814	41.80	PdO

oxides, as confirmed by experimental and calculated mass loss. The copper complex decomposed early as compared to other complexes, which supports the low thermal stability of the dimeric Cu(II) complex. The order (n) and activation energy (E_a) for thermal reactions were calculated using linearization method of Coats and Redfern²⁷. The activation energy values of the thermal decomposition reactions of complexes are found in the range of 23.22-41.80 kJ mol⁻¹. These low values of activation energies reveal that the ligand crystal field strength is a borderline case and may be slightly higher than that is required for producing low spin complexes. The Cu(II) complex has the lowest value of activation energy which indicates dimeric nature of the complex, which is also supported by jerks present in DTA curve and by other spectral evidences.

¹H NMR spectral study

The ¹H NMR spectra of the ligand and its Pd(II) complex have been recorded in DMSO-d₆. The integrations of the resonance signals are consistent with the assignments. The NMR spectrum of the ligand shows a resonance signal at 6.50 ppm (value in δ scale) due to amide NH proton in the range studied (0-15), not observed in the spectrum of the Pd(II) complex. It implies a large downshift of the amide NH proton, suggesting that the amide nitrogen is participating in coordination²⁸. In addition to this, a signal at 9.90 ppm (2H) was observed in the ligand spectrum due to -COOH proton, not observed in the spectrum of the complex indicating deprotonation of -COOH group and the coordination of Pd(II) through the oxygen of the carboxylate group in the complex.

EPR spectral study

The EPR spectra of the Cu(II) complex were recorded at X-band frequencies (~9.5 GHz) in the solid state at room temperature and liquid nitrogen temperature. (Fig. 1). The spectra of the Cu(II) complex showed four absorption bands at 460 G (moderately strong), 3000 G (moderate), 4600 G (strong) and 6000 G (weak), arising from the transition within the doublet state ($S = \frac{1}{2}$). The absorption band observed at 3000 G, with $g_{\parallel} = 2.41$, $g_{\perp} = 2.16$ ($g_{av} = 2.24$), is more likely due to the presence of a very small percentage of monomeric impurities²⁹. The intensity of the band at 3000 G increases at low temperature, whereas of other bands decreases, which might be due to a significant zero field splitting effect³⁰. Three absorption lines (H_{z1},

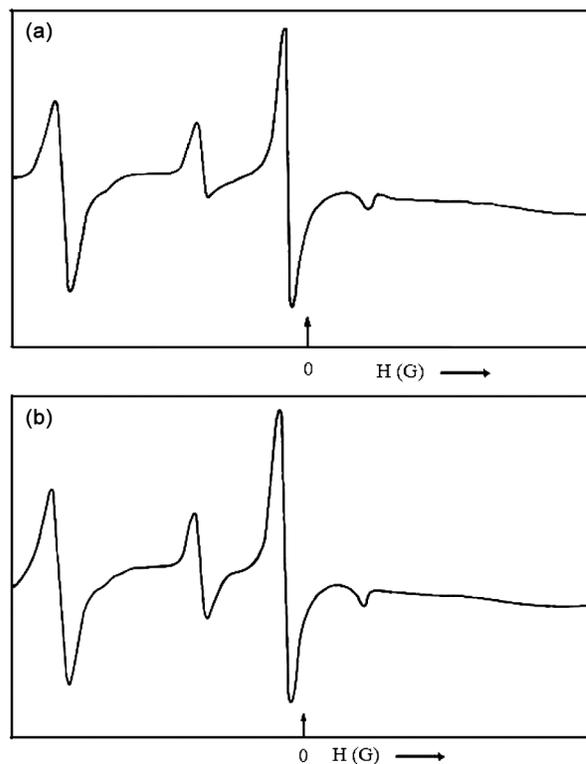


Fig.1 — EPR spectra of [CuL]₂ in solid state at (a) room temperature and (b) liquid nitrogen temperature

H_{z2}, H_{z1}) other than at 3000 G are due to transitions in the triplet state. It is noteworthy that the line width of high and low field absorption is approximately three times that of the middle one. It is clear that in such systems, intermolecular interactions are responsible for the exchange broadening in the spectra, which provides little information about the structure of the complex. All these features in the present Cu(II) complex are similar to those observed for the Cu(II) complexes of unsaturated carboxylic acids, di-carboxylic acids and acid amides³¹ for which a dimeric structure was proposed. Based on these studies, the present Cu(II) complex may be assigned a dimeric structure with small monomeric impurities.

pH-metric study

The potentiometric titrations of the ligand (0.1 M H₂L, at 298±0.5 K, I = 0.1 M NaClO₄) were carried out with tetramethyl ammonium hydroxide (TMAH) to determine acid-base equilibria. The pH values were plotted against the volume of TMAH used for the titrations (Fig. 2). The excellent σ_{fit} provides support for the complete experimental refinement as expected. The values for the logarithms of the stepwise protonation constants of the carboxylate

groups of the ligand are fairly close to the values reported for such types of ligands and are within the range observed for β -substituted carboxylic acids³². The protonation constants ($\log K_1^H = 9.67$, $\log K_2^H = 7.50$) of the ligand indicates that the ligand behaves as a relatively strong base. The determination of

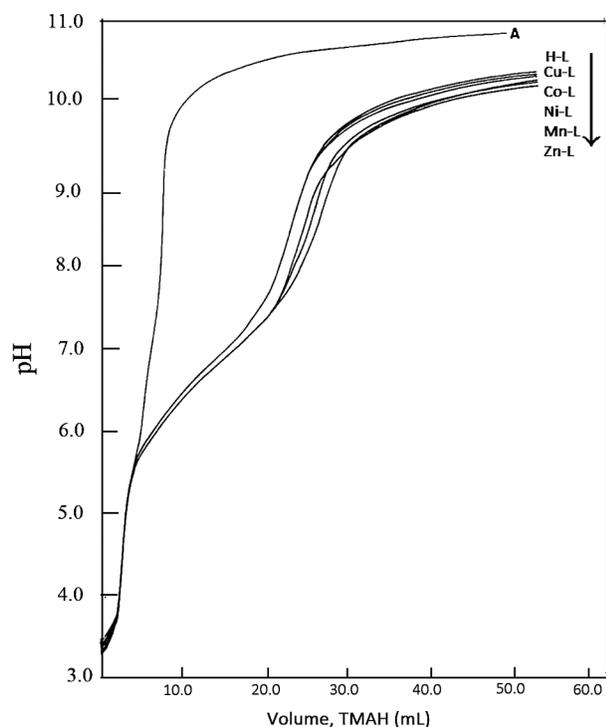


Fig. 2 — Potentiometric titrations curves of the ligand in the absence and presence of metal ions at 298 ± 0.5 K, $I=0.1$ M NaClO_4

deprotonation constants of $-\text{NH}$ group of amide ligands by potentiometric technique is not reliable since it requires a very basic medium¹.

The complex formation ability of the Ligand (H_2L) with respect to late 3d bivalent metal ions, i.e., Mn(II) , Co(II) , Ni(II) , Cu(II) and Zn(II) , has been investigated by potentiometric titrations in the pH range 3.0-10.4. It was revealed from the studies that precipitation of the complexes occurred at higher pH. The observed protonation constants of L^{2-} together with stability constants of its metal complexes, are given in Table 4. The values of stability constants of metal complexes are of the same order of magnitude as those reported for 1:1 and 1:2 ($\text{M(II)}:\text{carboxylate ligand}$) complexes in which the $-\text{COOH}$ group acts as a monodentate ligand³³. This indicates the possibility of coordination of deprotonated ligand to bivalent metal ions through the $-\text{COOH}$ group to yield mononuclear 1:1 and 1:2 species. The stability constant of the Cu(II) complex ($\log \beta = 11.38$) is greater as expected than that of the corresponding other M(II) complexes. The values of stability constants of M(II) complexes have been found in the order: $\text{Mn(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$. The proposed structures of the complexes are shown in Fig. 3.

The stability of the metal complexes depends on various factors. The radii of bivalent metal ions of 3d transition series decreases from Mn(II) to Cu(II) and then increases to Zn(II) . Also the crystal field stabilization energy for these metal ions increases from Mn(II) to Ni(II) and then decreases. Still the

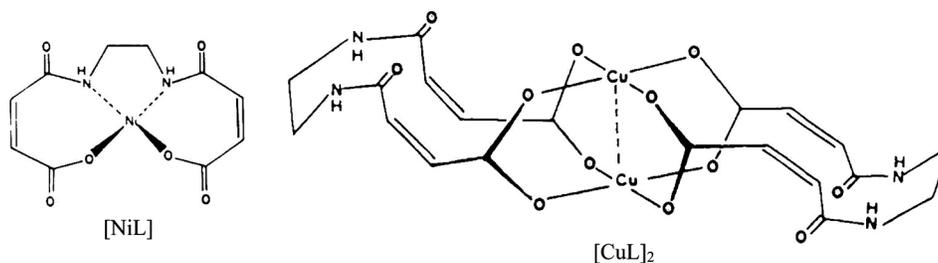


Fig. 3 — Proposed structures of the complexes

Table 4 — Stability constants of bivalent metal ions of H_2L in 75% DMF at 298 K in 0.1 M NaClO_4

Ligand/Complex	$\log K_1^H$	$\log K_2^H$	$\log K_1$	$\log K_2$	$\log \beta_2$	σ_{fit}
H_2L	9.67	7.50	-	-	-	0.0000
Mn(II)	-	-	4.75	4.30	9.05	0.0051
Co(II)	-	-	5.00	4.40	9.40	0.0078
Ni(II)	-	-	5.15	4.98	10.13	0.0059
Cu(II)	-	-	5.89	5.49	11.38	0.0074
Zn(II)	-	-	5.80	5.25	11.05	0.0087

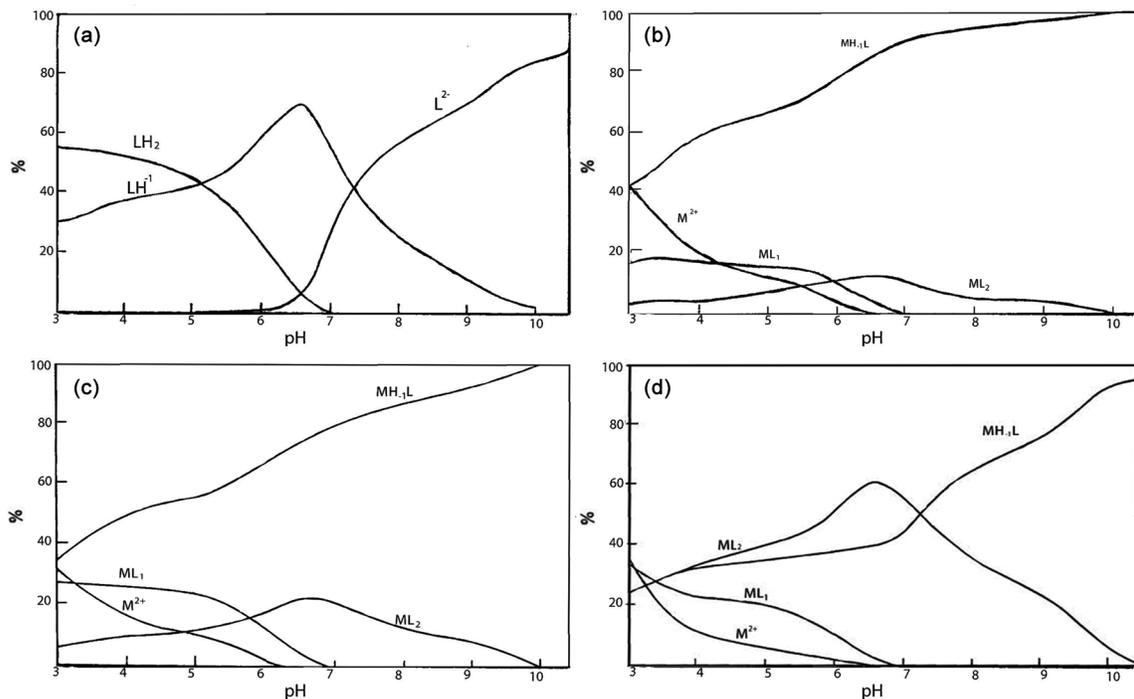


Fig. 4 — Species distribution curves for (a) H^+/L^{2-} , (b) $Mn(II)/L^{2-}$ system, (c) $Co(II)/L^{2-}$ system and (d) $Ni(II)/L^{2-}$ system

Cu(II) complex was found to be more stable due to distortions associated with these complexes. The observed trend is in good agreement with the Irving-Williams series³⁴. The values of stability constants observed for the complexes in the current study are higher than reported in the literature, which reveals the chelating character of the ligand.

The species distribution diagram for the system H^+/L^{2-} based on fitted equilibrium constants is presented in Fig. 4a. The prominent species at lower pH values are H_2L and HL^- , whereas the concentration of L^{2-} becomes significant at $pH > 6$ being the only species existing at $pH > 10$. Using the various equilibrium constants, percentage species distribution of L^{2-}/M^{2+} system as a function of pH were calculated and depicted in Fig. 4b-d. Only ML , ML_2 and MH_1L species exist in the pH range 3–10. A perusal of species distribution diagrams reveals that 1:1 complexes are formed in the pH range of 3–7. The 1:2 species formed at its maximum in the pH range of 5–8. The MH_1L species is significant throughout the pH range studied for $Mn(II)/L^{2-}$, $Co(II)/L^{2-}$ and $Ni(II)/L^{2-}$, being the only species present at $pH \geq 10$, for $Cu(II)/L^{2-}$ and $Zn(II)/L^{2-}$ system it becomes significant at $pH > 7$.

Conclusion

Keeping in mind the diverse coordinating behaviour and biological importance of carboxyamide ligands;

$Co(II)$, $Ni(II)$, $Cu(II)$ and $Pd(II)$ complexes of a novel carboxyamide ligand [H_2L] were prepared and characterized by IR, UV-visible, EPR and 1H NMR spectral studies. It was concluded that the metal ions coordinates to the ligand through deprotonated carboxylate oxygen and non-deprotonated amide nitrogen in all the complexes. $Co(II)$, $Ni(II)$ and $Pd(II)$ formed mononuclear square planar complexes, whereas $Cu(II)$ formed a binuclear complex. All the complexes showed stepwise decomposition to respective metal oxides. The complex formation between ligand and metal ions studied pH metrically, showed the stability constants in the order: $Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$, which was in good agreement with the Irving-Williams series. The probable structures of the complexes have been proposed.

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