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Synthesis and spectrothermal studies on group 12 metals coordination with novel carboxyamide ligands

Bibhesh K. Singh, Parshuram Mishra, Bhagwan S. Garg*

Department of Chemistry, University of Delhi, Delhi 110007, India Received 30 December 2006; accepted 12 April 2007

Abstract

Complexes of group 12 metals with new ligands N',N"-bis(3-carboxy-1-oxopropanyl) 2-amino-N-arylbenzamidine (H₂L) and N',N"-bis(3-carboxy-1-oxopropanyl) and N', carboxy-1-oxophenelenyl) 2-amino-N-arylbenzamidine (H₂L) have been synthesized and characterized by elemental analyses, vibrational spectra, electronic spectra, ¹H NMR spectra, TOF-mass spectra, thermal studies and molecular modeling studies. The infrared and ¹H NMR spectral data are in agreement with coordination of amide and carboxylate oxygen of the ligands giving a MO_4 tetrahedral chromophore. The elemental analyses and mass spectral data have justified the ML complexes. The thermal behaviour of complexes shows that water molecule is removed in first step-followed by decomposition of the rest of the molecule in the next steps. Kinetic and thermodynamic parameters were computed from the thermal data using Coats and Redfern method, which confirm first order kinetics. Molecular structures of the complexes have been optimized by MM2 calculations and supported tetrahedral geometry around metal(II) ions. © 2007 Elsevier B.V. All rights reserved.

Keywords: Amide; Group 12 metal complexes; Spectra; Thermal and molecular mechanics

1. Introduction

In recent years group 12 metal compounds, which have a stable d¹⁰ electronic configuration, have received a lot of attention in the fields of inorganic chemistry, biochemistry and environmental chemistry [1-5]. We are interested to establish spectroscopic model complexes of zinc(II), cadmium(II) and mercury(II) ions with biomimitic polydentate amide ligands, which have an amidine ring. The amidine unit is the key functional group in a wide range of biologically active molecules [6], including a variety of serine protease inhibitors [6-8] and antimicrobial agents [9]. Magainin-2-amide, the bioactive peptoid exhibit selective, potent antibacterial activity against both Gram-positive and Gram-negative bacteria [10]. These readily synthesized, protease-resistant peptoids represents an important advance in peptide biomimicry, the development of nonpeptide foldameric analogues of antibacterial peptides. Though, much work has been done on amide ligands in general and the amide ligands in combination with other functional groups, but only less work has been done on amide system contain-

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ing carboxylic anchors, which may act as biomimic to peptides and certain enzymes. Ligands containing carboxyamide chains having O₄ donor atoms, and their complexes, have been cited as possessing noteworthy pharmacological activity [11]. Thus, we have designed amide ligands containing carboxylic anchors condensed with amidines.

In general, the zinc(II) ion can coordinate to hard and soft atoms, while the cadmium(II) ion and mercury(II) ion prefer soft atoms and electron rich conditions [1]. Nitrogen donar ligands are regarded as hard ligands. The reactivities of complexes are affected by these differences in polarizability. In order to increase reactivity, we introduced new polydentate ligands to stabilize the complexes. In this context, the structure and mode of bonding of amide bond in a complexes of amide ligands, will be a great help in understanding the development in the area of amide-metal interactions [12,13]. Our research interest is centered on thermal stability and structure of metal ion complexes of newly synthesized biomimic amides. In view of the diverse coordinating behaviour of amide group, it was considered worthwhile to prepare and study some of the complexes. In the present manuscript, we report the preparation and study of Zn(II), Cd(II) and Hg(II) complexes of the newly synthesized ligands N', N''-bis(3-carboxy-1-oxopropanyl) 2-amino-*N*-arylbenzamidine and N', N''-bis(3-carboxy-1-oxophenelenyl)

Corresponding author. Tel.: +91 9868359781; fax: +91 27666250. E-mail address: bibheshksingh@yahoo.co.in (B.K. Singh).

2-amino-*N*-arylbenzamidine. The molecular modeling studies for energy minimization and optimization of geometry of the metal complexes have also been carried out.

2. Experimental

2.1. Material and methodology

All the chemicals used in this study were of analytical grade and used as procured. Solvents used were of analytical grade and were purified by standard procedures. The stoichiometric analyses(C, H and N) of the complexes were performed using Elementar vario EL III (Germany) model. Metal contents were estimated on an AA-640-13 Shimadzu flame atomic absorption spectrophotometer in solution prepared by decomposing the respective complex in hot concentrated HNO₃. Their IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer in KBr and polyethylene pellets. The electronic spectra were recorded in water on Beckman DU-64 spectrophotometer with quartz cells of 1 cm path length and mass spectra (TOF-MS) were recorded on Waters (USA) KC-455 model with ES⁺ mode in D₂O. ¹H NMR spectra were recorded in D₂O solvent (solvent peak 4.8 ppm) on a Bruker Advance 400 instrument. Rigaku model 8150 thermoanalyser (Thermaflex) was used for simultaneous recording of TG-DTA curves at a heating rate of 10° min⁻¹. For TG, the instrument was calibrated using calcium oxalate while for DTA, calibration was done using indium metal, both of which were supplied along with the instrument. A flat bed type aluminium crucible was used with α -alumina (99%) pure) as the reference material for DTA. The number of decomposition steps was identified using TG. The activation energy and Arrhenius constant of the degradation process was obtained by Coats and Redfern method.

2.2. 3D molecular modeling

3D molecular modeling of the proposed structure of the complexes was performed using CsChem3D Ultra 10-program package. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries. The potential energy of the molecule was the sum of the following terms: $E = E_{str} + E_{ang} + E_{tor} + E_{vdw} + E_{oop} + E_{ele}$, where all *Es* represent the energy values corresponding to the given types of interaction (kcal/mol). The subscripts str, ang, tor, vdw, oop and ele denote bond stretching, angle bonding, torsion deformation, Van der Waals interactions, out of plain bending and electronic interaction, respectively.

2.3. Synthesis of the ligands

2.3.1. Synthesis of 2-amino-N-arylbenzamidine $(C_{13}H_{13}N_3)$

2-Amino-*N*-arylbenzamidine ($C_{13}H_{13}N_3$) as precursor was synthesized by reported procedure [14]. This was characterized by elemental analysis, infrared spectra, ¹H NMR spectra and mass spectra. Satisfactory results were obtained.



Fig. 1. Ligand L1.

2.3.2. Synthesis of N', N''-bis(3-carboxy-1-oxopropanyl) 2-amino-N-arylbenzamidine ($C_{21}H_{21}N_3O_6$) (L^1) (Fig. 1)

A finely ground mixture of 2-amino-*N*-arylbenzamidine (0.5 mmol), succinic anhydride (1.0 mmol) and fused sodium acetate (0.5 mmol) in glacial acetic acid (25 ml) was refluxed on water bath for 3 h. After filtering the residue, filterate on slow evaporation forms fine crystals. This was recrystallized in acetic acid, washed with ethanol and dried over P_4O_{10} in vacuo. Ligand is soluble in common polar solvents.

Off white crystal; Yield: 83%; Anal. Calc. for $C_{21}H_{21}N_{3}O_{6}$ requires (%): C, 61.31; H, 5.11; N, 10.21; Found: C, 61.18; H, 5.37; N, 10.29 (mol. wt.: 411.4); FT-IR (KBr, cm⁻¹): ν (O–H) 2600(w), ν (N–H)_{amide} 3369(s), ν (C=O)_{amide I} 1650(w), $[\nu$ (C–N) + δ (N–H)]_{amide II} 1410(s), ν [(N–H) + δ (C–H)]_{amide III} 1300, ν_{as} (CO₂) 1558(s), ν_{s} (CO₂) 1402(s); ¹H NMR (ppm): 11.30(2H, s, –OH carboxylic acid), 8.15(2H, s, sec. amide), 7.45(4H, m, benzylidenimin), 7.35(5H, m, H-benzene), 1.43(8H, s, –CH₂ methylene group); TOF-MS (*m*/*z*): 412(14%, [*M*]⁺), 352(100%, [C₁₉H₁₉N₃O₄]⁺), 187(11%, [C₁₂H₁₄N₂]⁺). Electronic spectral data (cm⁻¹): 30,488 ($\pi \rightarrow \pi^*$, N-amide), 35,842 (n \rightarrow n*, C=O group).

2.3.3. Synthesis of N',N"-bis(3-carboxy-1-oxophenelenyl) 2-amino-N-arylbenzamidine $(C_{29}H_{21}N_3O_6)$ (L^2) (Fig. 2)

A finely ground mixture of 2-amino-*N*-arylbenzamidine (0.5 mmol), phthalic anhydride (1.0 mmol) and fused sodium



Fig. 2. Ligand L².

acetate (0.5 mmol) in glacial acetic acid (25 ml) was refluxed on water bath for 3 h. After filtering the residue, filterate on slow evaporation forms fine crystals. This was recrystallized in acetic acid, washed with ethanol and dried over P_4O_{10} in vacuo. Ligand is soluble in common polar solvents.

Light yellow crystal; Yield: 84%; Anal. Calc. for $C_{29}H_{21}N_3O_6$ requires (%): C, 68.64; H, 4.14; N, 8.28; Found: C, 68.64; H, 4.14; N, 8.28 (mol. wt.: 507); FT-IR (KBr, cm⁻¹): ν (O–H) 2602(w), ν (N–H)_{amide} 3370(s), ν (C=O)_{amide} I 1630(w), $[\nu$ (C–N) + δ (N–H)]_{amide} II 1485(s), ν [(N–H) + δ (C–H)]_{amide} III 1296, ν_{as} (CO₂) 1563(s), ν_s (CO₂) 1400(s); ¹H NMR (ppm): 11.25(2H, s, –OH carboxylic acid), 8.10(2H, s, sec. amide), 7.35(4H, m, benzylidenimin), 7.25(13H, m, H-benzene); TOF-MS (*m*/*z*): 507(15%, [*M*]⁺), 449(100%, [C₂₇H₁₉N₃O₄]⁺), 329(12%, [C₂₀H₁₄N₃O₂]⁺), 236(16%, [C₁₄H₁₀N₃O]⁺). Electronic spectral data (cm⁻¹): 31,447 ($\pi \rightarrow \pi^*$, N-amide), 35,842 (n \rightarrow n*, C=O group).

2.4. Synthesis of complexes

2.4.1. Synthesis of zinc(II), cadmium(II) and mercury(II) complexes of N',N"-bis(3-carboxy-1-oxopropanyl) 2-amino-N-arylbenzamidine

To a methanolic solution of $ZnCl_2$, $Cd(CH_3CO_2)_2 \cdot 2H_2O$ and $Hg(CH_3CO_2)_2$ (0.5 mmol) each in a separate flask was added a methanolic solution of the ligand (L¹) (0.5 mmol). The solution was stirred for 3 h, after which the volume was reduced on a warm water bath. The product obtained was washed with a small amount of methanol and air-dried. The above product was redissolved in excess warm methanol, and clear solution was left undisturbed for weeks to give beautiful white crystals of the complex.

2.4.2. Synthesis of zinc(II), cadmium(II) and mercury(II) complexes of N',N"-bis(3-carboxy-1-oxophenelenyl) 2-amino-N-arylbenzamidine

To a methanolic solution of $ZnCl_2$, $Cd(CH_3CO_2)_2 \cdot 2H_2O$ and $Hg(CH_3CO_2)_2$ (0.5 mmol) each in a separate flask was added a methanolic solution of the ligand (L²) (0.5 mmol). The solution was stirred for 3 h, after which the volume was reduced on a warm water bath. The product obtained was washed with a small amount of methanol and air-dried. The above product was redissolved in excess warm methanol, and clear solution was left

Table 1Color reaction yield and elemental analysis of complexes



Fig. 3. (a) Electronic spectra of complexes of ligand L^1 . (b) Electronic spectra of complexes of ligand L^2 .

undisturbed for weeks to give beautiful white/off white crystals of the complex.

3. Results and discussion

Satisfactory results of elemental analysis (Table 1) and spectral studies (IR, UV, ¹H NMR, TOF-MS) explained the bonding modes of ligands with metal ions. The complexes were of good purity and are of crystalline nature.

Complex	Empirical formula	Color	Yield (%)	Analysis:found (calculated) (%)			
				С	Н	Ν	М
$\overline{[Zn(L^1)]}$	C ₂₁ H ₁₉ N ₃ O ₆ Zn	White	78	53.04 (53.12)	3.96 (4.01)	8.80 (8.85)	13.70 (13.79)
$[Cd(L^1)] \cdot H_2O$	C ₂₁ H ₂₁ N ₃ O ₇ Cd	Silky white	81	46.48 (46.72)	3.81 (3.89)	7.72 (7.79)	20.78 (20.83)
$[Hg(L^1)] \cdot H_2O$	C ₂₁ H ₂₁ N ₃ O ₇ Hg	White	75	40.10 (40.15)	3.30 (3.35)	6.62 (6.69)	31.93 (31.96)
$[Zn(L^2)]$	$C_{29}H_{19}N_3O_6Zn$	White	80	60.93 (60.96)	3.30 (3.33)	7.31 (7.36)	11.41 (11.46)
$[Cd(L^2)]\cdot 2H_2O$	C ₂₉ H ₂₃ N ₃ O ₈ Cd	White	82	53.17 (53.23)	3.45 (3.52)	6.39 (6.42)	17.21 (17.19)
$[Hg(L^2)] \cdot H_2O$	$C_{29}H_{21}N_3O_7Hg$	Off white	77	48.00 (48.09)	2.79 (2.90)	5.73 (5.80)	27.69 (27.72)

Table 2	
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Important mass peaks for the complexes studied

Mass assignments	%	m/z
Complex I		
$[C_{21}H_{19}N_3O_6Zn]^+$	12	476
$[C_{18}H_{12}N_3O_3]^+$	16	318
$[C_{16}H_{12}N_3O_3]^+$	21	294
$[C_{14}H_{10}N_{3}O]^{+}$	26	236
$[C_{14}H_{12}N_2O]^+$	100	224
$[C_{14}H_{11}N_2]^+$	19	207
Complex II		
[C ₂₁ H ₂₁ N ₃ O ₇ Cd] ⁺	42	540/542
$[C_{21}H_{21}N_{3}O_{6}]^{+}$	100	414
$[C_{19}H_{15}N_{3}O_{2}]^{+}$	100	317
$[C_{15}H_{15}N_{3}O_{2}]^{+}$	100	269
$[C_{14}H_{12}N_2O]^+$	60	224
$[C_{14}H_{11}N_2]^+$	60	207
Complex III		
$[C_{21}H_{21}N_3O_7Hg]^+$	22	628/629
$[C_{21}H_{19}N_3O_6Hg]^+$	20	610
$[C_{20}H_{16}N_3O_3]^+$	45	346
$[C_{16}H_{12}N_3O_3]^+$	51	294
$[C_{16}H_{10}N_3O_2]^+$	100	276
$[C_{14}H_{10}N_{3}O]^{+}$	68	236
$[C_{14}H_{10}N_2O]^+$	67	222
Complex IV		
$[C_{29}H_{19}N_3O_6Zn]^+$	26	571/572
$[C_{27}H_{13}N_{3}O_{4}]^{+}$	30	443
$[C_{22}H_{11}N_3O_2]^+$	24	347/349
$[C_{20}H_{11}N_3O_2]^+$	100	324
$[C_{14}H_{10}N_3O]^+$	34	236
Complex V		
$[C_{29}H_{23}N_3O_8Cd]^+$	15	654/655
$[C_{22}H_{17}N_3O_6]^+$	72	417/419
$[C_{19}H_{13}N_3O_2]^+$	43	315
$[C_{14}H_7N_3O]^+$	100	233
Complex VI		
$[C_{29}H_{21}N_3O_7Hg]^+$	20	724/725
$[C_{27}H_{13}N_{3}O_{4}]^{+}$	100	442/443
$[C_{19}H_{13}N_3O_2]^+$	47	317
$[C_{14}H_6N_3O]^+$	90	232

3.1. Electronic spectra

The electronic spectra of the ligands and its metal complexes have been studied in the range 190–400 nm (Fig. 3(a) and (b)). The shoulder band observed at 279 nm in water solvent in ligands may be assigned to $n \rightarrow n^*$ transition within the C=O group of the amide moiety in the free ligands. This band is red shifted to 299 nm in case of complex IV and 284 nm in case of complex V, while it disappeared in other complexes of ligand L¹ and ligand L² revealing the involvement of the C=O of amide group or carboxylate oxygen in chelate formation. The band observed at 328 and 318 nm in ligands L¹ and L², respectively, may be assigned to $\pi \rightarrow \pi^*$ transition of the N-amino group of the amide ligand, remain at the same position in all the respective metal complexes, indicating they are not affected by metal chelation [15]. The result supports the mode of interaction of amide with group 12 metal ions.



Fig. 4. (a) TOF-MS spectra of complex I. (b) TOF-MS spectra of complex III. (c) TOF-MS spectra of complex V.

3.2. TOF-MS spectra

Mass spectrometry has been successfully used to investigate molecular species in solution [16–18]. The molecular ion peaks of the ligands and complexes have been used to confirm the proposed formula (Table 2). The multi-peaks pattern of the mass spectrum gives an impression of the successive degradation of the target compound with the series of peaks corresponding to the various fragments. Their intensity gives an idea of stability of fragments. The ligands have similar tendency of initial loss of two molecules of $[HC=O]^+$ with 100% *m*/*z* values. Ligand (L¹) starts degradation and it finally forms two molecules of $[C_6H_5NH_2]^+$, whereas Ligand (L²) finally degrades to [amidine]⁺. In the TOF-mass spectra of metal complexes initial fragmentation pattern is again similar (loss of one or two water molecules), a mononuclear nature



Fig. 5. (a) IR spectrum of complex I. (b) IR spectrum of complex II. (c) IR spectrum of complex III. (d) IR spectrum of complex IV. (e) IR spectrum of complex V. (f) IR spectrum of complex VI.

Table 3		
IR spectral data (cm ⁻	¹) of ligand and	metal complexes

Frequency	$\nu_{\rm NH}$	Amide I	Amide II	Amide III	$v_{as}(CO_2)$	$\nu_{sy}(CO_2)$	М–О
$[Zn(L^1)]$	3424(s)	1634(w)	1415(s)	1325(m)	1596(s)	1376(m)	489(m)
$[Cd(L^1)] \cdot H_2O$	3419(s,b)	1638(m)	1416(s)	1302(m)	1560(s)	1341(s)	510(m), 372(s), 306(s)
$[Hg(L^1)] \cdot H_2O$	3446(s,b)	1644(m)	1415(m)	1319(w)	1562(s)	1385(m)	644(s), 524(s)
$[Zn(L^2)]$	3421(s)	1614(w)	1489(s)	1305(w)	1580(s)	1395(s)	482(m)
$[Cd(L^2)]\cdot 2H_2O$	3417(s,b)	1626(w)	1488 (m)	1375(m)	1556(s)	1410(s)	519(m), 376(s), 300(s)
$[Hg(L^2)] \cdot H_2O$	3437(s,b)	1626(w)	1487(m)	1385(m)	1567(s)	1409(m)	526(m), 480(m)

b, broad; s, strong; m, medium; w, weak.

Table 4

¹H NMR δ values (ppm) of metal complexes

Compounds	Sec. amide	H-benzylidenimin	H-benzene	-CH ₂ methylene group	Proton of H ₂ O
$\overline{[Zn(L^1)]}$	8.00(2H,s)	7.44(4H,m)	7.34(5H,m)	1.42(8H,s)	_
$[Cd(L^1)] \cdot H_2O$	8.04(2H,s)	7.43(4H,m)	7.32(5H,m)	1.37(8H,s)	2.38
$[Hg(L^1)] \cdot H_2O$	8.09(2H,s)	7.42(4H,m)	7.30(5H,m)	1.41(8H,s)	2.27
$[Zn(L^2)]$	8.08(2H,s)	7.32(4H,m)	7.23(13H,m)	_	_
$[Cd(L^2)]\cdot 2H_2O$	8.00(2H,s)	7.30(4H,m)	7.22(13H,m)	_	2.50
$[Hg(L^2)] \cdot H_2O$	8.02(2H,s)	7.28(4H,m)	7.21(13H,m)	-	2.45

for these complexes $[M(L)]^+$ can be deduced (Fig. 4(a)–(c): TOF-MS spectrum of complexes I, III and V). The last two fragments appears in nearly all the complexes at positions (m/z)values) 233/236 (26% complex I, 68% complex III, 34% complex IV, 100% complex V and 90% complex VI) and 222/224 (100% complex I, 60% complex II and 67% complex III) corresponds to [C₁₄H₁₀N₃O]⁺ and [C₁₄H₁₀N₂O]⁺, respectively, which could be the result of demetallation and subsequently a partial intra-molecular hydrogen bonding. Another prominent peak in the middle of the degradation pathway of the complexes of ligand (L²) at position (m/z) 443 (30% complex IV, 100% complex VI) and 324 (100% complex IV) are $[C_{27}H_{13}N_3O_4]^+$ and [C₂₀H₁₁N₃O₂]⁺, respectively. Complex II (23%) and complex III (19%) have peak at 185 (m/z value) correspond to the formation of two molecules of C₆H₅NH₂ like a degradation of the ligand (L^1) . Likewise peaks attributable to unstable monomeric species as $[M(L)]^+$ and $[H_2L]^+$ are usually present in the mass spectra of these systems [19,20].



Fig. 6. ¹H NMR spectra of complex II.

3.3. IR spectra and mode of bonding

An ambidentate nature of the amide can coordinate with zinc(II), cadmium(II) and mercury(II) either through nitrogen of the -NH₂ or the oxygen of the C=O group. The bands due to the amide $v_{\rm NH}$ mode at 3200–3400 cm⁻¹ for the free ligands L¹ and L^2 are shifted towards higher frequencies, while the $v_{C=O}$ (amide I) frequency $(1630-1650 \text{ cm}^{-1})$ undergoes shift towards lower frequency $(1610-1645 \text{ cm}^{-1})$ in the metal complexes indicating non-involvement of the amide nitrogen and involvement of the carbonyl oxygen atom of amide group in coordination with the metal ion [21] (Fig. 5(a)–(f)). This result is explained by the decrease in the double bond character of C=O and the subsequent increase of C-N double bond character [22,23]. It is the lengthening of the C=O bond and shortening of the C-N bond which cause the decrease and increase of the frequencies, respectively. Amide II (1410–1485 cm⁻¹ in ligands) and amide III (1295–1301 cm⁻¹ in ligands) bands arising out of v_{C-N} as well as δ_{N-H} modes (coupled to one another), shift towards higher frequencies 1415–1490 and 1302–1385 cm⁻¹, respectively, in complexes further confirming the coordination through carbonyl oxygen (Table 3). The ν (C=O) and ν (C-O) stretching frequencies in the 1540–1590 and $1420-1400 \text{ cm}^{-1}$ region in the uncomplexed ligands have been assigned to $v_{as}(CO_2^{-})$ and $v_s(CO_2^{-})$ modes of the carboxylate group and these bands shows considerable shift in all the complexes. A positive and negative shift in complexes indicates a Δv enhancement upon complexation and suggests coordination of carboxylate groups in all the complexes of the three ligands in a monodentate fashion [24,25]. Here Δv implies the difference between $v_{as}(CO_2^{-})$ and $v_{s}(CO_{2}^{-})$ (i.e., asymmetric and symmetric stretching modes, respectively). The ν (O–H) due to carboxylic group appearing at $2600 \,\mathrm{cm}^{-1}$ in the free ligands disappears in the spectra of their complexes, indicates both carboxylic groups are involved in complexation. The vibrational bands due to rocking and wagging modes of water and metal–oxygen stretching modes are observed in the 800–350 cm⁻¹ region for all the complexes (except complexes I and IV) of both the ligands and may be attributed to the coordinated water [24]. This can be confirmed with the help of thermograms. A new band in the 650–300 cm⁻¹ regions in the spectra of the complexes is assignable to ν (M–O) [24].

3.4. ¹H NMR spectra

The ¹H NMR spectra of a D₂O solution of the amide ligands and its Zn(II), Cd(II) and Hg(II) complexes show well-resolved signals as expected (Fig. 6: ¹H NMR spectra of complex II). The solvent resonates near 4.8 ppm. The ¹H NMR resonances are summarized in Table 4, with the complexes slightly upfield compared to the free ligands, indicative of the presence of free carboxylate (absence of signals for COOH and OH–COOH group (11.2–11.3)). A similar trend has been observed in the ¹H NMR spectra of metal–acid complexes [26,27], in agreement with coordination by COO⁻, as also suggested by IR data. In all complexes, peaks in the range 2.50–2.20 ppm are from H₂O (water of crystallization).

3.5. Thermal studies

Recently, there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves [28-30]. Thermogravimetric (TG) and differential thermogravimetric analyses (DTA) were carried out for group 12 metal-amide complexes in ambient conditions. In thermogram of complexes (Fig. 7(a) and (b)), we have found that on heating at a rate of 10°C/min it loses nearly 2.5-5.6% of its weight between 75 and 110°C (except in complexes I and IV). This corresponds to the loss of water molecule(s). This has been supported by endothermic peak in DTA. In another steps, decomposition of organic moiety takes place with the formation of metal oxide as residue. In final steps an exothermic peak in the DTA suggests that conformational changes occurred in the amide chelate rings (Table 5). In the temperature range 320-530 °C, the complexes finally forms metal oxide that has been confirmed with the help of X-ray diffraction studies.

On the basis of above thermal decomposition, the kinetic analysis parameters such as activation energy (E^*), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), free energy change of decomposition (ΔG^*) were evaluated graphically by employing the Coats–Redfern relation [31]. The Coats and Redfern linearization plots (Fig. 7(a) and (b)), confirms the first order kinetics for the decomposition process. The calculated values of E^* (J mol⁻¹), A (s⁻¹), ΔS^* (J K⁻¹ mol⁻¹), ΔH^* (J mol⁻¹) and ΔG^* (J mol⁻¹) for the decomposition steps of the complexes are reported in Table 6. According to the kinetic data obtained from the TG curves, the activation energy relates the thermal stability of the metal complexes. Among metal complexes, activation energy increases as complex II ~ complex V < complex IV < complex VI < complex III < complex I, same



Fig. 7. (a) TG/DTA and Coats and Redfern linearization plot of complexes of ligand L^1 . (b) TG/DTA and Coats and Redfern linearization plot of complexes of ligand L^2 .

Table 5
Thermoanalytical data (TG, DTA) of group 12 metal-amide complexes

Complex	Step	TG _{range} (K)	DTA _{max} (K)	Thermal effect	Mass loss: obs. (cal.) (%)	Assignment	Metalic residue
$\overline{[Zn(L^1)]}$	Ι	493–598	528	Endo	9.15 (9.26)	CO ₂	
	II	693-773	728	Exo	72.95 (73.60)	Organic moiety	ZnO
$[Cd(L^1)] \cdot H_2O$	Ι	338-393	355	Endo	3.40 (3.33)	H_2O	
	II	473-573	527	Endo	8.20 (8.15)	CO_2	CdO
	III	663–738	717	Exo	64.35 (64.37)	Organic moiety	
$[Hg(L^1)] \cdot H_2O$	Ι	353-440	372	Endo	2.60 (2.87)	H_2O	
-	II	453-530	510	Endo	7.32 (7.00)	CO_2	HgO
	III	593-683	655	Exo	55.31 (55.67)	Organic moiety	
$[Zn(L^2)]$	Ι	413-493	445	Endo	8.00 (7.71)	CO_2	
	II	698–798	775	Exo	77.60 (78.03)	Organic moiety	ZnO
$[Cd(L^2)]\cdot 2H_2O$	Ι	348-423	393	Endo	5.60 (5.51)	H ₂ O	
	II	498-588	551	Endo	6.70 (6.73)	CO_2	610
	III	623-663	648	Exo	17.90 (17.89)	C9H9	CdO
	IV	723–793	781	Exo	50.10 (50.24)	Organic moiety	
$[Hg(L^2)] \cdot H_2O$	Ι	350-410	366	Endo	2.50 (2.49)	H ₂ O	
-	II	448-538	513	Endo	12.20 (12.15)	$2CO_2$	HgO
	III	615–673	637	Exo	55.50 (55.47)	Organic moiety	

trends happens with thermal stability of metal complexes. It is probably because of increase in bulkiness in ligand molecule from L^1 to L^2 . Cadmium complexes are thermally less stable than zinc and mercury complexes. All the complexes have negative entropy, which indicates that the complexes are formed spontaneously. The negative value of entropy also indicates a more ordered activated state that may be possible through the chemisorption of oxygen and other decomposition products. The negative values of the entropies of activation are compensated by the values of the enthalpies of activation, leading to almost the same values for the free energy of activation [32].

Table 6

3.6. Molecular structures and analysis of bonding modes

In order to ascertain the structural preferences and coordination behaviour of polydentate amide to metal ions, molecular mechanics calculations on the $[ML]^{n+}$ species were undertaken. We have optimized the molecular structure of complexes. The optimized molecular structure of complex I is given in Fig. 8. Energy minimization was repeated several times to find the global minimum. The energy minimization values for the optimized structure for the complex I is 62.12 kcal/mol. This supports tetrahedral geometry of the metal complexes. The selected bond length and bond angles of the complex I are rep-

Complex	Order (n)	Step	E^* (J mol ⁻¹)	$A(s^{-1})$	$\Delta S^* (\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$	$\Delta H^* (\mathrm{J} \mathrm{mol}^{-1})$	$\Delta G^* (\mathrm{kJ}\mathrm{mol}^{-1})$
$[Zn(L^1)]$	1	Ι	47.78	4.99×10^{4}	-159.46	02.91	84.20
		II	44.11	3.08×10^4	-166.13	51.75	120.99
$[Cd(L^1)] \cdot H_2O$	1	Ι	16.56	2.81×10^4	-160.93	12.72	57.14
		II	18.20	2.29×10^{4}	-165.91	35.26	87.47
		III	18.35	1.71×10^4	-170.89	185.98	122.71
$[Hg(L^1)] \cdot H_2O$	1	Ι	38.23	1.43×10^{4}	-166.92	13.23	62.11
		II	38.23	1.04×10^{4}	-172.19	95.74	87.91
		III	31.86	5.64×10^3	-179.34	656.42	118.12
$[Zn(L^2)]$	1	Ι	19.77	2.66×10^4	-163.26	20.61	72.67
		II	20.23	1.59×10^4	-172.14	62.75	133.47
$[Cd(L^2)]\cdot 2H_2O$	1	Ι	15.29	1.25×10^4	-168.49	46.76	66.26
		II	35.35	4.75×10^{4}	-160.22	59.55	88.34
		III	19.11	1.18×10^4	-173.13	31.94	112.22
		IV	15.93	6.79×10^{3}	-179.26	89.72	140.09
$[Hg(L^2)] \cdot H_2O$	1	Ι	21.25	3.41×10^{4}	-159.58	78.35	58.48
		II	20.23	2.20×10^4	-166.02	117.72	85.29
		III	20.23	1.77×10^4	-169.62	439.47	108.49



Fig. 8. The optimized molecular structure of complex I.

resented in Table 7, is comparable with tetrahedral geometry. The all bond lengths of Zn–O bond and bond angles O–Zn–O are same.

On the basis of above physiochemical data with consideration of ring strain, a tetrahedral geometry (Fig. 9(a) and (b)) is proposed for the group 12 metal–amide complexes.



Fig. 9. (a) Proposed structure of complexes. I: M = Zn(II), n = 0; II: M = Cd(II), n = 1; III: M = Hg(II), n = 1. (b) Proposed structure of complexes. IV: M = Zn(II), n = 0; V: M = Cd(II), n = 2, VI; M = Hg(II), n = 1.

Table 7 Data for selected bond lengths and bond angles of complex I

Bond length (Å)		
Zn(1) - O(5)	1.8900	
Zn(1)–O(4)	1.8900	
Zn(1)–O(3)	1.8900	
Zn(1)-O(2)	1.8900	
Bond angle ($^{\circ}$)		
O(5)-Zn(1)-O(4)	109.3272	
O(5)–Zn(1)–O(3)	109.5000	
O(5)-Zn(1)-O(2)	109.5000	
O(4)–Zn(1)–O(3)	109.5000	
O(4) - Zn(1) - O(2)	109.5000	
O(3)–Zn(1)–O(2)	109.5000	
C(14)–O(5)–Zn(1)	109.5000	
C(6)-O(4)-Zn(1)	109.5000	
C(7) - O(3) - Zn(1)	109.5000	
C(15)-O(2)-Zn(1)	109.5000	

4. Conclusion

It can be concluded that metal(II) complexes were found to be monomer and involved coordination through carboxylate oxygen of the amide ligands giving tetrahedral geometry. Vibrational spectra indicate the presence of H_2O molecule in the complexes (except zinc complexes) that has been supported by TG/DTA. Spectroscopic data in solution showed that the polydentate amide adopts similar coordination behaviour as suggested by vibrational spectra. Kinetic parameter shows that the decomposition follows first order kinetics and proceeds in two/three-step decomposition. The thermal behaviour of complexes shows that water molecule is removed in first step—followed by decomposition of the organic moiety in the second step. Thermal stability of the complexes has been compared. The molecular modeling studies for energy minimization and optimization of geometry of the metal complexes have also been carried out.

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