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Cobalt(II) complexes of new biomimetic polydentate amide: Spectroscopic, kinetics of thermal decomposition and XRPD studies

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

Department of Chemistry, University of Delhi, Delhi 110007, India Received 16 November 2006; received in revised form 12 May 2007; accepted 17 May 2007

Abstract

Complexes of Co(II) with new ligands N',N''-bis(3-carboxy-1-oxoprop-2-enyl) 2-amino-*N*-arylbenzamidine (C₂₁H₁₇N₃O₆), N',N''-bis(3-carboxy-1-oxophenelenyl) 2-amino-*N*-arylbenzamidine (C₂₉H₂₁N₃O₆) and N',N''-bis(3-carboxy-1-oxophenelenyl) 2-amino-*N*-arylbenzamidine (C₂₉H₂₁N₃O₆) have been synthesized and characterized by elemental analyses, vibrational spectra, electronic spectra, TOF-mass spectra, magnetic susceptibility measurements, thermal studies and X-ray powder diffraction studies. Vibrational spectra indicate coordination of amide and carboxylate oxygen of the ligands along with two water molecules giving a MO₆ weak field octahedral chromophore. Electronic spectra and magnetic susceptibility measurements reveal octahedral geometry for Co(II) complexes. The elemental analyses and mass spectral data have justified the ML complexes. Kinetic and thermodynamic parameters were computed from the thermal data using Coats and Redfern method, which confirm first-order kinetics. Powder diffraction determines the cell parameters of the complexes. (© 2007 Elsevier B.V. All rights reserved.

Keywords: Amide; Cobalt(II); Spectra; Thermal and X-ray powder diffraction studies

1. Introduction

The binding of metal ions to amide group(s) has been the subject of research over the past three decades, precisely due to ambidentate nature of amide bond and many of these reactions provide simple models for much more complex metal–peptide systems and enzymes [1]. There are numerous examples of the in vivo interactions of transition metal ions with the ligands containing amide group(s), and these interactions can be of biological importance [2–4]. Magainin-2-amide, the bioactive peptoid exhibit selective, potent antibacterial activity against both Gram-positive and Gram-negative bacteria [2]. These readily synthesized, protease-resistant peptoids represents an important advance in peptide biomimicry, the development of nonpeptide foldameric analogues of anti bacterial 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 containing carboxylic anchors, which may act as biomimic

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to peptides and certain enzymes. Thus, we have designed amide ligands containing carboxylic anchors condensed with amidines. The amidine unit is the key functional group in a wide range of biologically active molecules [5], including a variety of serine protease inhibitors [6,7] and antimicrobial agents [8].

Because of the number and variety of coordination sites in a biomimetic amide, its coordination chemistry is complicated and the most definitive information has been obtained by using results from combination of various techniques. Spectral characterization and the kinetic calculations of thermal decomposition reactions serve as important tools for the interpretation of structures of molecules of biological and analytical importance. Powder diffraction data is especially useful to deduce accurate cell parameters as well as particle size. The fact that the three-dimensional reciprocal lattice information is condensed onto a one-dimensional intensity profile with respect to 2θ in powder diffraction is the main concern. This leads to overlapping of the diffraction peaks, considerable and preferred orientation among the crystallites [9]. Therefore, we report herein the synthesis, spectral characterization (infrared, electronic, mass and ¹H NMR), magnetic susceptibility measurements, thermal and XRPD studies of the complexes of amide with cobalt(II) ions.

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

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 UV-vis 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. Magnetic susceptibility measurements were carried out at room temperature in powder form on a vibrating sample magnetometer PAR 155 with 5000G-field strength, using Co [Hg(SCN)₄] as the calibrant (magnetic susceptibility $\approx 1.644 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$). 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. The XRD powder pattern were recorded on a vertical type Philips 1130/00 X-ray diffractometer, operated at 40 kVand 50 Ma generator using the Cu K α line at 1.54056 Å as the radiation sources. Sample was scanned between 10° and 70° (2θ) at 25 °C. The crystallographic data was analyzed by using the CRYSFIRE-2000 powder indexing software package and the space group was found by GSAS program. Debye-Scherer relation with the help of 100% peak width, determined the particle size. The density was determined by Archimedes method.

2.2. Synthesis of the ligand

2.2.1. 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 [10]. This was characterized by elemental analysis, infrared spectra, ¹H NMR spectra and mass spectra. Satisfactory results were obtained.

2.2.2. Synthesis of N', N''-bis(3-carboxy-1-oxoprop-2-enyl) 2-amino-N-arylbenzamidine $(C_{21}H_{17}N_3O_6)$ (L^1) (Fig. 1)

A finely ground mixture of 2-amino-*N*-arylbenzamidine (0.5 mmol), maleic 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, filtrate on slow evaporation forms fine crystals. This was recrystallized in acetic



Fig. 1. L¹.

acid, washed with ethanol and dried over P_4O_{10} in vacuo. Ligand is soluble in common polar solvents.

Light yellow crystal—Yield: 85%; Anal. Calc. for $C_{21}H_{17}N_3O_6$ requires (%): C, 61.91; H, 4.18; N, 10.32. Found: C, 61.48; H, 4.67; N, 10.41 (M_W : 407.4); FTIR (KBr, cm⁻¹): ν (O–H) 2601(w), ν (N–H)_{Amide} 3407(s), ν (C=O)_{Amide I} 1645(w), [ν (C–N)+ δ (N–H)]_{Amide II} 1413(s), ν [(N–H)+ δ (C–H)]_{Amide III} 1275, ν as(CO₂) 1568(s), ν s(CO₂) 1401(s); TOF-MS (m/z): 408 (12%, M]⁺), 348 (100%, C₁₉H₁₅N₃O₄]⁺), 185 (11%, C₁₂H₁₄N₂]⁺). ¹H NMR (ppm): 11.20 (2H, s, –OH carboxylic acid), 8.25 (2H, s, sec. amide), 7.50 (4H, m, benzylidenimin), 7.20 (5H, m, H-benzene), 1.81 (4H, d, –CH methyne group); electronic spectral data (cm⁻¹): 30,120 ($\pi \rightarrow \pi^*$, *N*-amide), 35,842 ($n \rightarrow n^*$, C=O group).

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

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 $C_{21}H_{21}N_3O_6$ requires (%): C, 61.31; H, 5.11; N, 10.21. Found: C, 61.18; H, 5.37; N, 10.29 (M_W : 411.4); FTIR (KBr, cm⁻¹): ν (O–H) 2600 (w), ν (N–H)_{Amide} 3369(s), ν (C=O)_{Amide I} 1650(w), [ν (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);TOF-MS (m/z): 412 (14%, M]⁺), 352 (100%, C₁₉H₁₉N₃O₄]⁺), 187 (11%, C₁₂H₁₄N₂]⁺). ¹H NMR (ppm): 11.30 (2H, s, –OH carboxylic



Fig. 2. L².



Fig. 3. L³.

acid), 8.15 (2H, s, sec. amide), 7.45 (4H, m, benzylidenimin), 7.35 (5H, m, H-benzene), 1.43 (8H, s, $-CH_2$ methylene group); electronic spectral data (cm⁻¹): 30,488 ($\pi \rightarrow \pi^*$, *N*-amide), 35,842 ($n \rightarrow n^*$, C=O group).

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

A finely ground mixture of 2-amino-*N*-arylbenzamidine (0.5 mmol), phthalic 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.

Light yellow crystal—Yield: 84%; Anal. Calc. for C₂₉H₂₁N₃O₆ requires (%): C, 68.64; H, 4.14; N, 8.28. Found: C, 68.60; H, 4.11; N, 8.25 (M_W : 507); FTIR (KBr, cm⁻¹): ν (O–H) 2602(w), ν (N–H)_{Amide} 3370(s), ν (C=O)_{Amide I} 1630(w), [ν (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); TOF-MS (m/z): 507 (15%, M]⁺), 449 (100%, C₂₇H₁₉N₃O₄]⁺), 329 (12%, C₂₀H₁₄N₃O₂]⁺), 236 (16%, C₁₄H₁₀N₃O]⁺; 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); Electronic spectral data (cm⁻¹): 31,447 ($\pi \rightarrow \pi^*$, *N*-Amide), 35,842 ($n \rightarrow n^*$, C=O group).

2.3. Synthesis of cobalt(II) complexes

2.3.1. Synthesis of cobalt(II)
N',N"-bis(3-carboxy-1-oxoprop-2-enyl)
2-amino-N-arylbenzamidine complex[C₂₁H₁₉N₃O₈Co]
[Complex I] (Fig. 4)

To a methanolic solution of $CoCl_2 \cdot 6H_2O$ (0.5 mmol) was added a methanolic solution of the ligand (L¹) (0.5 mmol). The resulting dark pink-colored solution was stirred for 3 h, after which the volume was reduced on a warm water bath. The dark pink 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 pink crystals of the complex.

Dark pink crystal—Yield: 80%; Anal. Calc. for $C_{21}H_{19}N_3O_8Co$ requires (%): C, 50.41; H, 3.80; N, 8.40; Co, 11.78. Found: C, 50.64; H, 4.00; N, 8.34 (M_W : 499.9); electronic spectral data (cm⁻¹): 16,393 [${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F)(\nu_2)$],



Fig. 4. Complex I.

19,380 [${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)(\nu_{3})$], 30,120 ($\pi \rightarrow \pi^{*}$, *N*-amide); μ_{eff} (BM): 4.82; FTIR (KBr, cm⁻¹): ν (N–H)_{Amide} 3420(s), ν (C=O)_{Amide I} 1635(w), [ν (C–N) + δ (N–H)]_{Amide II} 1460(s), ν [(N–H) + δ (C–H)]_{Amide III} 1296, ν_{as} (CO₂) 1574(s), ν_{s} (CO₂) 1406(s), ν (M–O) 372(m); TOF–MS (*m*/*z*): 500 (12%, M]⁺), 464 (8%, C₂₁H₁₅N₃O₆CO]⁺), 407 (6%, C₁₉H₁₃N₃O₄CO]⁺), 364 (35%, C₁₇H₁₂N₃O₃ CO]⁺), 305 (50%, C₁₇H₁₁N₃O₃]⁺, 236 (100%, C₁₄H₁₀N₃O]⁺, 222 (46%, C₁₄H₁₀N₂O]⁺;TG [Step I, Step II] *E** (J mol⁻¹): 68.81, 70.90; *A* (×10⁵ s⁻¹): 7.63, 5.23; ΔS^{*} (J K⁻¹ mol⁻¹): -133.64, -140.38; ΔH^{*} (J mol⁻¹): 104.90, 140.3 and ΔG^{*} (kJ mol⁻¹): 48.22, 78.19.

2.3.2. Synthesis of cobalt(II) N',N"-bis(3-carboxy-1-oxopropanyl)

2-amino-N-arylbenzamidine complex $(C_{21}H_{23}N_3O_8C_0)$ [Complex II] (Fig. 5)

To a methanolic solution of $CoCl_2 \cdot 6H_2O$ (0.5 mmol) was added a methanolic solution of the ligand (L²) (0.5 mmol). The resulting dark brown-colored solution was stirred for 3 h, after which the volume was reduced on a warm water bath. The dark brown 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 brown crystals of the complex.

Dark brown crystal—Yield: 85%; Anal. Calc. for $C_{21}H_{23}N_3O_8Co$ requires (%): C, 50.01; H, 4.56; N, 8.33; Co, 11.69. Found: C, 50.23; H, 4.67; N, 8.39; Co, 11.71 (M_W : 503.9); Electronic spectral data (cm⁻¹): 15,600 [${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F)(\nu_2)$], 20,408 [${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)(\nu_3)$], 30,488 ($\pi \rightarrow \pi^*$, *N*-amide), 34,965 ($n \rightarrow n^*$, C=O group); μ_{eff} (BM): 5.01; FTIR (KBr, cm⁻¹): ν (N–H)_{Amide} 3434(s), ν (C=O)_{Amide I} 1640(w), [ν (C–N) + δ (N–H)]_{Amide II} 1425(s), ν [(N–H) + δ (C–H)]_{Amide III} 1320, ν_{as} (CO₂) 1563(s), ν_s (CO₂)



Fig. 5. Complex II.



Fig. 6. Complex III.

1408(s), ν (M–O) 365 (m); TOF-MS (*m*/*z*): 504 (10%, M]⁺), 468 (6%, C₂₁H₁₉N₃O₆Co]⁺), 292 (100%, C₁₆H₁₀N₃O₃]⁺), 246 (56%, C₁₅H₈N₃O]⁺), 220 (40%, C₁₄H₈N₂O]⁺ TG [Step I, Step II] *E*^{*} (J mol⁻¹): 35.04, 38.23; *A* (×10⁵ s⁻¹): 1.74, 1.32; ΔS^* (J K⁻¹ mol⁻¹): -146.34, -152.27; ΔH^* (J mol⁻¹): 100.75, 142.78 and ΔG^* (kJ mol⁻¹): 55.56, 90.80.

2.3.3. Synthesis of cobalt(II)
N',N''-bis(3-carboxy-1-oxophenelenyl)
2-amino-N-arylbenzamidine complex (C₂₉H₂₃N₃O₈Co)
[Complex III] (Fig. 6)

To a methanolic solution of $CoCl_2 \cdot 6H_2O$ (0.5 mmol) was added a methanolic solution of the ligand (L³) (0.5 mmol). The resulting dark brown-colored solution was stirred for 3 h, after which the volume was reduced on a warm water bath. The dark brown 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 brown crystals of the complex.

Dark brown crystal—Yield: 79%; Anal. Calc. for $C_{29}H_{23}N_3O_8Co$ requires (%): C, 58.01; H, 3.91; N, 7.00; Co, 9.82. Found: C, 58.13; H, 3.99; N, 7.06; Co, 9.92 (M_W : 599.9); electronic spectral data (cm⁻¹): 15,898 [${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F)(\nu_2)$], 19,646 [${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)(\nu_3)$], 31,447 ($\pi \rightarrow \pi^*$, *N*-amide); μ_{eff} (BM): 4.95; FTIR (KBr, cm⁻¹): ν (N–H)_{Amide} 3396(s), ν (C=O)_{Amide I} 1610(w), [ν (C–N) + δ (N–H)]_{Amide II} 1493(s), ν [(N–H) + δ (C–H)]_{Amide III} 1338, ν_{as} (CO₂) 1559(s), ν_{s} (CO₂) 1409(s), ν (M–O) 380 (m); TOF-MS (m/z): 601 (12%, M]⁺), 564 (8%, C₂₉H₁₉N₃O₆Co]⁺), 292 (89%, C₁₆H₁₀N₃O₃]⁺), 236 (100%, C₁₄H₁₀N₃O]⁺), 222 (47%, C₁₄H₁₀N₂O]⁺. TG [Step I, Step II]: E^* (J mol⁻¹): 32.77, 35.04; A (×10⁵ s⁻¹): 1.81, 1.39; ΔS^* (J K⁻¹ mol⁻¹): -146.10, -151.62; ΔH^* (J mol⁻¹): 148.80, 76.54 and ΔG^* (kJ mol⁻¹): 56.03, 86.80.

3. Results and discussion

Satisfactory results of elemental analysis and spectral studies revealed that the ligands and complexes were of good purity.

3.1. TOF-MS

Mass spectrometry has been successfully used to investigate molecular species in solution [11,12]. The molecular ion peaks of the ligands and complexes have been used to confirm the pro-

posed formula. All three ligands have similar tendency of initial loss of two molecules of HC=O]⁺ with 100% m/z values. Ligands $(L^1 \text{ and } L^2)$ seem to be almost of similar trend of degradation and finally forms two molecules of $C_6H_5NH_2$ ⁺, whereas ligand (L³) finally degrades to amidine]⁺. In the spectra of $Co(L^1)2H_2O$, $Co(L^2)2H_2O$, and $Co(L^3)2H_2O$ initial fragmentation pattern is again similar (loss of two water molecules), a mononuclear nature for these complexes can be deduced. The selected range of m/z for the spectrum of complexes allows the observation of $[Co(L)]^+$ and 100% 236 m/z species $[C_{14}H_{10}N_3O]^+$. A conclusive proof of a strict attribution of these signals is shown in (Fig. 7: TOF-MS spectra of Complex I), where the isotopic profile observed at 236/238 in the spectrum is in good agreement with that calculated for $[C_{14}H_{12}N_3O]^+$ species, which could be the result of demetallation and subsequently a partial intra molecular hydrogen bonding. Likewise peaks attributable to unstable monomeric species as $[Co(L)]^+$ and $[H_2L]^+$ are usually present in the mass spectra of these systems [13,14].

3.2. IR spectra and mode of bonding

An ambidentate nature of the amide can coordinate with cobalt(II) either through nitrogen of the-NH₂ or the oxygen of the C=O group. The bands due to the amide ν (N-H) mode at 3200–3400 cm⁻¹ for the free ligands L_1 , L_2 and L_3 are shifted towards higher frequencies, while the ν (C=O) (amide I) frequency $(1630-1650 \text{ cm}^{-1})$ undergoes shift towards lower frequency $(1600-1640 \text{ cm}^{-1})$ in the cobalt complexes indicating non-involvement of the amide nitrogen and involvement of the carbonyl oxygen atom of amide group in coordination with the metal ion [15] (Fig. 8a and b). 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 [16,17]. 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 (1410–1480 cm^{-1} in ligands) and Amide III (1275–1305 cm⁻¹ in ligands) bands arising out of ν (C–N) as well as δ (N–H) modes (coupled to one another), shift towards higher frequencies $1430-1530 \text{ cm}^{-1}$ and $1295-1340 \text{ cm}^{-1}$, respectively, in complexes further confirming the coordination through carbonyl oxygen. 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 $v_{\rm s}({\rm CO_2}^-)$ 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 [18,19]. Here Δv implies the difference between $v_{as}(CO_2^{-})$ and $v_{\rm s}({\rm CO}_2^-)$ (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 $800-350 \text{ cm}^{-1}$ region for all the complexes of all the ligands and may be attributed to coordinated water in



Fig. 7. TOF-MS spectrum of Complex I.

all the complexes [18]. This can be confirmed with the help of thermograms. A new band in the 390–360 cm⁻¹ regions in the spectra of the complexes is assignable to ν (Co–O) [20].

3.3. Magnetic susceptibility measurement and electronic spectra

The magnetic susceptibility measurements were carried out in the solid state at 298 K. The magnetic moment (μ_{eff}) value of the complexes lie in the range of 4.7–5.2 BM, which is in agreement with high-spin state of Co(II) and middle in strength crystal field [21]. The electronic spectra of the ligands and its cobalt complexes have been studied in the range 200-900 nm. In the UV region, 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 286 nm in case of Complex II, while it disappeared in the Complexes I and III revealing the involvement of the C=O of amide group or carboxylate oxygen in chelate formation. The band observed at 332, 328 and 318 nm in ligands L^1 , L^2 and L^3 , 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 cobalt complexes, indicating they are not affected by metal chelation [22]. In the visible absorption spectra of complexes (Fig. 9a and b), two bands in the range of 15,475-16,500 and 20,900-21,300 cm⁻¹ were observed. The first one is attributed to d-d transition and the second one to O (σ) \rightarrow Co(II) transition. Assuming an octahedral coordination for Co(II) complexes, three spin allowed transitions are expected: ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{2g}({}^{4}F) (\nu_{1}), {}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}A_{2g}({}^{4}F) (\nu_{2}),$ ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P) (\nu_{3}).$ The first band appeared in the region $8080-8650 \text{ cm}^{-1}$ usually in the IR region, so v_1 transition due to

transition ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{2g}({}^{4}F)$ could not be observed in all the complexes. The second transition is two-electronic process and therefore its bands are with low-intensity. The broad band with maximum at 21,250 cm⁻¹ corresponds to the highest energy ${}^{4}T_{1g}({}^{4}F) \rightarrow {}^{4}T_{1g}({}^{4}P)$ (ν_{3}) transition.

3.4. Kinetics of thermal decomposition

Recently, there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves [23,24]. Thermogravimetric (TG) and differential thermogravimetric (DTA) analyses were carried out for Co(II)-amide complexes in ambient conditions (Fig. 10). The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formula of the complexes.

The Complex I with the molecular formula $[C_{21}H_{19}N_3O_8C_0]$ is thermally decomposed in two successive decomposition steps. The first estimated mass loss of 7.40% (calculated mass loss = 7.20%) within the temperature range 349–413 K may be attributed to the loss of two water molecules. The DTA curve gives an endothermic peak at 360 K (the maximum peak temperature). The second step occurs within the temperature range 540–593 K with the estimated mass loss 45.01% (calculated mass loss = 44.65%) which corresponds to the loss of organic moiety leaving CoO and Co₃O₄ as residue. The DTA curve gives an exothermic peak at 556 K (the maximum peak temperature). Total estimated mass loss is 52.41% (calculated mass loss = 51.85%).

The thermal decomposition of Complex II with the molecular formula $[C_{21}H_{23}N_3O_8C_0]$ proceeds with two main degrada-



Fig. 8. (a) IR spectrum of Complex II. (b) IR spectrum of Complex III.

tion steps. The first step occurs within the temperature range 365-421 K with an estimated mass loss 7.10% (calculated mass loss = 7.14%) which is reasonably accounted for the loss of two water molecules. The DTA curve gives an endothermic peak at 379 K (the maximum peak temperature). The second step occurs within the temperature range 570-684 K with an estimated mass loss 44.40% (calculated mass loss = 45.10%), which is reasonably accounted for the loss of organic moiety, leaving CoO and Co₃O₄ as residue. The DTA curve gives an exothermic peak at

595 K (the maximum peak temperature). Total estimated mass loss is 51.50% (calculated mass loss = 52.24%).

The thermal decomposition of Complex III with the molecular formula $[C_{29}H_{23}N_3O_8Co]$ also proceeds with two main degradation steps. The first estimated mass loss of 6.05% (calculated mass loss = 6.00%) within the temperature range 360–403 K could be attributed to the liberation of two water molecules. The DTA curve gives an endothermic peak at 383 K (the maximum peak temperature). The second step occurs within



Fig. 9. (a) Electronic spectra of Complexes I and II. (b) Electronic spectra of Complex III.

the temperature range 563–691 K with an estimated mass loss 53.55% (calculated mass loss = 53.88%), which is reasonably accounted for the decomposition of organic moiety leaving CoO and Co_3O_4 as residue. The DTA curve gives an exothermic peak at 572 K (the maximum peak temperature). Total estimated mass loss is 59.60% (calculated mass loss = 59.88%).

The final product of decomposition at 878 K corresponds to the formation of CoO and Co_3O_4 as the end product, which was confirmed by comparing the observed/estimated and the calculated mass of the pyrolysis product [25].

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 [26] (1):

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{\theta E^*}\left(\frac{1-2RT}{E^*}\right)\right] -\frac{E}{2.303RT}$$
(1)



Fig. 10. Thermograms of complexes.

where α is the mass loss up to the temperature *T*, *R* the gas constant, *E** the activation energy in J mol⁻¹, θ the linear heating rate and the term $(1 - 2RT/E^*) \cong 1$. A straight line plot of left hand side of Eq. (1) against 1/T gives the value of *E** while its intercept corresponds to *A* (Arrhenius constant). The linearization plots (Fig. 11a–c), 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 experi-



Fig. 11. Linearization plot of complexes.

Empirical formula	$C_{21}H_{17}N_3O_6~(L^1)$	$C_{21}H_{21}N_3O_6 (L^2)$	$C_{29}H_{21}N_{3}O_{6}\ (L^{3})$
Formula weight	407.4	411.4	507.5
Temperature (K)	298	298	298
Wavelength (Å)	1.54056	1.54056	1.54056
Crystal system	Tetragonal	Triclinic	Tetragonal
Space group	P_{422}	P_1	P_{422}
Unit cell dimensions (Å)	a = 10.253400, b = 10.253400,	<i>a</i> = 7.089918, <i>b</i> = 8.763797, <i>c</i> = 12.380810,	a = 12.240700, b = 12.240700,
	$c = 12.78373, \alpha = \beta = \gamma = 90^{\circ}$	$\alpha = 69.31414^{\circ}, \beta = 72.2477^{\circ}, \gamma = 104.1482^{\circ}$	$c = 20.354620, \alpha = \beta = \gamma = 90^{\circ}$
Volume (A^3)	1343.98	628.12	3049.86
2θ range	$10 - 70^{\circ}$	$10-70^{\circ}$	$10-70^{\circ}$
Limiting indices	$0 \le h \le 5$	$-4 \le h \le 4$	$0 \le h \le 4$
	$0 \le k \le 4$	$-4 \leq k \leq 4$	$0 \le k \le 4$
	$0 \le l \le 7$	$0 \le \le 7$	$0 \le 1 \le 9$
Density (g/cm ³)	1.005	1.086	1.104
Ζ	2	1	4
Avs. Eps	0.0000537	0.0000685	0.000089
Merit of fitness	M(7) = 15, F(7) = 4	M(22) = 4, F(22) = 3	M(20) = 6, F(20) = 8
Particle size (nm)	0.932	0.8036	13.873

Table 1 Crystallographic data of ligands

Table 2

Crystallographic data of cobalt(II) complexes

Empirical formula	$C_{21}H_{19}N_3O_8$ Co (Complex I)	$C_{21}H_{23}N_3O_8Co$ (Complex II)	C ₂₉ H ₂₃ N ₃ O ₈ Co (Complex III)
Formula weight	499.9	503.9	599.9
Temperature (K)	298	298	298
Wavelength (Å)	1.54056	1.54056	1.54056
Crystal system	Cubic	Hexagonal	Tetragonal
Space group	P_{432}	P _{6/mmm}	P_{422}
Unit cell dimensions (Å)	<i>a</i> =4.861712, <i>b</i> =4.861712,	a = 17.445040, b = 17.445040, c = 9.833171,	<i>a</i> = 9.419596, <i>b</i> = 9.419596,
	$c = 9.499986, \alpha = \beta = \gamma = 90^{\circ}$	$\alpha = 90^\circ, \ \beta = 90^\circ, \ \gamma = 120^\circ$	$c = 19.160880, \alpha = \beta = \gamma = 90^{\circ}$
Volume (A ³)	224.54	2591.59	1698.32
2θ range	$10-70^{\circ}$	$10-70^{\circ}$	$10-70^{\circ}$
Limiting indices	$1 \le h \le 3, 0 \le k \le 2, 0 \le l \le 3$	$0 \le h \le 10, 0 \le k \le 3, 0 \le l \le 6$	$0 \le h \le 5, 0 \le k \le 4, 0 \le l \le 9$
Density (g/cm ³)	1.66	1.29	1.173
Ζ	1	4	2
Avs. Eps	0.0000101	0.0000512	0.0000723
Merit of fitness	M(6) = 37, F(6) = 10	M(10) = 13, F(10) = 4	M(8) = 10, F(8) = 3
Particle size (nm)	2.684	10.292	13.78

mental section. 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 III < Complex II < Complex I, same trends happens with thermal stability of metal complexes. It is probably because of increase in bulkiness in ligand molecule from L^1 to L^3 . 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 [27].

3.5. X-ray powder diffraction studies

X-ray powder data is especially useful to deduce accurate cell parameters. The diffraction pattern reveals the crystalline nature

of the complex. The indexing procedures were performed using (CCP₄, UK) Crysfire programme [28] giving different crystal system with varying space group. The merit of fitness and particle size of ligands and its cobalt complexes has been calculated. The cell parameters of the ligands and complexes are shown in Tables 1 and 2, respectively.

4. Conclusion

Cobalt(II) complexes were found to be monomer and involved coordination through carboxylate oxygen of the amide ligands along with two water molecules giving octahedral geometry. Vibrational spectra indicate the presence of H_2O molecule in the complexes that has been supported by TG/DTA. Kinetic parameter shows that the decomposition follows first-order kinetics and proceeds in two-step decomposition. The thermal behaviour of complexes shows that water molecule is removed in first step—followed by decomposition of the ligand molecule in the second step. Magnetic susceptibility measurements and electronic spectra also support octahedral coordination geometry around the Cobalt(II) ions. The complex crystallizes in the cubic/hexagonal/tetragonal crystal system.

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