Chapter IX

Lewis-base modulated coordination polymers
derived from metal(II) 1,3,5-benzenetricarboxylates

Abstract: As a continuation of our studies on metal isophthalates and their Lewis-base derivatives we considered the case of 1,3,5-benzenetricarboxylic acid (H$_3$btc) as an extended analogue of isophthalic acid (1,3-benzenedicarboxylic acid). As in the previous cases we attempted to synthesize new Lewis-base incorporated ternary type coordination polymers of various metal-btc compounds. We employed only monodentate or chelating type Lewis-bases for our study with the intention of getting low-dimensional coordination polymers rather than three-dimensional frameworks. Several new derivatives could be isolated in phase pure form through one pot synthesis in aqueous medium which included [Co$_3$(btc)$_2$(dap)$_6$]$n$.18nH$_2$O 45, [Ni$_3$(btc)$_2$(dap)$_9$(H$_2$O)$_9$]$n$.6nH$_2$O 46, [Cu$_3$(btc)$_2$(dap)$_9$(H$_2$O)$_9$]$n$.12nH$_2$O 47, [Zn$_3$(btc)$_2$(dap)$_9$(H$_2$O)$_9$]$n$.12nH$_2$O 48, [Cu(Hbtc)(en)(H$_2$O)]$n$ 49, [Zn(Hbtc)(en)$_3$]$_n$.9nH$_2$O 50, [Co$_3$(btc)$_2$(im)$_9$(H$_2$O)$_9$]$n$.12nH$_2$O 51, [Ni$_3$(btc)$_2$(im)$_9$(H$_2$O)$_9$]$n$.9nH$_2$O 52, [Cu$_3$(btc)$_2$(bipy)$_3$(H$_2$O)$_9$]$n$.9nH$_2$O 53 and [Zn$_3$(btc)$_2$(bipy)$_3$(H$_2$O)$_9$]$n$.9nH$_2$O 54. While in 49 and 50 the H$_3$btc acts like an isophthalate analogue by deprotonating only two -COOH units, in the rest of the compounds H$_3$btc behaves as a tricarboxylic acid through deprotonation and coordination through all the carboxylate moieties. Based on analytical, spectral (FTIR, UV-vis and EPR), magnetic and thermal analysis we were able to propose some tentative structures for all the compounds. SEM analysis showed different textural and morphological features for all the compounds. The details are discussed.
**9.1 Introduction**

Even though the focus of our thesis has been on developing coordination polymers of benzenedicarboxylates we thought it would be worthwhile to look at the role of additional –COOH groups on the benzene moiety of the benzenedicarboxylic acids on the overall properties of the resulting coordination polymers. In this connection we have considered two polycarboxylic acids, 1,3,5-benzenetricarboxylic acid (H$_3$btc) and 1,2,4,5-benzenetetracarboxylic acid (H$_4$pm). The benzenetricarboxylic acid can be considered as a ‘higher analogue’ of isophthalic acid because positions of all the three –COOH groups are ‘meta’ to each other. However, compared to isophthalic acid which generally prefers to form mainly low-dimensional coordination polymers H$_3$btc is known to generate mostly higher-dimensional coordination polymers and frameworks. Symmetrically disposed H$_3$btc molecules posses interesting features that are conducive to the formation of versatile coordination structures. Firstly the multicarboxylate groups on the molecule may be completely or partially deprotonated. Secondly the carboxylate groups may not lie coplanar with the aromatic ring upon coordination to metal ions and as a result the btc moieties may act as an excellent connector species by ligating to metal ions in different directions generating mostly three-dimensional architectures. In addition it can act not only as hydrogen bond acceptor but also as hydrogen bond donor depending on the number of deprotonated carboxylic groups. Also the high symmetry that the molecule exhibits may be helpful for generating more structured compounds with pores and cavities which are of appreciable size. A wide variety of metal-btc compounds with composition M$_3$(btc)$_2$ have
been reported which are known to exhibit interesting functional properties. However, not many ternary systems containing auxiliary ligands are seen to be reported for $\text{M}_3(\text{btc})_2$. While $\text{M(II)}$-$\text{btc}$ derivatives themselves can take up diverse structural features incorporation of auxiliary ligand can bring about substantial structural tuning which would be very relevant for the many functional applications. The work embodied in the present chapter was taken up mainly because of the relatively less number of reports available on such systems.

As a continuation of our studies on developing structurally and electronically modulated Lewis-base incorporated metal-benzenedicarboxylates we have attempted to generate a series of metal-$\text{btc}$-Lewis-base ternary systems by employing diverse N-bases. We have chosen only chelating and monodentate ligands mainly because of their ability to generate low-dimensional coordination polymers from higher-dimensional/framework systems. Given in Scheme 9.1 are the N-bases employed by us for the generation of $\text{M(II)}$-$\text{btc}$-Lewis-base ternary systems.

\begin{center}
\begin{tabular}{ccc}
\text{dap} & \text{en} & \text{im} & \text{bipy} \\
\end{tabular}
\end{center}

\textbf{Scheme 9.1} N-bases employed in the synthesis of $\text{M(II)}$-$\text{btc}$-Lewis-base ternary systems
9.2 Experimental

**Preparation of [Co₃(C₆H₃(COO)₃]₂(NH₂-(CH₂)₃-NH₂)₆]₁₈nH₂O 45**

To a warm methanolic solution of cobalt chloride (5 mM, 20 mL), solution of dap in methanol (10 mM, 10 mL) was added slowly with constant stirring. The reaction mixture was kept warm for 15 minutes and a methanolic solution of H₃btc (3.33 mM, 10 mL) was added. The solution was kept warm for 10 minutes more and filtered. The filtrate on keeping undisturbed developed pink coloured compound after three days. The solid was collected, washed with methanol and dried in air. (yield : 60%)

**Preparation of [Ni₃(C₆H₃(COO)₃]₂(NH₂-(CH₂)₃-NH₂)₈(H₂O)₆]₆nH₂O 46**

Nickel chloride dissolved in water (5 mM, 10 mL) was warmed and mixed with an aqueous solution of dap (10 mM, 10 mL). Then a solution of H₃btc in methanol (3.33 mM, 10 mL) was added and kept stirred for some more time. The solution was filtered and kept undisturbed for a few days. The filtrate developed a blue crystalline solid after two days. The solid compound was dried in air after washing with water. (yield : 60%)

**Preparation of [Cu₃(C₆H₃(COO)₃]₂(NH₂-(CH₂)₃-NH₂)₁₅(H₂O)₉]₉₄ 47**

Solution of copper acetate in water (5 mM, 15 mL) was allowed to react with aqueous solution of dap (10 mM, 10 mL) under warm condition. The resulting solution was mixed with a solution of H₃btc in a mixture of water and methanol (3.33 mM, 10 mL). A blue coloured solid appeared immediately. The compound was dried in air after washing with water. The filtrate, slightly blue coloured did not develop any crystals on keeping for a long period. Yield : 65%)
Preparation of $[Zn_3(C_6H_3(COO)_3)_2(NH_2-(CH_2)_3-NH_2)_3(H_2O)_6]_n$ 48

Warm zinc acetate solution in water (5 mM, 15 mL) was mixed with a solution of dap in water (10 mM, 10 mL) with constant stirring. A solid complex appeared and on addition of a solution of H$_3$btc in a mixture of water and methanol (3.33 mM, 10 mL) developed the appearance of a gel. Heated for some more time and filtered. The solid residue was dried in air after washing with water. (yield : 65%)

Preparation of $[Cu(HOOC_6H_3(COO))_2(NH_2-(CH_2)_2-NH_2)_2H_2O]_n$ 49

Copper acetate solution in water (5 mM, 15 mL) was made to react with aqueous solution of en (10 mM, 10 mL). The complex formation was indicated by a change of colour to deep blue. Then a solution of H$_3$btc in a mixture of water and methanol (3.33 mM, 10 mL) was added with constant stirring under warm conditions. The solution was filtered and the filtrate developed blue crystalline powder after a half an hour. The solid was washed with water and dried in air. (yield : 60%)

Preparation of $[Zn(HOOC_6H_3(COO))_2(NH_2-(CH_2)_3-NH_2)_2]_nH_2O$ 50

Zinc acetate was dissolved in water (5 mM, 15 mL) and warmed on a water bath. Then solution of en in water (10 mM, 10 mL) was added with constant stirring. Solid complex appeared and dissolved on the addition of H$_3$btc solution (3.33 mM, 10 mL) in a mixture of water and methanol. A colourless powder appeared in a few minutes. The solid was collected, washed with water and dried in air after. (yield : 60%)

Preparation of $[Co_3(C_6H_3(COO))_3_(C_3H_4N_2)_3(H_2O)_6]_n$ 51

A warm solution of cobalt nitrate in water (5 mM, 10 mL) was treated with a solution of im (20 mM, 15 mL) in water. A solid complex appeared
and it disappeared on addition of H$_3$btc solution in a mixture of water and methanol (3.33 mM, 10 mL). The solution was filtered and kept undisturbed after concentration. Pink crystals were obtained after seven days. (yield: 65%)

*Preparation of [Ni$_3$(C$_6$H$_3$(COO)$_3$)$_2$(C$_3$H$_4$N$_2$)$_4$(H$_2$O)$_3$]$n$ 52*

Nickel carbonate was dispersed in water (5 mM, 15 mL) and warmed on a water bath. To the warm aqueous solution of nickel carbonate, solution of im in water (20 mM, 10 mL) was added and kept stirred for half an hour. The nickel-im complex was then treated with solid H$_3$btc (3.33 mM). The acid reacted with effervescence and then filtered. The filtrate after concentration on keeping for five days developed blue crystalline complex. (yield : 60%)

*Preparation of [Cu$_3$(C$_6$H$_3$(COO)$_3$)$_2$(C$_3$H$_4$N$_2$)$_{12}$]$n$.12nH$_2$O 53*

A warm aqueous solution of copper acetate (2.5 mM, 10 mL) was warmed and treated with aqueous solution of im (10 mM, 5 mL). The deep blue solution thus obtained was treated with H$_3$btc solution in a mixture of water and methanol (1.66 mM, 5 mL). Initially there was a solid separation, but gradually the solid disappeared and a clear solution was obtained. The solution was filtered and concentrated. The concentrated solution developed blue compound on keeping undisturbed overnight. (yield : 65%)

*Preparation of [Zn$_3$(C$_6$H$_3$(COO)$_3$)$_2$(C$_{10}$H$_8$N$_2$)$_3$(H$_2$O)$_6$]$n$.9nH$_2$O 54*

Zinc acetate was dissolved in water (2.5 mM, 10 mL) and warmed which was then treated with a solution of H$_3$btc in a mixture of water and methanol (1.66 mM, 5 mL). The solid zinc-btc complex was allowed to
react with a methanolic solution of bipy (5 mM, 10 mL). The solid complex disappeared and a clear solution was obtained. The solution was filtered and kept undisturbed after concentration. The concentrated solution developed crystals after 24 hours. (yield : 65%)

9.3 Results and discussion

One of the main reasons for considering H$_3$btc in our studies is because it can be taken as an extended analogue of isophthalic acid. As we have seen, while isophthalate has tendency to form mainly low-dimensional coordination polymers on reacting with various metal salts the additional –COOH groups present in H$_3$btc might, therefore, will have ability to generate coordination polymers/frameworks of higher dimension by linking with neighboring metal centers. Even though there are diverse carboxylate specific linking modes for btc ligand the most common forms of linking seen in metal-btc derivatives are as shown in Scheme 9.2 (b, c, d). The overall structural and topological features of the resulting coordination polymers/frameworks are quite different and depend on the type of the ligation mode of btc moiety. As an extension of our work presented in previous three chapters we have attempted to develop some new Lewis-base modulated metal-btc derivatives and study their structural and electronic features. We have considered either chelating or monodentate type N-bases for developing the ternary systems mainly because the resulting coordination polymers can be of lower dimension. Our preparative method involved mainly reacting metal salt, H$_3$btc and Lewis-bases in aqueous or methanol solution under ordinary conditions. Sometimes varying extents of Lewis-bases had been employed with a view to develop new types of ternary systems. However, it was
seen that only one type of ternary compound is getting formed. Care was taken to isolate all the compounds in phase pure form by controlling the reaction or by repeated crystallization. Even though all the products were crystalline materials we were not able to separate any good quality crystals for single crystal X-ray diffraction. The composition of all the pure ternary type compounds could be obtained by elemental analysis and the amount of water content in them (either ligated or guests) by TG analysis. Presented in Table 9.1 are the various products and their elemental analytical data. All the compounds showed data that are matching with the composition given in Table 9.1

**Scheme 9.2** Structure of H$_3$btc and bonding modes of btc
Table 9.1 Analytical data of the btc complexes

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<th>Complex</th>
<th>Formula Weight/ colour</th>
<th>Elemental % obs (cal)</th>
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<td>C</td>
</tr>
<tr>
<td>[Co(_3)(C_6H_3(COO))(_3)]_2((NH_2-(CH_2)_3-NH_2))_n(18nH_2O)</td>
<td>452.93 (pink)</td>
<td>31.60 (31.79)</td>
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<td>[Ni(_3)(C_6H_3(COO))(_3)]_2((NH_2-(CH_2)_3-NH_2))_n(6nH_2O)</td>
<td>1028.07 (blue)</td>
<td>31.96 (31.51)</td>
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<tr>
<td>[Cu(_3)(C_6H_3(COO))(_3)]_2((NH_2-(CH_2)_3-NH_2))_n(3(H_2O))</td>
<td>877.62 (blue)</td>
<td>30.31 (30.76)</td>
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<td>[Zn(_3)(C_6H_3(COO))(_3)]_2((NH_2-(CH_2)_3-NH_2))_n(9nH_2O)</td>
<td>940.17 (colourless)</td>
<td>33.95 (34.46)</td>
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<tr>
<td>[Cu{HOOCC(_6H_3(COO))}_2((NH_2-(CH_2)_3-NH_2))_n(3(H_2O))</td>
<td>349.54 (blue)</td>
<td>38.05 (37.76)</td>
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<tr>
<td>[Zn{HOOCC(_6H_3(COO))}_2((NH_2-(CH_2)_3-NH_2))_n(9nH_2O)</td>
<td>351.39 (colourless)</td>
<td>37.01 (37.56)</td>
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<tr>
<td>[Co(_3)(C_6H_3(COO))(_3)]_2(C_3H_4N_2)(3(H_2O))_n\</td>
<td>957.03 (pink)</td>
<td>34.31 (33.85)</td>
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<td>[Ni(_3)(C_6H_3(COO))(_3)]_2(C_6H_4N_2)(3(H_2O))_n\</td>
<td>1256.79 (blue)</td>
<td>42.01 (42.96)</td>
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<tr>
<td>[Cu(_3)(C_6H_3(COO))(_3)]_2(C_6H_4N_2)(12nH_2O)</td>
<td>1637.58 (blue)</td>
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<td>[Zn(_3)(C_6H_3(COO))(_3)]_2(C_10H_8N_2)(9nH_2O)</td>
<td>1348.74 (colourless)</td>
<td>41.99 (42.70)</td>
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</table>
9.3.1 Infrared spectra

**Table 9.2** IR spectral data of the btc compounds (cm⁻¹)

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<th>Assignments</th>
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<th>47</th>
<th>48</th>
<th>49</th>
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<th>51</th>
<th>52</th>
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<td>νNH₂</td>
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<td>νC=C</td>
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<tr>
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The presence of the Lewis-bases and the bonding mode of the carboxylate functions in the metal-organic coordination networks were confirmed by their characteristic peaks in the IR spectra. The relevant IR absorption frequencies of the metal(II) coordination networks are presented in Table 9.2. The asymmetric and symmetric stretching vibrations of the NH₂ group in 45 were observed at 3201 and 3101 cm⁻¹ respectively. The bending mode (δNH₂) was seen at 1620 cm⁻¹. The
presence of guest water molecules in the compound is indicated by the high energy band at 3417 cm\(^{-1}\). The bands at 1558 and 1346 cm\(^{-1}\) are assigned to \(\nu_{\text{as}}\text{COO}^-\) and \(\nu_{\text{s}}\text{COO}^-\) of the carboxylate group of the btc moiety. The \(\Delta\nu\) value of 212 cm\(^{-1}\) confirms the unidentate behavior of the carboxylate function.\(^{219}\) The IR spectrum of the Ni(II) compound \(46\) having the same secondary ligand shows similar features. \(\nu_{\text{as}}\text{COO}^-\) and \(\nu_{\text{s}}\text{COO}^-\) of the carboxylate group of the btc moiety are observed at 1550 and 1365 cm\(^{-1}\) respectively. The corresponding \(\Delta\nu\) value of 185 cm\(^{-1}\) clearly indicates the monodentate behavior of the carboxylate group. The peaks at 3317 and 3247 cm\(^{-1}\) indicates that the compound \(46\) consists of both coordinated and uncoordinated water molecules. The \(\text{NH}_2\) stretching vibrations appear at 3170 and 3074 cm\(^{-1}\) while the bending mode is seen at 1620 cm\(^{-1}\).

Compound \(47\), the Cu(II) analogue of \(46\) also consists of water molecules, but only in the coordinated manner. The stretching vibration of the coordinated water molecule is seen at 3313 cm\(^{-1}\). The asymmetric and symmetric stretching vibrations of the carboxylate group are observed at 1566 and 1365 cm\(^{-1}\) respectively with a \(\Delta\nu\) value of 201 cm\(^{-1}\) confirming the monodentate behavior of the carboxylate function. The stretching vibrations of the \(\text{NH}_2\) group appear at 3274 and 3160 cm\(^{-1}\) whereas the bending mode is seen at 1623 cm\(^{-1}\). Compound \(48\) also exhibits peaks characteristic of the auxiliary ligands as well as the carboxylate function and coordinated water molecules. The peak at 3298 cm\(^{-1}\) is characteristic of coordinated water molecules. \(\nu_{\text{as}}\text{COO}^-\) and \(\nu_{\text{s}}\text{COO}^-\) frequencies are respectively 1531 and 1365 cm\(^{-1}\). The corresponding \(\Delta\nu\) value is 166 cm\(^{-1}\).
While the NH$_2$ stretching frequencies appear at 3209 and 3132 cm$^{-1}$ the $\delta$NH$_2$ vibration is seen at 1612 cm$^{-1}$.

Compounds 49 and 50 consist of en as the auxiliary ligand and exhibit peaks characteristic of the primary amine. In addition to the presence of water either in the coordinated or uncoordinated form the compounds exhibit vOH stretching of the non-deprotonated carboxyl group. vOH stretching of the carboxyl groups of 49 and 50 appear at 3001 and 2974 cm$^{-1}$ respectively. The peaks have been assigned by comparing with that of H$_3$btc. vOH of H$_3$btc appears at 3001 cm$^{-1}$. The shift of vOH frequency of 50 to lower wave number may be due to H-bonding. The stretching frequencies of the water molecules in 49 appear at 3278 cm$^{-1}$ while that of 50 is seen at 3300 cm$^{-1}$. The vibration is observed at comparatively high energy in 50 as the water molecules remain uncoordinated in it. The NH$_2$ vibrations of 49 is exhibited at 3228 and 3151 cm$^{-1}$ and the bending mode appears at 1612 cm$^{-1}$. These frequencies are 3200, 3055 and 1608 cm$^{-1}$ respectively for 50. $\nu_{as}$COO$^-$, $\nu_{s}$COO$^-$ and $\Delta$v for 49 are 1558, 1361 and 197 cm$^{-1}$ respectively while in the FTIR spectrum of 50 they appear at 1539, 1357 and 182 cm$^{-1}$ respectively. The $\Delta$v values are consistent with monodentate coordination (197 cm$^{-1}$ for 49 and 182 cm$^{-1}$ for 50).

Compounds 51, 52 and 53 have im as the auxiliary ligand. 51 and 52 contain coordinated water molecules indicated by the peaks at 3220 and 3182 cm$^{-1}$ respectively. The water molecule present in the complex 53 exhibit the vibration at a comparatively higher frequency and is seen at 3282 cm$^{-1}$ and indicates that it is present in the lattice. While vNH vibrations of 51 appear at 3139 and 3060 cm$^{-1}$ that of 52 are observed at
3058 and 2950 cm\(^{-1}\) whereas 53 exhibit them at 3178 and 3128 cm\(^{-1}\). Carboxylate stretching frequencies of 51 are seen at 1542 and 1361 cm\(^{-1}\) with \(\Delta\nu\) 181 cm\(^{-1}\). The same frequencies for 52 appear almost in the same range and are seen at 1542, 1357 and 185 cm\(^{-1}\). The corresponding frequencies for 53 are 1554, 1353 and 201 cm\(^{-1}\) respectively. Compound 54 is the only compound having bipy as the auxiliary ligand. The coordination of bipy through both of its pyridyl nitrogen atoms is indicated by the peaks at 767, 1022, 1438 and 1620 cm\(^{-1}\).\(^{226-231}\) The \(\nu_{as}\text{COO}^{-}\) and \(\nu_{s}\text{COO}^{-}\) vibrations of the btc moiety in 54 appear at 1562 and 1361 cm\(^{-1}\) and the corresponding \(\Delta\nu\) value is 201 cm\(^{-1}\). Presence of water molecules in the coordinated and non-coordinated fashion are confirmed by the peaks at 3350 and 3280 cm\(^{-1}\).

We have monitored the trend in \(\Delta\nu\) among the various compounds and found that no specific trend could be assigned. The only observation worthy to highlight is that the \(\Delta\nu\) values for Ni(II) are the same for both the dap and im ligands. So also for Cu(II). Another important observation is that FTIR could prove the existence of one of the carboxylate functions of btc in non-deprotonated form in compounds 49 and 50.

9.3.2 Electronic spectra and magnetic data of the Co(II), Ni(II) and Cu(II) coordination networks

We have tried to look at the structural details of various Lewis-base modulated coordination polymers of Co-btc system by examining their electronic spectra. The electronic spectral data and the assignments are given in Table 9.3. The Co(II) complexes 45 and 51 exhibit two absorptions each in the visible region of the spectrum. The absorption at 14260 cm\(^{-1}\) of 45 corresponds to \(^{4}\text{T}_{1g} \rightarrow ^{4}\text{A}_{2g}\) (\(\nu_2\)) transition expected of a
Co(II) ion in an octahedral environment. The other transition at 19600 cm\(^{-1}\) pertains to \(^{4}T_{1g} \rightarrow ^{4}T_{1g}(P)\) (\(v_3\)) of the same ion in the same environment. Generally three spin allowed transitions are expected for an octahedrally coordinated Co(II) ion.\(^{176}\) The low energy transition corresponding to \(^{4}T_{1g} \rightarrow ^{4}T_{2g}\) (\(v_1\)) usually occurs at \(\sim 8000\) cm\(^{-1}\) and is outside the measurement range selected for scanning the spectrum. In addition to these two transitions a charge transfer transition is also observed in the spectrum at 38550 cm\(^{-1}\). The absorption maxima seen at 14710, 19600 and 38500 cm\(^{-1}\) in the electronic spectrum of 51 correspond to \(^{4}T_{1g} \rightarrow ^{4}A_{2g}\) (\(v_2\)), \(^{4}T_{1g} \rightarrow ^{4}A_{2g}\) (\(v_2\)) and CT respectively.

A Ni(II) ion having octahedral coordination is expected to exhibit three peaks in the UV-vis spectrum in the ranges 8000-13000 (\(v_1\)), 15000-19000 (\(v_2\)) and 25000-30000 (\(v_3\)) corresponding to \(^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)\) (\(v_1\)), \(^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)\) (\(v_2\)) and \(^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)\) (\(v_3\)) respectively.\(^{176}\) The lowest energy transition may or may not be visible as the maximum wavelength selected was only 800 nm. Out of the two Ni(II) compounds 46 exhibits only \(v_2\) and \(v_3\) at 15970 and 26310 cm\(^{-1}\) respectively. Another peak maximum observed in the spectrum of 46 is assigned to CT. The other Ni(II) compound 52 exhibits all the three peaks at 13000, 16130 and 26390 cm\(^{-1}\) respectively for \(v_1\), \(v_2\) and \(v_3\). CT observed in the spectrum of 52 is seen at 38610 cm\(^{-1}\). Dq, B’ and β values evaluated for 52 are 1300 cm\(^{-1}\), 234 cm\(^{-1}\) and 0.22 respectively. The low value of β is a clear indication for the strong covalent bonding present in the complex. These parameters could not be evaluated for 46 as only two bands were visible in the spectrum.
Table 9.3 | Electronic spectra and magnetic data of the M(II)-btc coordination networks

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absor. Max. ν' (cm⁻¹)</th>
<th>Assignments</th>
<th>μ eff BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co₃(btc)₂(dap)₆]ₙ.18nH₂O</td>
<td>14260 19600 38550</td>
<td>⁴T₁g→⁴A₂g ν² ⁴T₁g→⁴T₁g(P) ν³ CT</td>
<td>1.82</td>
</tr>
<tr>
<td>[Ni₃(btc)₂(dap)₃(H₂O)₆]ₙ.6nH₂O</td>
<td>15970 26310 40000</td>
<td>³A₂g→³T₁g(F) ν₂ ³A₂g→³T₁g(P) ν³ CT</td>
<td>2.91</td>
</tr>
<tr>
<td>[Cu₃(btc)₂(dap)₁.₅(H₂O)₉]ₙ</td>
<td>14810 33560</td>
<td>dz²→dx²-y² CT</td>
<td>2.15</td>
</tr>
<tr>
<td>[Cu(Hbtc)(en)(H₂O)]ₙ</td>
<td>15220 32900</td>
<td>dz²→dx²-y² CT</td>
<td>1.70</td>
</tr>
<tr>
<td>[Co₃(btc)₂(im)₃(H₂O)₉]ₙ</td>
<td>14710 19960 35710</td>
<td>⁴T₁g→⁴A₂g ν² ⁴T₁g→⁴T₁g(P) ν³ CT</td>
<td>4.10</td>
</tr>
<tr>
<td>[Ni₃(btc)₂(im)₅(H₂O)₃]ₙ</td>
<td>13000 16130 26390 38610</td>
<td>³A₂g→³T₂g(F) ν¹ ³A₂g→³T₁g(F) ν₂ ³A₂g→³T₁g(P) ν³ CT</td>
<td>2.74</td>
</tr>
<tr>
<td>[Cu₃(btc)₂(im)₁₂]ₙ.12nH₂O</td>
<td>12740 36230</td>
<td>dz²→dx²-y² CT</td>
<td>2.01</td>
</tr>
</tbody>
</table>

Electronic spectrum of Cu(II) is not much informative. In the electronic spectrum of copper complexes of any geometry a broad band with a peak maximum near 15000 cm⁻¹ is observed.¹⁷²,¹⁷⁶ All three copper compounds 47, 49 and 53 exhibit one broad peak each in the visible region. The ground state of the Cu(II) ion in an elongated tetragonally distorted octahedral field of D₄h symmetry may be described as a single electron in dₓ²-ᵧ² orbital or ²B₁g spectroscopic state. The transitions observed in these complexes may,
therefore, could be assigned to $d^2 \rightarrow d_{x^2-y^2}$. The absorption maxima observed are 14810, 13642 and 12740 cm$^{-1}$ respectively for 47, 49 and 53.

The magnetic susceptibility of the coordination polymers were found to be in the range expected for the respective ions in the geometry indicated above. The $\mu_{\text{eff}}$ value of 45 was found to be 1.82BM which corresponds to the low spin configuration of a $d^7$ ion in an octahedral ligand field. $^{272}$ The $\mu_{\text{eff}}$ values of other compounds are slightly higher than $\mu_{\text{so}}$ and could be due to some orbital contribution. $^{245}$ The magnetic moment values of the coordination compounds are presented along with the electronic spectral data in Table 9.3.

9.3.3 EPR spectra of the Cu(II) compounds

In the case of the three Cu(II) derivatives ([Cu$_3$(btc)$_2$(dap)$_{1.5}$(H$_2$O)$_9$]$_n$ 47, [Cu(Hbtc)(en)(H$_2$O)]$_n$ 49 and [Cu$_3$(btc)$_2$(im)$_{12}$]$_n$.12nH$_2$O 53) we have made attempts to get some useful information from EPR spectra. Since all the compounds were insoluble in nature EPR spectra were recorded at room temperature and DPPH was used as ‘g’ marker in the measurements. Represented in Fig 9.1 are the EPR spectral traces of the compounds. While the dap adduct 47 gives a featureless spectrum the en adduct 49 gives a broad absorption but indicative of exchange coupling. However, the imidazole adduct 53 showed some anisotropy in the spectrum. Various spin-Hamiltonian Parameters evaluated for the compounds are given in Table 9.4. We could observe hyperfine splitting in the EPR spectrum of 53 in the solid state itself. $\alpha^2$Cu was evaluated using the equation.

$$\alpha^2_{\text{Cu}} = -(A_{||}/0.036) + g_{||} - 2.002) + 3/7(g_{\perp} - 2.002) + 0.04$$
and the value is 0.4091 which is indicates a moderately strong covalent character in all its bonds. The EPR spectrum of 53 is suggestive of axial symmetry consistent with elongated tetragonal octahedral stereochemistry.\textsuperscript{221}

Even though one can expect superhyperfine splitting due to the I = 1 state of nitrogen nucleus in the three Lewis-base coordinated compounds we were not able to identify them in their spectra because of strong dipolar interaction and also because of the broadness seen in the spectra.

**Fig 9.1** EPR traces of the Cu(II) compounds

**Table 9.4** EPR spin Hamiltonian parameters of Cu(II)-btc Lewis-base ternary type coordination polymers.

| Compound | $A_{||}$ (gauss) | $A_{\perp}$ (gauss) | $g_{||}/g_1$ | $g_{\perp}/g_2$ | $g_{iso}$ | $G$ |
|----------|-----------------|-------------------|--------------|---------------|-----------|-----|
| 47       | -               | -                 | 2.03         | -             | -         | -   |
| [Cu$_3$(btc)$_2$(dap)$_{1.5}$(H$_2$O)$_9$]$_n$ | 80.33           | 15                | 2.130        | 2.044         | 2.072     | 3.04 |
9.3.4 SEM images

Even though we have made repeated trials to get good quality single crystals of the M(II)-btc-Lewis-base ternary type complexes our attempts met with failure. Since we could not characterize any of the compounds by solving the crystal structure we have recorded the SEM images of the coordination networks to get an idea about the surface morphology. Given in Fig 9.2 are the SEM micrographs of the phase pure products. We have expected nano dimensions for Zn(II)-btc Lewis-base ternary complexes 48, 50 and 54 from their fine textures. Compound 48 appears like plates. No definite order is seen in the packing. 50 and 54 appear like rods. Rods of nano dimension can be seen adhering on the surface of bigger rods in 50. As expected 54 appeared to be highly ordered long needle like rods with almost nano dimension. The Ni(II) compounds 46 and 52 have surface morphologies similar to plates with cracks. The Co(II) compounds 45 and 51 have almost similar appearance, like small crystals stacked over each other. Surface morphologies of copper compounds modulated by different auxiliary bases are different. While 47 having pn as the secondary ligand have the appearance of rods of sub micron size packed in regular manner 49 with en as auxiliary ligand appears as plates of nano thickness packed one over the other. The other copper compound 53 modulated by im has the appearance of small rods of sub micron radius packed in small bundles.
[Co₃(btc)₂(dap)₆]ₙ·18nH₂O 45

[Ni₃(btc)₂(dap)₃(H₂O)₆]ₙ·6nH₂O 46

[Cu₃(btc)₂(dap)₁.₅(H₂O)₉]ₙ 47

[Zn₃(btc)₂(dap)₃(H₂O)₆]ₙ 48

[Cu(Hbtc)(en)(H₂O)]ₙ 49

[Zn(Hbtc)(en)]ₙ·nH₂O 50
coordination polymers derived from metal(II) 1,3,5-benzenetricarboxylates

[Co$_3$(btc)$_2$(im)$_3$(H$_2$O)$_9$]$_n$ 51  [Ni$_3$(btc)$_2$(im)$_9$(H$_2$O)$_3$]$_n$ 52

[Co$_3$(btc)$_2$(im)$_3$(H$_2$O)$_9$]$_n$ 51  [Ni$_3$(btc)$_2$(im)$_9$(H$_2$O)$_3$]$_n$ 52

Fig 9.2. SEM micrographs of the coordination polymers

9.3.5 Structural aspects

FTIR data of the Co(II) derivatives 45 and 51 indicate that the carboxylate groups are η$^1$ coordinated in both the compounds (Δν = 212 and 181 cm$^{-1}$ respectively). Elemental analytical data showed that metal : btc ratio is 3 : 2 in both compounds. Also that in 45 metal : dap ratio is 1 : 2. Electronic spectral data suggest an octahedral environment in both the compounds. TG data also supports the elemental analytical data. Based on these observations we propose an octahedral geometry around the Co(II) ion in [Co$_3$(btc)$_2$(dap)$_6$]$_n$.18nH$_2$O 45 with a chromophore CoN$_4$O$_2$. FTIR
data of 51 indicates the presence of coordinated water molecules in it (νOH = 3220 cm\(^{-1}\)) and TG data confirms that there are three water molecules/cobalt ion. Analytical data indicates that the metal : im ratio in 51 is 1 : 1. Based on these available data we propose a polymeric nature to [Co\(_3\)(btc)\(_2\)(im)\(_3\)(H\(_2\)O)\(_9\)]\(_n\) 51 in which the chromophore is CoNO\(_5\). We could synthesize two phase pure auxiliary ligand incorporated Ni(II)-btc derivatives (46 and 52). FTIR spectra of these complexes correspond to monodentate coordination of the carboxylate functions (Δν = 185 cm\(^{-1}\) for both). Elemental analytical data indicate that metal : btc ratio is 3 : 2 in both compounds. Metal : dap ratio is 1 :1 in the case of 46 and metal : im ratio is 1 : 3 for 52. The presence of coordinated water molecules in both the compounds is suggested by their FTIR spectra (νOH = 3247 cm\(^{-1}\) for 46 and νOH = 3132 cm\(^{-1}\)for 52). TG data could confirm that there are two coordinated water molecules/nickel ion in 46 and 52 consists of one water molecule/nickel ion. Based on these observations we can propose polymeric nature for both [Ni\(_3\)(btc)\(_2\)(dap)\(_3\)(H\(_2\)O)\(_6\)]\(_n\)6nH\(_2\)O 46 and [Ni\(_3\)(btc)\(_2\)(im)\(_9\)(H\(_2\)O)\(_3\)]\(_n\) 52 where the chromophores are respectively NiN\(_2\)O\(_4\) and NiN\(_2\)O\(_3\). Lewis-base incorporated Cu(II)-btc derivatives, we could characterize were 47, 49 and 53. FTIR spectral data of all the three compounds exhibit peaks characteristic of monodentate coordination of the carboxylate functions in btc (Δν = 201, 197 and 201 cm\(^{-1}\) respectively). Elemental analytical data show that metal : btc ratio is 3 :2 for 47 and 53 while it is 1 : 1 for 49. FTIR data indicates the presence of coordinated water molecules in both 47 and 49 (νOH = 3313 and 3001 cm\(^{-1}\) respectively). TGA could confirm that there are three water molecules/copper ion in 47 while 49 consists of one water molecule/copper ion. Elemental analytical data is suggestive of metal :
dap in the ratio 1 : ½ in 47, metal : en in the ratio 1 : 1 in 49 and metal : im in the ratio 1 : 4 in 53. Based on these observations we could propose polymeric structures for all the three Cu(II) derivatives. The chromophoric units in [Cu$_3$(btc)$_2$(dap)$_{1.5}$(H$_2$O)$_9$]$_n$ 47, [Cu(Hbtc)(en)(H$_2$O)]$_n$ 49 and [Cu$_3$(btc)$_2$(im)$_{12}$]$_n$.12nH$_2$O 53 are respectively CuNO$_5$, CuN$_2$O$_3$ and CuN$_4$O$_2$.

We could characterize three phase pure Zn(II)-btc-Lewis-base derivatives (48, 50 and 54). Infrared spectral data of all the three compounds indicate the η$_1$ mode of coordination of the carboxylate functions of btc (Δν = 166, 182 and 201 cm$^{-1}$ respectively for 48, 50 and 54). FTIR spectral data also indicates the presence of coordinated water molecules in 48 and 54 (νOH = 3298, 3350 cm$^{-1}$ respectively). TG data confirmed that the metal : water ratio is 1 : 2 in both the compounds. CHN analysis showed that metal and acid are in the ratio 3 : 2, 1 : 1 and 3 : 2 respectively for 48, 50 and 54. Elemental analysis could confirm the ratio between metal and auxiliary ligands (metal : dap is 1 : 1 for 48, metal : en is 1 : 1 for 50 and metal : bipy is 1 : 1 for 54). Based on these data we could propose polymeric structures to all the three Zn(II) derivatives. The chromophores were seen to be ZnN$_2$O$_4$, ZnN$_2$O$_2$ and ZnN$_2$O$_4$ respectively for [Zn$_3$(btc)$_2$(dap)$_3$(H$_2$O)$_6$]$_n$ 48, [Zn(Hbtc)(en)]$_n$.nH$_2$O 50 and [Zn$_3$(btc)$_2$(bipy)$_3$(H$_2$O)$_6$]$_n$.9nH$_2$O 54. Interestingly all the M(II)-btc-Lewis-base derivatives are seen to be polymeric in nature. The polymers can be expected to have 3D nature (except 49 and 50) because deprotonation of all the carboxylate groups will result in extended structures.
9.3.6 Thermal characteristics

The dissociation features of the compounds were studied under N₂ atmosphere for all the ternary coordination polymers to understand their thermal characteristics and also to infer their stability. The rate of heating employed was 10°C/min. The thermal characteristics of the various coordination compounds are presented in Table 9.5. An interesting and noteworthy feature is that there is no compound which does not contain water molecules, either coordinated or uncoordinated. Usually lattice water molecules are eliminated at comparatively lower temperature than coordinated water molecules. We have studied the thermal behavior of four complexes modulated by dap. While the Co(II) compound 45 and Ni(II) compound 46 undergo decomposition in three stages each the Cu(II) compound 47 and the Zn(II) compound 48 are completely oxidized in two stages each. The elimination of lattice water molecules of 45 is initiated at 51°C and ends at 96°C with a peak temperature of 71°C. The second stage corresponds to elimination of one molecule of dap where the initial temperature (Tᵢ) is 286°C while the final temperature (Tᶠ) is 321°C. The third and final stage in which one molecule of dap and btc each are eliminated is initiated at 439°C which comes to completion at 498°C resulting in the formation of cobalt oxide. Ti for the first stage of decomposition of the dap modulated Ni(II) compound 46 is 70°C while Tᶠ is 82°C and this step corresponds to the elimination of two lattice water molecules. The second stage also corresponds to the elimination of two water molecules, but coordinated. Tᵢ and Tᶠ for this step are respectively 129 and 141°C. In the final stage which is initiated at 390°C and completed at 434°C dap and btc molecules are removed yielding nickel oxide as the final product. Cu(II) compound 47 loses two coordinated water molecules in the first step for which Tᵢ and Tᶠ are respectively 120 and 140°C. The remaining fractions are
eliminated in the second step which occurs in the temperature range 280-325°C. In this case also metal oxide is the final product.

**Table 9.5** Thermal characteristics of the btc complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stages</th>
<th>Temp. range (°C)</th>
<th>Peak temp. (°C)</th>
<th>Weight loss%</th>
<th>Probable reaction</th>
<th>Residue</th>
<th>Wt. % of residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1</td>
<td>51-96</td>
<td>71</td>
<td>23.44</td>
<td>Loss of six water mol.</td>
<td>CoO</td>
<td>17.12 16.54</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>286-321</td>
<td>304</td>
<td>16.62</td>
<td>Loss of one dap</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>439-498</td>
<td>464</td>
<td>42.85</td>
<td>Loss of one dap and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>1</td>
<td>70-82</td>
<td>77</td>
<td>10.26</td>
<td>Loss of two water mol.</td>
<td>NiO</td>
<td>21.44 21.79</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>129-141</td>
<td>134</td>
<td>9.96</td>
<td>Loss of two water mol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>390-434</td>
<td>420</td>
<td>56.73</td>
<td>Loss of dap and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>1</td>
<td>120-140</td>
<td>130</td>
<td>17.83</td>
<td>Loss of two water mol.</td>
<td>CuO</td>
<td>27.99 27.18</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>280-325</td>
<td>300</td>
<td>52.61</td>
<td>Loss of dap and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>1</td>
<td>114-130</td>
<td>120</td>
<td>11.19</td>
<td>Loss of two water mol.</td>
<td>ZnO</td>
<td>26.77 25.97</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>380-430</td>
<td>420</td>
<td>61.95</td>
<td>Loss of dap and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>1</td>
<td>95-120</td>
<td>109</td>
<td>5.24</td>
<td>Loss of one water mol.</td>
<td>Cu</td>
<td>16.81 17.16</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>301-352</td>
<td>340</td>
<td>58.80</td>
<td>Formation of copper carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>360-420</td>
<td>396</td>
<td>17.55</td>
<td>Formation of metallic copper from CuCO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>75-90</td>
<td>82</td>
<td>5.33</td>
<td>Loss of water mol.</td>
<td>ZnO</td>
<td>23.99 23.16</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>117-140</td>
<td>129</td>
<td>12.29</td>
<td>Loss of CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>420-475</td>
<td>462</td>
<td>58.50</td>
<td>Loss of en and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>1</td>
<td>104-121</td>
<td>111</td>
<td>16.76</td>
<td>Loss of three water mol.</td>
<td>Co</td>
<td>19.22 18.47</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>410-470</td>
<td>443</td>
<td>65.26</td>
<td>Loss of im and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>1</td>
<td>80-101</td>
<td>92</td>
<td>4.56</td>
<td>Loss of one water mol.</td>
<td>Ni</td>
<td>13.83 14.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>396-438</td>
<td>421</td>
<td>81.33</td>
<td>Loss of im and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>1</td>
<td>81-97</td>
<td>92</td>
<td>12.87</td>
<td>Loss of four water mol.</td>
<td>CuO</td>
<td>15.86 14.57</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>280-326</td>
<td>310</td>
<td>71.11</td>
<td>Loss of im and btc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>1</td>
<td>79-92</td>
<td>85</td>
<td>11.85</td>
<td>Loss of three water mol.</td>
<td>Zn</td>
<td>14.01 14.54</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>180-190</td>
<td>188</td>
<td>8.29</td>
<td>Loss of two water mol.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>348-428</td>
<td>383</td>
<td>64.13</td>
<td>Loss of bipy and btc</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A similar disintegration pattern is followed by 48 also. The first stage corresponding to the elimination of two coordinated water molecules takes place in the temperature range 114-130°C. The second step is initiated at 380°C and completed at 430°C and pertains to the removal of dap and btc fractions giving zinc oxide as the stable end product. We have followed the thermal dissociation features of two compounds modulated by en. Each compound undergoes the complete decomposition in three stages. The Cu(II) compound 49 consists of coordinated water molecules and loses it in the temperature range 95-120°C. The en and btc fractions are eliminated in the second step resulting in the formation of copper carbonate which occurs in the temperature range 301-352°C. In the final stage copper carbonate yields metallic copper in the range of temperature 360-420°C. The other en modulated compound 50 loses the lattice water molecules in the temperature range 75-90°C (Fig 9.3). The second stage which is initiated at 117°C and completed at 140°C corresponds to the removal of one molecule of carbon dioxide. In the last stage the remaining fractions are lost yielding zinc oxide as the final product which occurs in the temperature range 420-475°C.

Fig 9.3  TG/DTA curve of 50 showing the removal of water at very low temperature
We have studied the thermal characteristics of three complexes having im as the secondary ligand. Each complex undergoes decomposition in two stages. The coordinated water molecules of 51 are removed in the first step and the elimination is completed at 121°C. In the last step moieties such as im and btc are completely eliminated resulting in the formation of metallic cobalt itself. The formation of cobalt occurs in the temperature range 410-470°C. The coordinated water molecules of 52 are removed at a comparatively lower temperature range. The elimination is complete by 101°C. In the final step occurring in the range of temperature of 396-438°C the im and btc moieties are completely removed yielding metallic nickel as the end product. The Cu(II) compound having im as the secondary ligand loses the lattice water molecules in the range 81-97°C and converted to copper oxide in the temperature range 280-326°C. The thermal dissociation characteristics of Zn(II) modulated by bipy was studied and found that dissociation takes place in three stages. The first step initiated at 79°C and completed at 92°C indicates the removal of three lattice water molecules while the second step occurring in the temperature range 180-190°C corresponds to the removal of coordinated water molecules. Cases of removal of water molecules at such higher temperature are rare. The Last stage initiated at 348°C and terminated at 428°C with a peak temperature of 383°C indicates the removal of bipy and btc leading to the formation of metallic zinc.

When we analyze the thermal dissociation characteristics of the dap modulated complexes we see that the stability of the compounds follows the order Co > Ni > Zn > Cu. A similar trend is seen with respect to im modulated complexes also; Co > Ni > Cu. When we compare the relative
thermal stability of the en modulated complexes of copper and zinc we see that the order is Zn > Cu. This is in agreement with the trend observed for dap modulated complexes. The calculated and observed weight losses are in good agreement, as seen from Table 9.5. We could also evaluate the thermal and kinetic parameters associated with various stages of decomposition of all the complexes complex using Coats-Redfern equation.\textsuperscript{160} The results are presented in Table 9.6. We cannot cite any special trend in the variation of $E_a$ or A or $\Delta S$ of the compounds. The only observation is that when the value of $\Delta S$ is positive or less negative the value of A is much higher. The negative values for the entropies of activation indicate that the activated complexes have a more ordered structure than the reactants and the reaction are slower than the normal.$^{249-251}$ However we could not find any definite trends in the values for both $E_a$ and $\Delta S$.

From the table, it is evident that in most cases the form of $g(\alpha)$ with the highest value of correlation coefficients is $-\ln(1-\alpha)$, random nucleation, one nucleus on each particle, Mampel equation. Another major mechanism obeyed by the thermal decompositions in the solid state was found to be one dimensional diffusion corresponding to the form $\alpha^2$ of $g(\alpha)$. A few steps were found to follow three dimensional diffusion, spherical symmetry, Ginstling-Brounshetin equation and only one step is seen obeying phase boundary reaction, spherical symmetry. The corresponding forms of $g(\alpha)$ are $(1- \frac{2}{3} \alpha)(1- \alpha)^{2/3}$ and $1-(1-\alpha)^{1/3}$ respectively.
Table 9.6 Thermal and kinetic parameters associated with the various stages of decomposition of the btc complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stages</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$\Delta S$ (JK$^{-1}$mol$^{-1}$)</th>
<th>Form of $g(\alpha)$</th>
<th>Rate controlling process</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1</td>
<td>28.23</td>
<td>1.64x10$^{-2}$</td>
<td>-261.72</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation, one nucleus on each particle, Mampel equation</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>144.52</td>
<td>8.01x10$^{2}$</td>
<td>-194.74</td>
<td>$(1-\frac{2}{3}\alpha)-(1-\alpha)^{23}$</td>
<td>Three dimensional diffusion, spherical symmetry, Ginstling-Brounshetin equation</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>101.99</td>
<td>9.25</td>
<td>-234.11</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation, one nucleus on each particle, Mampel equation</td>
</tr>
<tr>
<td>46</td>
<td>1</td>
<td>77.38</td>
<td>4.31x10$^{2}$</td>
<td>-195.80</td>
<td>$(1-\frac{2}{3}\alpha)-(1-\alpha)^{23}$</td>
<td>Three dimensional diffusion, spherical symmetry, Ginstling-Brounshetin equation</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>75.33</td>
<td>83.94</td>
<td>-210.66</td>
<td>$\alpha^2$</td>
<td>One dimensional diffusion</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>191.42</td>
<td>1.18x10$^{4}$</td>
<td>-173.90</td>
<td>$\alpha^2$</td>
<td>One dimensional diffusion</td>
</tr>
<tr>
<td>47</td>
<td>1</td>
<td>29.77</td>
<td>14.33x10$^{-2}$</td>
<td>-263.56</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation, one nucleus on each particle, Mampel equation</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>73.77</td>
<td>5.26</td>
<td>-236.53</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation, one nucleus on each particle, Mampel equation</td>
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<tr>
<td>48</td>
<td>1</td>
<td>51.83</td>
<td>1.07</td>
<td>-246.63</td>
<td>$(1-\frac{2}{3}\alpha)-(1-\alpha)^{23}$</td>
<td>Three dimensional diffusion, spherical symmetry, Ginstling-Brounshetin equation</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>227.60</td>
<td>12.4x10$^{4}$</td>
<td>-154.35</td>
<td>$(1-\frac{2}{3}\alpha)-(1-\alpha)^{23}$</td>
<td>Three dimensional diffusion, spherical symmetry, Ginstling-Brounshetin equation</td>
</tr>
<tr>
<td>49</td>
<td>1</td>
<td>18.52</td>
<td>1.48x10$^{-2}$</td>
<td>-284.52</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation, one nucleus on each particle, Mampel equation</td>
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<tr>
<td></td>
<td>2</td>
<td>295.22</td>
<td>6.38x10$^{8}$</td>
<td>-63.33</td>
<td>$-\ln(1-\alpha)$</td>
<td>Random nucleation, one nucleus on each particle, Mampel equation</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>272.70</td>
<td>2.04x10$^{-7}$</td>
<td>-111.67</td>
<td>$\alpha^2$</td>
<td>One dimensional diffusion</td>
</tr>
</tbody>
</table>
In summary this chapter describes our studies on metal isophthalates and their Lewis-base derivatives. We considered H₃btc as an extended analogue of H₂ipt. By employing monodentate or chelating type Lewis-bases we could synthesize ten new ternary compounds and characterize them using elemental analytical, spectral, thermal and magnetic studies. SEM analysis showed different textural and morphological features for all the compounds.