Chapter 5

Thermal Studies on Transition Metal Complexes of Some Antipyrine Derivatives

The kinetics and mechanism of thermal decomposition of the complexes of Fe(III), Co(II), Ni(II) and Cu(II) with two Schiff bases, viz., 1,2-(diimino-4'-antipyrinyl)ethane (GA) and 4-N-(4'-antipyrylmethylidene)aminoantipyrine (AA) have been studied by thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses.

The kinetic parameters for the major decomposition stages are calculated using Coats-Redfern equation with the aid of a computer programme. The phenomenological and kinetic aspects of thermal decomposition of the complexes are discussed in this chapter.

5.1. Experimental

5.1.1 Preparation of the ligands and the complexes

The methods used for the preparation of the ligand GA and its complexes are presented in chapter 3 and that of the Schiff base AA and its complexes are described in chapter 4.
5.2. Results and discussion

All these complexes have been characterised by elemental analyses, electrical conductance in non-aqueous solvents, magnetic susceptibility as well as infrared, ESR and electronic spectra as described in chapters 3 and 4.

Wendlandt and co-workers studied the relationship between the thermal stability of metal chelates and the structure of chelating ligands.\textsuperscript{143-146} Usually non-isothermal methods are used to study the kinetics and mechanism of thermal decomposition of compounds.\textsuperscript{146} Here, in the present investigation non-isothermal analysis is used as the tool for the investigation of thermal stability of complexes and also for the evaluation of the kinetic parameters of thermal decomposition reactions. The theory of the evaluation of the kinetic parameters are discussed in chapter 2. The studies are based on TG and DTG, which were recorded in nitrogen atmosphere. Both the phenomenological and kinetic aspects of thermal decomposition are discussed here. The TG and DTG curves are presented in Figures 5.1 to 5.38.

5.3. Phenomenological aspects

5.3.1 Complexes of GA

The phenomenological data of the iron(III), cobalt(II), nickel(II) and copper(II) complexes of GA are presented in Tables 5.1 to 5.4.

Iron(III) complexes

The perchlorate complex is formulated as [Fe(GA)(ClO$_4$)](ClO$_4$)$_2$. It undergoes a two stage decomposition process in the range 146-482°C. There is no mass loss up to 146°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 146°C and ends at 220°C.
The observed mass loss (24.52%) is due to the conversion of three perchlorates into chlorides. The presence of chloride and absence of perchlorate after the first stage are confirmed by the chemical analysis and the infrared spectrum of the intermediate compound. The maximum rate of mass loss occurs at 197°C as indicated by the DTG peak. The second stage begins at 220°C and ends at 482°C with the DTG peak at 369°C. The corresponding mass loss (54.72%) is attributed to the removal of the ligand molecule of GA. The final residue is anhydrous ferric chloride as confirmed by qualitative analysis.

The nitrate complex, [Fe(GA)(NO\textsubscript{3})\textsubscript{2}]NO\textsubscript{3}, undergoes a three stage decomposition process. There is no mass loss up to 142°C revealing the absence of either water or solvent molecules in this complex. The first stage begins at 142°C and ends at 264°C. The observed mass loss (27%) is due to the decomposition of three nitrate ions. This result is supported by the absence of nitrate ion in the intermediate compound obtained at 264°C as confirmed by infrared spectral analysis. The second stage starts at 264°C and comes to an end at 497°C and the corresponding mass loss (31%) is due to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The third stage begins at 497°C and ends at 910°C. The observed mass loss (31.50%) is due to the removal of the remaining half of the ligand molecule. The rate of mass loss is found to be maximum at 192, 325 and 583°C respectively for the first, second and third stages of decomposition as indicated by the DTG peaks. The decomposition gets completed at 910°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The thiocyanate complex, [Fe(GA)(SCN)\textsubscript{2}]SCN, undergoes decomposition in three stages. There is no mass loss up to 190°C indicating the absence of either water or solvent molecules in this complex. The first stage starts at 190°C and ends at 313°C. The observed mass loss (31%) is due to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the
presence of GA indicating only a partial removal of the ligand at this stage. The maximum rate of mass loss is indicated by the DTG peak at 303°C. The second stage of decomposition starts at 313°C and comes to an end at 515°C with the DTG peak at 453°C. The observed mass loss (25.87%) is due to the decomposition of three thiocyanate ions. This result is supported by the absence of thiocyanate ion in the intermediate compound obtained at 515°C as confirmed by infrared spectral analysis. The third stage occurs in the temperature range 515-801°C with the DTG peak at 636°C. The corresponding mass loss (32.02%) is due to the decomposition of the remaining half of the ligand molecule. The decomposition gets completed at 801°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex is represented as [Fe(GA)Cl2]Cl. It undergoes a two stage decomposition process and there is no mass loss up to 211°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 211°C and ends at 400°C. The observed mass loss (36.01%) is due to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The corresponding DTG peak occurs at 307°C. The second stage begins at 400°C and ends at 874°C with the DTG peak at 637°C. The corresponding mass loss (36.17%) is attributed to the decomposition of the remaining half of the ligand molecule. The final product is anhydrous ferric chloride as confirmed by qualitative analysis.

The bromide complex, [Fe(GA)Br2]Br, undergoes decomposition in two stages. There is no mass loss up to 240°C proving the absence of either water or solvent molecules in this complex. The first stage starts at 240°C and ends at 408°C. The observed mass loss (29.10%) is attributed to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The DTG peak corresponding to this stage is observed at 350°C. The second stage of decomposition starts at 408°C and comes to an end at 856°C with the DTG peak
at 620°C. The corresponding mass loss (29%) is due to the expulsion of the remaining half of the ligand molecule. The final residue is anhydrous ferric bromide as confirmed by qualitative analysis.

**Cobalt(II) complexes**

The perchlorate complex is represented as [Co(GA)(ClO₄)]ClO₄. There is no mass loss up to 252°C indicating that either water or solvent molecules are absent in this complex. It undergoes a three stage decomposition process in the range 252-641°C. The first stage starts at 252°C and ends at 374°C. The observed mass loss (31.42%) is attributed to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The DTG peak corresponding to this stage is observed at 305°C. The second stage starts at 374°C and comes to an end at 540°C. The corresponding mass loss (18.56%) is due to the conversion of two perchlorates into chlorides. Absence of perchlorate ion after this stage is confirmed by infrared spectral analysis of the intermediate compound obtained at 540°C. The rate of mass loss is maximum at 431°C as indicated by the DTG peak. The third stage, which occurs in the temperature range 540-641°C with the DTG peak at 580°C, amounts to a mass loss (31.78%) corresponding to the decomposition of the remaining half of the ligand molecule. The final residue is qualitatively proved to be anhydrous metal chloride.

The cobalt(II) nitrate complex is formulated as [Co(GA)(NO₃)]NO₃. There is no mass loss up to 156°C revealing that molecules of either water or solvent molecules are absent in this complex. It also undergoes a three stage decomposition pattern. The first stage starts at 156°C and ends at 327°C. The observed mass loss (34.07%) is due to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The maximum
rate of mass loss is indicated by the DTG peak obtained at 270°C. The second stage of decomposition starts at 327°C and comes to an end at 423°C. The observed mass loss (19.92%) is due to the decomposition of two nitrate ions. The DTG peak of this stage is observed at 389°C. The third stage of decomposition starts at 423°C and comes to an end at 499°C. The DTG peak of this stage is observed at 440°C. The corresponding mass loss (35.35%) may be attributed to the removal of the remaining half of the ligand molecule. The decomposition gets completed at 499°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex, [Co(GA)Cl₂], undergoes a two stage decomposition process. There is no mass loss up to 172°C revealing that small molecules like water or solvents are absent in this complex. The first stage of decomposition begins at 172°C and comes to an end at 463°C. The observed mass loss (37.64%) is due to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The second stage starts at 463°C and comes to an end at 636°C and the corresponding mass loss (38.36%) is due to the removal of the remaining half of the ligand molecule, yielding anhydrous metal chloride as the final product. The rate of mass loss is found to be maximum at 354 and 610°C respectively for the first and second stages of decomposition as indicated by the DTG peaks.

The bromide complex is represented as [Co(GA)Br₂]. There is no mass loss up to 283°C indicating that either water or solvent molecules are absent in this complex. It undergoes decomposition in two stages. The first stage starts at 283°C and comes to an end at 450°C. The observed mass loss (34.60%) is attributed to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The DTG peak of this stage is observed at 372°C. The second stage of decomposition starts at 450°C and it is a continuous one. The
steady mass loss observed in this stage may be due to the expulsion of the remaining part of the ligand molecule together with volatilisation of the residue of anhydrous cobalt bromide above 678°C.

The iodide complex of GA have the formula [Co(GA)]$_2$. It undergoes a two stage decomposition process. There is no mass loss up to 179°C indicating the absence of either water or solvent molecules in this complex. The first stage starts at 179°C and ends at 461°C with the DTG peak at 326°C. The observed mass loss (58.56%) is due to the decomposition of GA. The second stage of decomposition starts at 461°C and comes to an end at 539°C with the DTG peak at 483°C. The corresponding mass loss (35.71%) is due to the decomposition of two iodide ions. The decomposition gets completed at 539°C and the final residue is qualitatively proved to be anhydrous metal oxide.

**Nickel(II) complexes**

The perchlorate complex, [Ni(GA)](ClO$_4$)$_2$, undergoes decomposition in two stages in the range 249-421°C. There is no mass loss up to 249°C revealing that small molecules like water or solvents are absent in this complex. The first stage of decomposition begins at 249°C and ends at 307°C. The observed mass loss (63.01%) is due to the decomposition of the molecule of GA. The second stage starts at 307°C and comes to an end at 421°C and the corresponding mass loss (19.81%) is due to the conversion of two perchlorates into chlorides. The rate of mass loss is found to be maximum at 278 and 410°C respectively for the first and second stages of decomposition as indicated by the DTG peaks. The final residue is anhydrous nickel chloride as confirmed by qualitative analysis.

The nitrate complex is formulated as [Ni(GA)](NO$_3$)$_2$. It undergoes a two stage decomposition process and there is no mass loss up to 235°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 235°C and comes to an end at 350°C. The observed mass
loss (44.34%) is due to the decomposition of one nitrate ion and half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA and the nitrate ion indicating only partial decomposition of the ligand and the nitrate ion at this stage. The maximum rate of mass loss occurs at 313°C as indicated by the DTG peak. The second stage begins at 350°C and ends at 501°C with the DTG peak at 438°C. The corresponding mass loss (44.67%) is attributed to the decomposition of the remaining nitrate ion and half of the molecule of GA. The decomposition gets completed at 501°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex, [Ni(GA)]Cl₂, undergoes decomposition in two stages in the range 193-768°C. There is no mass loss up to 193°C revealing that small molecules like water or solvents are absent in this complex. The first stage begins at 193°C and ends at 456°C. The observed mass loss (39.51%) is due to the decomposition of half of the molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The second stage starts at 456°C and comes to an end at 768°C, and the corresponding mass loss (38.38%) is due to the decomposition of the remaining half of the ligand molecule. The rate of mass loss is found to be maximum at 289 and 675°C respectively for the first and second stages of decomposition as indicated by the DTG peaks. The final residue is anhydrous metal chloride as confirmed by qualitative analysis.

The bromide complex, [Ni(GA)]Br₂, undergoes a two stage decomposition pattern and there is no mass loss up to 221°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 221°C and ends at 471°C with the DTG peak at 313°C. The observed mass loss (44.63%) is due to the decomposition of half of the ligand molecule and one bromide ion. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The second stage begins at 471°C and ends at 629°C with the DTG peak at 564°C. The
corresponding mass loss (44.28%) is attributed to the removal of the remaining half of GA and one bromide ion. The decomposition gets completed at 629°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The iodide complex, [Ni(GA)]I₂, undergoes a two stage decomposition process in the range 168-599°C. The first stage begins at 168°C and ends at 434°C. The observed mass loss (45.01%) is due to the decomposition of half of the molecule of GA and one iodide ion. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The second stage starts at 434°C and comes to an end at 599°C and the corresponding mass loss (45.70%) is due to the decomposition of the remaining half of GA and one iodide ion. The rate of mass loss is found to be maximum at 276 and 537°C respectively for the first and second stages of decompositions as indicated by the DTG peaks. The decomposition gets completed at 599°C and the final residue is qualitatively proved to be anhydrous metal oxide.

**Copper(II) complexes**

The perchlorate complex, [Cu(GA)](ClO₄)₂, undergoes decomposition in three stages. There is no mass loss up to 137°C indicating the absence of either water or solvent molecules in this complex. The first stage starts at 137°C and ends at 266°C. The corresponding mass loss (30.90%) is due to the decomposition of half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The maximum rate of mass loss is at 220°C as indicated by the DTG peak. The second stage of decomposition starts at 266°C and comes to an end at 513°C. The observed mass loss (18.75%) is due to the conversion of two perchlorates into chlorides. The DTG peak corresponding to this stage is observed at 350°C. The third stage, which starts at 513°C, is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining ligand.
molecule together with the volatilisation of the residue of anhydrous cupric chloride above 620°C.

The nitrate complex is formulated as [Cu(GA)](NO₃)₂. There is no mass loss up to 228°C revealing that molecules of either water or solvent are absent in this complex. It follows a two stage decomposition pattern in the range 228-611°C. The first stage starts at 228°C and comes to an end at 464°C with the DTG peak at 245°C. The corresponding mass loss (43.57%) is due to the decomposition of half of the ligand molecule and one nitrate ion. The infrared spectrum of the residue after this stage shows the presence of GA and nitrate ion indicating partial removal of the ligand and the nitrate ion at this stage. The second stage begins at 464°C and comes to an end at 611°C with the DTG peak at 561°C. The corresponding mass loss (44.28%) is due to the decomposition of the remaining half of GA and one nitrate ion. The decomposition gets completed at 611°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex of GA is formulated as [Cu(GA)Cl₂]. It undergoes a two stage decomposition pattern and there is no mass loss up to 178°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 178°C and ends at 427°C with DTG peak at 348°C. The corresponding mass loss (38.08%) is due to the decomposition of half of the molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The second stage, which begins at 427°C, is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining part of the ligand molecule together with the volatilisation of the residue of anhydrous cupric chloride above 620°C.

The bromide complex, [Cu(GA)Br₂], undergoes a two stage decomposition process. There is no mass loss up to 197°C revealing the absence of either water or solvent molecules in this complex. The first stage begins at 197°C and ends at
492°C. The observed mass loss (33.33%) is due to the decomposition of half of the molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The second stage starts at 492°C and comes to an end at 893°C and the corresponding mass loss (32.74%) is due to the decomposition of the remaining half of the ligand molecule. The rate of mass loss is found to be maximum at 297 and 684°C respectively for the first and second stages of the decomposition as indicated by the DTG peaks. The final product is anhydrous cupric bromide as confirmed by qualitative analysis.

5.3.1.1 Structure-thermal stability relation

Iron(III) complexes

The analyses of the results show that though the molecular composition of the complexes is the same, i.e., Fe(GA)X₃ (where X = ClO₄⁻, NO₃⁻, SCN⁻, Cl⁻ or Br⁻), the nature of the decomposition pattern is entirely different. The nitrate and thiocyanate complexes show a three stage decomposition pattern while the perchlorate, chloride and bromide complexes exhibit a two stage decomposition process. The nitrate complex is the least stable and the bromide complex is the most stable among the series. The difference in the thermal stability of the complexes indicates that the anion may have some marked influence on the thermal stability of the complexes and it is in the order:

Bromide > Chloride > Thiocyanate > Perchlorate > Nitrate

Cobalt(II) complexes

The TG data reveal that though the molecular composition of the cobalt(II) complexes is the same, viz., Co(GA)X₂ (where X = ClO₄⁻, NO₃⁻, Cl⁻, Br⁻ or I⁻), the
nature of the decomposition pattern is different. The perchlorate and nitrate complexes exhibit a three stage decomposition pattern while a two stage decomposition pattern is observed in the case of chloride, bromide and iodide complexes. Among the series the nitrate complex is the least stable and the bromide complex is the most stable. The difference in thermal stability of the complexes reveals that the anion may have some marked influence on the thermal stability of the complexes and it is in the order:

Bromide > Perchlorate > Iodide > Chloride > Nitrate

**Nickel(II) complexes**

The TG results show that all the nickel(II) complexes of GA follow a two stage decomposition pattern. Even though the anions are not involved in coordination in these complexes, they exhibit a wide range in stability. Among the series the iodide complex is the least stable and the perchlorate complex is the most stable. The difference in thermal stability of the complexes indicates that even though the anions are not involved in coordination they may have some marked influence on the thermal stability of the complexes and it is found in the order:

Perchlorate > Nitrate > Bromide > Chloride > Iodide

**Copper(II) complexes**

The analyses of the results show that though the molecular composition of the complexes is the same, viz., Cu(GA)X2 (where X = ClO4−, NO3−, Cl− or Br−), the nature of the decomposition pattern is different. The perchlorate complex follows a three stage decomposition process while the nitrate, chloride and bromide complexes show a two stage decomposition pattern. Among the series the perchlorate complex is the least stable and the nitrate complex is the most stable.
The difference in thermal stability of the complexes reveals that the anion may have some marked influence on the thermal stability of the complexes and it is in the order.

Nitrate > Bromide > Chloride > Perchlorate

5.3.2 Complexes of AA

The phenomenological data of the iron(III), cobalt(II), nickel(II) and copper(II) complexes of AA are presented in Tables 5.5 to 5.8.

Iron(III) complexes

The perchlorate complex is formulated as \([\text{Fe(AA)}_2(\text{ClO}_4)](\text{ClO}_4)_2\). There is no mass loss up to 205°C indicating that either water or solvent molecules are absent in this complex. It undergoes decomposition in two stages in the range 205-533°C. The first stage starts at 205°C and ends at 320°C with the DTG peak at 256°C. The corresponding mass loss (68.56%) is attributed to the decomposition of two ligand molecules. The second stage starts at 320°C and comes to an end at 533°C with the DTG peak at 485°C. The corresponding mass loss (15.71%) is due to the conversion of three perchlorates into chlorides. The final residue is anhydrous ferric chloride as confirmed by qualitative analysis.

The nitrate complex is formulated as \([\text{Fe(AA)}_2(\text{NO}_3)_2]\text{NO}_3\). It undergoes a three stage decomposition process in the range 157-496°C. There is no mass loss up to 157°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 157°C and ends at 241°C. The observed mass loss (17.14%) is due to the decomposition of three nitrate ions. This result is supported by the absence of nitrate ion in the intermediate compound obtained at 241°C as confirmed by infrared spectral analysis. The maximum rate of
mass loss occurs at 231°C as indicated by the DTG peak. The second stage starts at 241°C and ends at 420°C with the DTG peak at 348°C. The corresponding mass loss (37.14%) is attributed to the decomposition of one ligand molecule. The third stage starts at 420°C and comes to an end at 496°C with DTG peak at 473°C and the corresponding mass loss (37.91%) is due to the decomposition of the remaining ligand molecule. The decomposition gets completed at 496°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The thiocyanate complex of AA is formulated as [Fe(AA)(SCN)₃]. There is no mass loss up to 218°C indicating that either water or solvent molecules are absent in this complex. It undergoes a two stage decomposition process. The first stage starts at 218°C and ends at 455°C with the DTG peak at 321°C. The corresponding mass loss (39.28%) is attributed to the decomposition of half of the ligand molecule and one thiocyanate ion. The infrared spectrum of the residue after this stage shows the presence of AA and thiocyanate ion indicating only partial removal of AA and thiocyanate at this stage. The second stage starts at 455°C and comes to an end at 564°C with the DTG peak at 529°C. The corresponding mass loss (50.70%) is due to the decomposition of the remaining half of the ligand molecule and two thiocyanate ions. The decomposition of the complex gets completed at 564°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex is represented as [Fe(AA)Cl₃] and there is no mass loss up to 260°C indicating that either water or solvent molecules are absent in this complex. It undergoes a two stage decomposition process. The first stage starts at 260°C and ends at 573°C with the DTG peak at 398°C. The corresponding mass loss (34.49%) is attributed to the decomposition of half of the molecule of AA. The infrared spectrum of the residue after this stage shows the presence of AA indicating only partial removal of the ligand at this stage. The second stage of
decomposition, which starts at $573^\circ C$, is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining part of the ligand molecule together with the volatilisation of the residue of anhydrous metal chloride.\textsuperscript{147}

The bromide complex is formulated as [Fe(AA)$_2$Br$_2$]Br. It undergoes a two stage decomposition process and there is no mass loss up to $171^\circ C$ revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at $171^\circ C$ and ends at $426^\circ C$ with the DTG peak at $335^\circ C$. The corresponding mass loss (36.54\%) is due to the decomposition of one molecule of AA. The second stage, which begins at $426^\circ C$, is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining ligand molecule together with the volatilisation of the residue of anhydrous metal bromide.\textsuperscript{147}

**Cobalt(II) complexes**

The perchlorate complex, [Co(AA)$_2$](ClO$_4$)$_2$, undergoes a two stage decomposition process in the range 363-625\(^\circ\)C. There is no mass loss up to 363\(^\circ\)C revealing the absence of either water or solvent molecules in this complex. The first stage begins at 363\(^\circ\)C and ends at 498\(^\circ\)C. The corresponding mass loss (75.70\%) is due to the decomposition of two ligand molecules. The second stage starts at 498\(^\circ\)C and comes to an end at 625\(^\circ\)C and the corresponding mass loss (12.85\%) is due to the conversion of two perchlorates into chlorides. The rate of mass loss is found to be maximum at 421 and 574\(^\circ\)C respectively for the first and second stages of the decomposition as indicated by the DTG peaks. The decomposition of the complex leaves anhydrous cobalt chloride as the final residue as confirmed by qualitative analysis.
The nitrate complex is represented as $[\text{Co(AA)}_2(\text{NO}_3)_2]$. There is no mass loss up to 269°C indicating that either water or solvent molecules are absent in this complex. It undergoes decomposition in two stages. The first stage starts at 269°C and ends at 296°C with the DTG peak at 280°C. The observed mass loss (12.57%) is attributed to the decomposition of two nitrate ions. This result is supported by the absence of nitrate ion in the intermediate obtained at 296°C as confirmed by infrared spectral analysis. The second stage starts at 296°C and comes to an end at 666°C. The corresponding mass loss (80.43%) is attributed to the decomposition of two molecules of AA. The rate of mass loss is maximum at 553°C as indicated by the DTG peak. The decomposition of the complex gets completed at 666°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex, $[\text{Co(AA)}_2\text{Cl}_2]$, undergoes a two stage decomposition pattern. There is no mass loss up to 278°C revealing that small molecules like water or solvent are absent in this complex. The first stage begins at 278°C and ends at 433°C. The corresponding mass loss (36.59%) is due to the decomposition of half of the molecule of AA. The infrared spectrum of the residue after this stage shows the presence of AA indicating only partial removal of the ligand at this stage. The second stage starts at 433°C and comes to an end at 720°C and the corresponding mass loss (36.95%) is due to the removal of the remaining half of the ligand molecule. The final residue is anhydrous metal chloride as confirmed by qualitative analysis. The rate of mass loss is found to be maximum at 332 and 677°C respectively for the first and second stages of decomposition as indicated by the DTG peaks.

The bromide complex is formulated as $[\text{Co(AA)}_2\text{Br}_2]$. There is no mass loss up to 236°C indicating that either water or solvent molecules are absent in this complex. It undergoes decomposition in two stages. The first stage starts at 236°C and ends at 442°C with the DTG peak at 311°C. The corresponding mass loss
(39.13%) is attributed to the decomposition of one molecule of AA. The second stage of decomposition, that starts at 442°C, is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining part of the ligand molecule together with volatilisation of the residue anhydrous metal bromide\textsuperscript{147} above 678°C.

The iodide complex, [Co(AA)]\textsubscript{2}I\textsubscript{2}, undergoes a three stage decomposition pattern in the range 167-543°C. There is no mass loss up to 167°C indicating the absence of either water or solvent molecules in this complex. The first stage starts at 167°C and ends at 238°C with the DTG peak at 222°C. The corresponding mass loss (23.18%) is due to the decomposition of two iodide ions. The second stage of decomposition starts at 238°C and comes to an end at 433°C with the DTG peak at 326°C. The corresponding mass loss (35.50%) is attributed to the decomposition of a molecule of AA. The third stage occurs in the temperature range 433-543°C with the DTG peak at 519°C. The corresponding mass loss (36.23%) is due to the decomposition of the remaining molecule of AA. The decomposition gets completed at 543°C and the final residue is qualitatively proved to be anhydrous metal oxide.

**Nickel(II) complexes**

The perchlorate complex is formulated as [Ni(AA)]\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2}. It follows a two stage decomposition pattern in the range 281-593°C. There is no mass loss up to 281°C indicating the absence of either water or solvent molecules in this complex. The first stage starts at 281°C and ends at 387°C with the DTG peak at 350°C. The corresponding mass loss (75.77%) is due to the decomposition of two ligand molecules. The second stage of decomposition starts at 387°C and comes to an end at 593°C with the DTG peak at 518°C. The corresponding mass loss (13.84%) is due to the conversion of two perchlorates into chlorides. The
decomposition gets completed at 593°C yielding anhydrous nickel chloride as the final residue as confirmed by qualitative analysis.

The nitrate complex is formulated as [Ni(AA)₂](NO₃)₂. It follows a two stage decomposition pattern and there is no appreciable mass loss up to 201°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 201°C and ends at 456°C. The corresponding mass loss (46.92%) is due to the decomposition of one nitrate ion and one molecule of AA. The maximum rate of mass loss occurs at 293°C as indicated by the DTG peak. The second stage begins at 456°C and ends at 684°C with the DTG peak at 652°C. The corresponding mass loss (46.01%) is attributed to the decomposition of the remaining nitrate and ligand molecule. The decomposition gets completed at 884°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex, [Ni(AA)₂]Cl₂, undergoes decomposition in two stages. There is no mass loss up to 228°C which indicates that small molecules like water or solvents are absent in this complex. The first stage of decomposition begins at 228°C and ends at 412°C. The corresponding mass loss (42.47%) is due to the removal of one molecule of AA. The second stage starts at 412°C and comes to an end at 718°C and the corresponding mass loss (42.92%) is due to the removal of the remaining ligand molecule. The rate of mass loss is found to be maximum at 369 and 637°C respectively for the first and second stages of decomposition as indicated by the DTG peaks. The decomposition of the complex leaves the residue of anhydrous nickel chloride as confirmed by qualitative analysis.

The bromide complex is formulated as [Ni(AA)₂]Br₂. It undergoes a three stage decomposition pattern and there is no mass loss up to 193°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 193°C and ends at 293°C. The observed mass loss (14.28%) is due to the decomposition of two bromide ions. The maximum rate of
mass loss occurs at 220°C as indicated by the DTG peak. The second stage begins at 293°C and ends at 450°C with the DTG peak at 358°C. The corresponding mass loss (40.17%) is attributed to the removal of one molecule of AA. The third stage occurs in the temperature range 450-881°C with a DTG peak at 683°C. The corresponding mass loss (39.28%) is due to the removal of the remaining ligand molecule. The decomposition gets completed at 881°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The iodide complex, \([\text{Ni}(\text{AA})_2]_2\), undergoes a three stage decomposition process. The first stage begins at 168°C and ends at 256°C. The observed mass loss (21.87%) is due to the decomposition of two iodide ions. The second stage starts at 256°C and comes to an end at 431°C and the corresponding mass loss (34.37%) is due to the decomposition of one molecule of AA. The third stage, which occurs in the temperature range 431-618°C with a mass loss (35.15%) amounts to the expulsion of the remaining one molecule of AA. The rate of mass loss is found to be maximum at 230, 357 and 537°C respectively for the first, second and third stages of the decomposition as indicated by the corresponding DTG peaks. The decomposition gets completed at 618°C and the final residue is qualitatively proved to be anhydrous metal oxide.

Copper(II) Complexes

The perchlorate complex, \([\text{Cu}(\text{AA})_2](\text{ClO}_4)_2\), undergoes a two stage decomposition pattern between 190 and 615°C. There is no mass loss up to 190°C indicating the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 190°C and ends at 328°C. The observed mass loss (43.47%) is due to the expulsion of one molecule of AA and the conversion of one perchlorate into chloride. The rate of mass loss is maximum at 314°C as indicated by the respective DTG peak. The second stage of decomposition starts
at 328°C and comes to an end at 615°C with the DTG peak at 564°C. The corresponding mass loss (43.11%) is due to the removal of the remaining molecule of AA and the conversion of the second perchlorate into chloride. The decomposition gets completed at 615°C yielding anhydrous cupric chloride as the final residue as confirmed by qualitative analysis.

The nitrate complex is formulated as [Cu(AA)$_2$](NO$_3$)$_2$. There is no mass loss up to 206°C revealing that molecules of either water or solvent are absent in this complex. It follows a two stage decomposition pattern between 206 and 615°C. The first stage starts at 206°C and comes to an end at 464°C with the DTG peak at 245°C. The corresponding mass loss (46.37%) is due to the decomposition of one nitrate ion and one molecule of AA. The second stage begins at 464°C and comes to an end at 615°C with the DTG peak at 561°C. The corresponding mass loss (46.10%) is due to the decomposition of the remaining nitrate ion and ligand molecule. The decomposition gets completed at 615°C and the final residue is qualitatively proved to be anhydrous cupric oxide.

The chloride complex of AA is formulated as [Cu(AA)$_2$]Cl$_2$. It undergoes a two stage decomposition pattern and there is no mass loss up to 181°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 181°C and ends at 489°C. The corresponding mass loss (41.10%) is due to the decomposition of one molecule of AA. The maximum rate of mass loss occurs at 347°C as indicated by the DTG peak. The second stage begins at 489°C and ends at 807°C with the DTG peak at 718°C. The corresponding mass loss (41.01%) is attributed to the decomposition of the remaining molecule of AA. The decomposition gets completed at 807°C yielding anhydrous cupric chloride as the final residue as confirmed by qualitative analysis.

The bromide complex, [Cu(AA)Br]Br, undergoes a two stage decomposition process. The first stage begins at 186°C and ends at 549°C. The
corresponding mass loss (32.78%) is due to the decomposition of half of the molecule of AA. The infrared spectrum of the residue after this stage shows the presence of AA indicating only partial removal of the ligand at this stage. The second stage starts at 549°C and comes to an end at 719°C and the corresponding mass loss (32.17%) is due to the removal of the remaining half of the ligand molecule. The rate of mass loss is found to be maximum at 330 and 698°C respectively for the first and second stages of the decomposition as indicated by the corresponding DTG peaks. The decomposition gets completed at 719°C yielding the residue of anhydrous cupric bromide as confirmed by qualitative analysis.

5.3.2.1 Structure-thermal stability relation

Iron(III) complexes

The TG results show that though the stoichiometry of the perchlorate, nitrate and bromide complexes is the same, the perchlorate complex is thermally more stable than the other two complexes. The nitrate complex undergoes a three stage decomposition process while the perchlorate and bromide complexes decompose in two stages. The thiocyanate and chloride complexes, the molecular compositions of which are different from that of the nitrate, perchlorate and bromide complexes follow a two stage decomposition pattern and undergo decomposition at higher temperatures compared to that of the perchlorate, nitrate and bromide complexes. The chloride complex decomposes at higher temperature than the thiocyanate complex. The chloride complex is the most stable and the nitrate complex is the least stable among the series. Thus the difference in thermal stability of these complexes indicate that the anion may have some marked influence on the thermal stability of the complexes and it follows the order:

Chloride > Thiocyanate > Perchlorate > Bromide > Nitrate
Cobalt(II) complexes

The TG data reveal that even though the molecular composition of the perchlorate, nitrate, bromide and iodide complexes are the same, the perchlorate complex is more stable than the other three and all of these except the iodide complex undergo a two stage decomposition pattern. In the case of the iodide complex, a three stage decomposition pattern is observed. The chloride complex, the molecular composition of which is different from the other complexes, follows a two stage decomposition process. Among the series, the iodide complex is the least stable and the perchlorate complex is the most stable. Based on the foregoing facts, it may be concluded that the nature of the anion may have some marked influence on the thermal stability of the complexes and it is in the order:

Perchlorate > Chloride > Nitrate > Bromide > Iodide

Nickel(II) complexes

The TG results show that even though the molecular composition of the complexes is the same, i.e., [Ni(AA)₂]X₂ (where X = ClO₄⁻, NO₃⁻, Cl⁻, Br⁻ or I⁻), the nature of decomposition pattern is different. The perchlorate, nitrate and chloride complexes show a two stage decomposition pattern while the bromide and iodide complexes decompose in three stages. Even though the anions are not involved in coordination in these complexes, they exhibit a wide range in stability. Among the series, the iodide complex is the least stable and the perchlorate complex is the most stable. The TG data indicate that even though the anions are not involved in coordination, they may have some marked influence on the thermal stability of the complexes and it is in the order:

Perchlorate > Chloride > Nitrate > Bromide > Iodide
Copper(II) complexes

The TG results show that though the molecular composition of the perchlorate, nitrate and chloride complexes is the same, the nitrate complex is more stable than the other two and all of them undergo a two stage decomposition process. The bromide complex, even though the molecular composition of which is different from the other complexes, also exhibits a two stage decomposition pattern. Among the series, the nitrate complex is the most stable and the chloride complex is the least stable. The TG data indicate that the anion may have some marked influence on the thermal stability of the complexes and it is found to be in the order:

Nitrate > Perchlorate > Bromide > Chloride.

5.4. Kinetic aspects

The kinetic parameters like the activation energy (E) and the pre-exponential factor (A) are calculated for well defined stages of decomposition using Coats-Redfern equation.\(^{113}\)

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

In the present investigation \(\log[g(\alpha)/T^2]\) is plotted against \(10^3/T\). From the graph so obtained (Figures 5.39 to 5.46), the slope and intercept of the straight line are determined. Using these values, the kinetic parameters are calculated by the least square method. The goodness of fit was evaluated by calculating the correlation coefficient.
The entropy of activation ($\Delta S$) is also calculated for each stage of thermal decomposition in these complexes using the relationship,

$$A = \frac{kT_s}{h} e^{\Delta S_R}$$

All the calculations are done with the help of a computer programme.

### 5.4.1 Complexes of GA

The kinetic parameters calculated for the iron(III), cobalt(II), nickel(II) and copper(II) complexes of GA are presented in Tables 5.9-5.12

**Iron(III) complexes**

The activation energies ($E$) in the different stages of thermal decomposition of iron(III) complexes are in the range 31.75-82.23 kJ mol$^{-1}$. The corresponding values of pre-exponential factor ($A$) of these complexes vary in the range $1.56 \times 10^2$ to $66.20$ S$^{-1}$. The respective values of entropy of activation ($\Delta S$) of these complexes fall in the range $-288.61$ to $-213.83$ J mol$^{-1}$. There is no definite trend either in the values of $E$ or in the values of $\Delta S$ among the different stages of decomposition in the present series. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal $^{148,149}$

**Cobalt(II) complexes**

The activation energies ($E$) in the different stages of the thermal decomposition of cobalt(II) complexes are in the range 30.16-306.99 kJ mol$^{-1}$. The respective values of the pre-exponential factor ($A$) vary from $2.72 \times 10^2$ to $7.84 \times 10^7$ S$^{-1}$. The corresponding values of the entropy of activation ($\Delta S$) are in the
range -281.02 to -100.89 J mol\(^{-1}\). There is no definite trend either in the values of \(E\) or in the values of \(\Delta S\) among the different stages of decomposition in the present series. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.\(^{148,149}\)

**Nickel(II) complexes**

The observed activation energies (\(E\)) in both the stages of thermal decomposition of nickel(II) complexes are in the range 31.95-155.04 kJ mol\(^{-1}\). The corresponding values of the pre-exponential factor (\(A\)) vary from \(4.61 \times 10^{-2}\) to \(2.20 \times 10^{4}\) S\(^{-1}\). The respective values of the entropy of activation (\(\Delta S\)) are in the range -275.56 to -167.35 J mol\(^{-1}\). There is no definite trend either in the values of \(E\) or in the values of \(\Delta S\) among the different stages of decomposition in the present series. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal\(^{148,149}\).

**Copper(II) complexes**

The activation energies (\(E\)) in the different stages of the thermal decomposition of copper(II) complexes are in the range 33.98-140.72 kJ mol\(^{-1}\). The corresponding values of pre-exponential factor (\(A\)) vary from \(4.15 \times 10^{-2}\) to \(175.98\) S\(^{-1}\). The respective values of the entropy of activation (\(\Delta S\)) are in the range -281.04 to -209.40 J mol\(^{-1}\). There is no definite trend either in the values of \(E\) or in the values of \(\Delta S\) among the different stages of decomposition in the present series. But the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal\(^{148,149}\).
5.4.2 Complexes of AA

The kinetic parameters calculated for the iron(III), cobalt(II), nickel(II) and copper(II) complexes of AA are presented in Tables 5.13-5.16.

Iron(III) complexes

The activation energies (E) in the different stages of thermal decomposition of iron(III) complexes are in the range 28.25 to 419.26 kJ mol\(^{-1}\). The corresponding values of pre-exponential factor (A) are in the range \(2.40 \times 10^{-2}\) to \(1.69 \times 10^{8}\) S\(^{-1}\). The respective values of the entropy of activation (\(\Delta S\)) are in the range -281.81 to -60.93 J mol\(^{-1}\). There is no definite trend either in the values of \(E\) or in the values of \(\Delta S\) among the different stages of decomposition in the present series. But, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.\(^{148,149}\)

Cobalt(II) complexes

The values of activation energies (E) in the different stages of decomposition of cobalt(II) complexes are in the range 51.09 to 292.24 kJ mol\(^{-1}\). The corresponding values of pre-exponential factor (A) vary from \(9.38 \times 10^{-2}\) to \(1.25 \times 10^{10}\) S\(^{-1}\). The respective values of the entropy of activation (\(\Delta S\)) are in the range -272.17 to -56.89 J mol\(^{-1}\). There is no definite trend either in the values of \(E\) or in the values of \(\Delta S\) among the different stages of decomposition in the present series. However, negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.\(^{148,149}\)
Nickel(II) complexes

The activation energies (E) in the different stages of thermal decomposition of nickel(II) complexes are in the range 29.03-182.63 kJ mol\(^{-1}\). The corresponding values of pre-exponential factor (A) vary from \(2.01 \times 10^2\) to \(2.57 \times 10^6\) S\(^{-1}\). The respective values of the entropy of activation (\(\Delta S\)) fall in the range -283.76 to -126.39 J mol\(^{-1}\). There is no definite trend either in the values of E or in the values of \(\Delta S\) among the different stages of decomposition in the present series. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.\(^{148,149}\)

Copper(II) complexes

The activation energies (E) in the different stages of the thermal decomposition of copper(II) complexes are in the range 38.96-179.58 kJ mol\(^{-1}\). The corresponding values of pre-exponential factor (A) vary from \(6.46 \times 10^2\) to \(2.22 \times 10^4\) S\(^{-1}\). The respective values of the entropy of activation (\(\Delta S\)) fall in the range -273.52 to -180.17 J mol\(^{-1}\). There is no definite trend either in the values of E or in the values of \(\Delta S\) among the different stages of decomposition in the present series. But, the negative values of the entropy of activation indicate that the activated complex has a more ordered structure than reactants and the reactions are slower than normal.\(^{148,149}\)

5.5. Mechanistic aspects

The elucidation of mechanism for the solid state thermal decomposition reaction is a complicated one. All the heterogeneous processes can be classified into three categories, viz., (1) nucleation and growth, (2) diffusion and (3) phase
boundary reactions. Several kinetic equations have been derived corresponding to the above three possible rate determining steps. The kinetic equations which govern the reaction mechanism are based on the assumption that the form of \( g(\alpha) \) depends on the reaction mechanism. In the present investigation, nine forms of \( g(\alpha) \) proposed by Satava\textsuperscript{[115]} have been used.

The form of \( g(\alpha) \) representing the best experimental data is considered as the mechanism of the reaction. In the present investigation thirtyeight complexes derived from two Schiff bases (GA and AA) are selected. The correlation coefficients obtained for the nine forms of \( g(\alpha) \) are presented in Tables 5.17-5.24.

Except in two cases, i.e., the second stage decomposition of copper(II) nitrate complex of GA and the second stage decomposition of cobalt(II) nitrate complex of AA, the highest values of the magnitude of correlation coefficient is obtained for the equation:

\[
g(\alpha) = -\ln(1-\alpha)
\]

and hence the mechanism is ‘random nucleation with one nucleus on each particle’ representing ‘Mampel Model’.

But for the second stage decomposition of copper(II) nitrate complex of GA and the second stage decomposition of cobalt(II) nitrate complex of AA, the highest value of the magnitude of correlation coefficient is obtained for the equation:

\[
g(\alpha) = \alpha + (1-\alpha) \ln (1-\alpha)
\]

and hence the mechanism is ‘two dimensional diffusion’. 
5.6. Summary and conclusion

The thermogravimetric analyses of the iron(III), cobalt(II), nickel(II) and copper(II) complexes of two Schiff bases (GA and AA) indicate that thermal stability of these complexes are in the range 137-363°C.

In iron(III) complexes of GA, the thermal stability is in the order: bromide > chloride > thiocyanate > perchlorate > nitrate. Among the series, the thiocyanate and nitrate complexes undergo a three stage decomposition pattern while the perchlorate, chloride and bromide complexes decompose in two stages. In cobalt(II) complexes of GA, the perchlorate and nitrate complexes undergo a three stage decomposition process, while the chloride, bromide and iodide complexes follow a two stage decomposition pattern. The thermal stability of the complexes is in the order: bromide > perchlorate > iodide > chloride > nitrate. In nickel(II) complexes of GA, all of them undergo a two stage decomposition pattern and the thermal stability is in the order: perchlorate > nitrate > bromide > chloride > iodide. In copper(II) complexes of GA, the perchlorate complex follows a three stage decomposition pattern while the nitrate, chloride and bromide complexes decompose in two stages. The thermal stability of the complexes is in the order: nitrate > bromide > chloride > perchlorate.

In iron(III) complexes of AA, the thermal stability is in the order: chloride > thiocyanate > perchlorate > bromide > nitrate. Among the series, the nitrate complex undergoes decomposition in three stages while the thiocyanate, perchlorate, chloride and bromide complexes decompose in two stages. In cobalt(II) complexes of AA, all of them except the iodide complex (which decomposes in three stages) exhibit a two stage decomposition pattern. The thermal stability of the complexes is in the order: perchlorate > chloride > nitrate > bromide > iodide. In nickel(II) complexes of AA, the perchlorate, nitrate and chloride complexes decompose in two stages while the bromide and iodide complexes decompose in three stages. The thermal stability of the complexes is in
the order: perchlorate > chloride > nitrate > bromide > iodide. In copper(II) complexes of AA, all of them follow a two stage decomposition pattern and the thermal stability of the complexes follow the order: nitrate > perchlorate > bromide > chloride.

The observed values of activation energy in different stages of thermal decomposition of the present complexes are in the range 28.25-419.26 kJ mol\(^{-1}\). The values of entropy of activation are observed in the range -56.89 to -288.6 J mol\(^{-1}\). But no definite trend is observed either in the values of activation energy or in the values of entropy of activation among the different stages of decomposition in the present complexes. The negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.

The thermal decomposition mechanism is found to be ‘random nucleation with one nucleus on each particle’ representing the ‘Mampel Model’ in different stages of decomposition in all the present complexes studied except in the second stage decomposition of the copper(II) nitrate complex of GA and the second stage decomposition of the cobalt(II) nitrate complex of AA where the mechanism is found to be ‘two dimensional diffusion’.
Chapter 6

Summary and Conclusion

The work incorporated in this thesis deals with the synthesis and characterisation of some first row transition metal complexes of two antipyrine derivatives, viz.,

(a) 1,2-(diamino-4'-antipyrinyl)ethane (GA), and

(b) 4-N-(4'-antipyrylmethylidene)aminoantipyrine (AA)

The metal ions used in the present study are Fe(III), Co(II), Ni(II) and Cu(II).

The complexes of both GA and AA have been synthesised and characterised by elemental analyses, molar conductance in non-aqueous solvents, infrared, electronic and ESR spectra, magnetic susceptibility measurements as well as thermogravimetric analyses.

6.1. Complexes of GA

Iron(III) complexes have the formulae [Fe(GA)(ClO₄)](ClO₄)₂ and [Fe(GA)X₂]X (where X = NO₃⁻, SCN⁻, Cl⁻ or Br⁻). GA acts as a neutral tetradentate ligand coordinating through both the carbonyl oxygens and both the azomethine nitrogens in all these complexes. In the perchlorate complex, one of the
perchlorate ion is coordinated bidentately while in the nitrate and thiocyanate complexes, two of the anions are coordinated monodentately to the metal ion. In the chloride and bromide complexes, two of the anions are coordinated to the metal ion. From the electronic spectra and magnetic moment data, a high spin octahedral geometry is proposed around the Fe(III) ion in all these complexes.

The cobalt(II) complexes of GA can be represented as [Co(GA)X]X (where $X = \text{ClO}_4^-$ or $\text{NO}_3^-$) and [Co(GA)X$_2$] (where $X = \text{Cl}^-, \text{Br}^-$ or $\Gamma$). In all these complexes, GA acts as a neutral tetradentate ligand, coordinating through both the carbonyl oxygens and both the azomethine nitrogens. One of the anions is coordinated bidentately in the perchlorate and nitrate complexes while both the anions are coordinated in the halide complexes. The electronic spectra and magnetic moment values suggest an octahedral geometry around the Co(II) ion in all these complexes.

Nickel(II) complexes of GA are of the type [Ni(GA)]X$_2$ (where $X = \text{ClO}_4^-$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{Br}^-$ or $\Gamma$). GA acts as a neutral tetradentate ligand, coordinating through both the carbonyl oxygens and both the azomethine nitrogens in all these complexes. Also, both the anions remain as counter ions in all these complexes. From the electronic spectra and magnetic moment values, a square planar geometry is proposed around the Ni(II) ion in all these complexes.

Copper(II) complexes of GA have the general formulae [Cu(GA)]X$_2$ (where $X = \text{ClO}_4^-$ or $\text{NO}_3^-$) and [Cu(GA)X$_2$] (where $X = \text{Cl}^-$ or $\text{Br}^-$). GA acts a neutral tetradentate ligand, coordinating through both the carbonyl oxygens and both the azomethine nitrogens in all these complexes. In the perchlorate and nitrate complexes, both the anions remain as counter ions while in the halide complexes, both the anions are coordinated to the metal ion. Electronic spectral studies suggest a square planar geometry around the Cu(II) ion in the perchlorate and nitrate complexes while a distorted octahedral geometry in the halide complexes.
6.2. Complexes of AA

Iron(III) complexes of AA are represented by the general formulae \([\text{Fe}(\text{AA})_2(\text{ClO}_4)](\text{ClO}_4)\), [\(\text{Fe}(\text{AA})_2X_2\)](where \(X = \text{NO}_3^-\) or Br') and [\(\text{Fe}(\text{AA})X_3\)] (where \(X = \text{SCN}^-\) or Cl'). AA acts as a neutral bidentate ligand, coordinating through the carbonyl oxygen (derived from the aldehydic part) and the azomethine nitrogen in perchlorate, nitrate and bromide complexes while the coordination of AA occurs in a neutral tridentate fashion through both the carbonyl oxygens and the azomethine nitrogen in thiocyanate and chloride complexes. In the perchlorate complex, one of the perchlorate ion is coordinated in a bidentate fashion, while in the nitrate complex two of the nitrate ions are coordinated monodentately. In the thiocyanate complex, all the thiocyanate ions are coordinated monodentately and in the chloride complex all the chloride ions are coordinated. In the bromide complex, two of the bromide ions are coordinated. From the electronic spectra and magnetic moment data, a high spin octahedral geometry is assigned around the Fe(III) ion in all these complexes.

The cobalt(II) complexes of AA are represented as [\(\text{Co}(\text{AA})_2\)](where \(X = \text{ClO}_4^-, \text{NO}_3^-, \text{Br}^-\) or I) and [\(\text{Co}(\text{AA})\text{Cl}_2\)]. AA acts as a neutral bidentate ligand, coordinating through the carbonyl oxygen (derived from the aldehydic part) and the azomethine nitrogen in all these complexes. Both the anions remain as counter ions in the perchlorate, nitrate, bromide and iodide complexes, while both the anions are coordinated to the metal ion in the chloride complex. The electronic spectra and magnetic moment data suggest a tetrahedral geometry around the Co(II) ion in all these complexes.

Nickel(II) complexes of AA are formulated as [\(\text{Ni}(\text{AA})_2\)](where \(X = \text{ClO}_4^-, \text{NO}_3^-, \text{Cl}^-, \text{Br}^-\) or I). In all these complexes AA acts as a neutral bidentate ligand coordinating through the carbonyl oxygen (derived from the aldehydic part) and the azomethine nitrogen. Both the anions remain as counter ions in these complexes. From the electronic spectra and magnetic moment, a tetrahedral geometry is assigned around the Ni(II) ion in all these complexes.
The copper(II) complexes are represented as \([Cu(AA)_{2}]X_2\)
(where \(X = ClO_4^-, NO_3^-\) or Cl') and \([Cu(AA)Br]Br\). AA acts as a neutral bidentate ligand coordinating through the carbonyl oxygen (derived from the aldehydic part) and the azomethine nitrogen in the perchlorate, nitrate and chloride complexes, while the coordination of AA occurs in a neutral tridentate fashion through both the carbonyl oxygens and the azomethine nitrogen in the bromide complex. In the perchlorate, nitrate and chloride complexes both the anions remain as counter ions, while in the bromide complex, one of the bromide ions is coordinated to the metal ion. Electronic spectral studies suggest a square planar geometry around the Cu(II) ion in these complexes.

6.3. Thermal studies on complexes of GA and AA

The thermal studies (TG and DTG) of the 38 complexes of iron(III), cobalt(II), nickel(II) and copper(II) complexes of the Schiff bases GA and AA indicate that they are thermally stable up to the temperature range 137-363°C.

In the iron(III) complexes of GA, the thermal stability is in the order: bromide > chloride > thiocyanate > perchlorate > nitrate. Among the series, the thiocyanate and nitrate complexes decompose in three stages while the perchlorate, chloride and bromide complexes follow a two stage decomposition pattern. In the cobalt(II) complexes of GA, the perchlorate and nitrate complexes undergo a three stage decomposition pattern while the chloride, bromide and iodide complexes decompose in two stages. The thermal stability of the complexes follow the order: bromide > perchlorate > iodide > chloride > nitrate. In the nickel(II) complexes of GA, the thermal stability is in the order: perchlorate > nitrate > bromide > chloride > iodide and all of them undergo a two stage decomposition pattern. In the copper(II) complexes of GA, the perchlorate complex undergoes a three stage decomposition pattern while the nitrate, chloride and bromide complexes
decompose in two stages. The thermal stability of the complexes is in the order: nitrate > bromide > chloride > perchlorate.

In the case of iron(III) complexes of AA, the thermal stability is in the order: chloride > thiocyanate > perchlorate > bromide > nitrate. Among the series, the nitrate complex undergoes decomposition in three stages while the perchlorate, thiocyanate, chloride and bromide complexes decompose in two stages. In the cobalt(II) complexes, all of them except the iodide complex (which decompose in three stages) exhibit a two stage decomposition pattern. The thermal stability of the complexes is in the order: perchlorate > chloride > nitrate > bromide > iodide. In the nickel(II) complexes of AA, the thermal stability is in the order: perchlorate > chloride > nitrate > bromide > iodide. Among the series, the perchlorate, nitrate and chloride complexes undergo a two stage decomposition process while the bromide and iodide complexes decompose in three stages. In the copper(II) complexes, all of them follow a two stage decomposition pattern and thermal stability of the complexes is in the order: nitrate > perchlorate > bromide > chloride.

The activation energy and entropy of activation in the different stages of thermal decomposition of the complexes are in the range 28.25 to 419.26 kJ mol\(^{-1}\) and -288.61 to -56.89 J mol\(^{-1}\) respectively. There is no definite trend in the values of activation energy and entropy of activation among the different stages of decomposition in the present complexes. But the negative values of entropy of activation in all cases indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.

The mechanism of thermal decomposition is found to be 'random nucleation with one nucleus on each particle' representing 'Mampel Model' for different stages of decomposition in all the present complexes studied except in the second stage decomposition of copper(II) nitrate complex of GA and second stage decomposition of cobalt(II) nitrate complex of AA, where the mechanism is found to be 'two dimensional diffusion.'
Tables and Figures
Table 3.1 Analytical data of the iron(III) complexes of GA.

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Table 3.2 Analytical data of the cobalt(II) complexes of GA.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal%</th>
<th>Anion%</th>
<th>Carbon%</th>
<th>Hydrogen%</th>
<th>Nitrogen%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calculated</td>
<td>Found</td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td>[Co(GA)(ClO₄)]ClO₄</td>
<td>8.48</td>
<td>8.58</td>
<td>28.89</td>
<td>28.97</td>
<td>-</td>
</tr>
<tr>
<td>[Co(GA)(NO₃)₂]NO₃</td>
<td>9.59</td>
<td>9.63</td>
<td>-</td>
<td>-</td>
<td>47.06</td>
</tr>
<tr>
<td>[Co(GA)Cl₂]</td>
<td>10.44</td>
<td>10.55</td>
<td>12.61</td>
<td>12.70</td>
<td>-</td>
</tr>
<tr>
<td>[Co(GA)Br₂]</td>
<td>9.12</td>
<td>9.16</td>
<td>24.60</td>
<td>24.69</td>
<td>-</td>
</tr>
<tr>
<td>[Co(GA)I₂]</td>
<td>7.92</td>
<td>7.95</td>
<td>34.14</td>
<td>34.24</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3.3  Analytical data of the nickel(II) complexes of GA.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal%</th>
<th>Anion%</th>
<th>Carbon%</th>
<th>Hydrogen%</th>
<th>Nitrogen%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calculated</td>
<td>Found</td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Ni(GA)</a>₂</td>
<td>8.60</td>
<td>8.55</td>
<td>28.87</td>
<td>28.99</td>
<td>-</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Ni(GA)</a>₂</td>
<td>9.68</td>
<td>9.60</td>
<td>-</td>
<td>-</td>
<td>47.05</td>
</tr>
<tr>
<td>[Ni(GA)]Cl₂</td>
<td>10.57</td>
<td>10.52</td>
<td>12.65</td>
<td>12.70</td>
<td>-</td>
</tr>
<tr>
<td>[Ni(GA)]Br₂</td>
<td>9.10</td>
<td>9.07</td>
<td>24.61</td>
<td>24.70</td>
<td>-</td>
</tr>
<tr>
<td>[Ni(GA)]I₂</td>
<td>7.88</td>
<td>7.90</td>
<td>34.21</td>
<td>34.25</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.4  Analytical data of the copper(II) complexes of GA.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Metal%</th>
<th>Anion%</th>
<th>Carbon%</th>
<th>Hydrogen%</th>
<th>Nitrogen%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calculated</td>
<td>Found</td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td><a href="ClO%E2%82%84">Cu(GA)</a>₂</td>
<td>9.23</td>
<td>9.19</td>
<td>28.51</td>
<td>28.78</td>
<td>-</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Cu(GA)</a>₂</td>
<td>10.40</td>
<td>10.31</td>
<td>-</td>
<td>-</td>
<td>46.61</td>
</tr>
<tr>
<td>[Cu(GA)]Cl₂</td>
<td>11.10</td>
<td>11.28</td>
<td>12.41</td>
<td>12.59</td>
<td>-</td>
</tr>
<tr>
<td>[Cu(GA)]Br₂</td>
<td>9.60</td>
<td>9.74</td>
<td>24.56</td>
<td>24.52</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3.5  Molar conductance data of the iron(III) complexes of GA (in ohm⁻¹ cm² mol⁻¹)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆H₅NO₂</td>
</tr>
<tr>
<td>[Fe(GA)(ClO₄)]₂(ClO₄)₂</td>
<td>49.09</td>
</tr>
<tr>
<td>[Fe(GA)(NO₃)₂]NO₃</td>
<td>22.16</td>
</tr>
<tr>
<td>[Fe(GA)(SCN)₂]SCN</td>
<td>-</td>
</tr>
<tr>
<td>[Fe(GA)Cl₂]Cl</td>
<td>21.05</td>
</tr>
<tr>
<td>[Fe(GA)Br₂]Br</td>
<td>22.64</td>
</tr>
</tbody>
</table>

*10⁻³ M solutions used.

Table 3.6  Molar conductance data of the cobalt(II) complexes of GA (in ohm⁻¹ cm² mol⁻¹)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆H₅NO₂</td>
</tr>
<tr>
<td>[Co(GA)(ClO₄)]ClO₄</td>
<td>24.34</td>
</tr>
<tr>
<td>[Co(GA)(NO₃)₃]NO₃</td>
<td>17.03</td>
</tr>
<tr>
<td>[Co(GA)Cl₂]</td>
<td>2.43</td>
</tr>
<tr>
<td>[Co(GA)Br₂]</td>
<td>5.84</td>
</tr>
<tr>
<td>[Co(GA)I₂]</td>
<td>10.11</td>
</tr>
</tbody>
</table>

*10⁻³ M solutions used.