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Research Article

## A Review on the Characterization of Metal Hydrazine Complexes

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**Abstract:** Hydrazine is a potential ligand and forms a wide variety of complexes with various metal ions, organic and inorganic acids. The emerging interests in these hydrazine complexes are mainly due to their structure and thermal behavior. An approach was made herein to review the characterizations such as Electronic spectra, Infra-red spectra (IR) and Thermogravimetric/Differential Thermogravimetric Analysis (TG/DTA) of mono metal and mixed metal hydrazine complexes with various acids.

**Keywords:** Electronic spectra, Infra-red spectra (IR), Thermogravimetric/Differential Thermogravimetric analysis (TG/DTA).

### INTRODUCTION

Hydrazine ( $\text{H}_2\text{N}-\text{NH}_2$ ) is a powerful reducing agent and also called as diazane. It is a versatile ligand with two free lone pairs of electrons. The chemistry of hydrazine is interesting with respect to its ability to form complexes with various metals and variety of organic and inorganic acids<sup>1-4</sup>. In acidic solution hydrazine exists in the form of either hydrazinium( $1^+$ ), ( $\text{N}_2\text{H}_5^+$ ) or hydrazinium( $2^+$ ), ( $\text{N}_2\text{H}_6^{2+}$ ) ion, among which the protonated form  $\text{N}_2\text{H}_5^+$  is still capable of coordinating with metal ions. The hydrazine content of the precursor is determined volumetrically under Andrew's condition<sup>5</sup>. The metal percentage of the precursors is estimated by gravimetry as given in the Vogel's book<sup>5</sup>.

IR spectra of hydrazine and its derivatives are studied in the finger print region between 1300 and 650  $\text{cm}^{-1}$ . The unidentate and bidentate bridging coordination of the hydrazine molecule on complexation has been well documented<sup>6</sup>. The thermal reactivity of metal hydrazine complexes is noteworthy and the stability of complexes changes dramatically depending upon the cation and anion<sup>7</sup>. Being a fuel,

hydrazine not only supports combustion but also lowers the decomposition temperature of the metal hydrazine complexes<sup>8</sup>.

Nowadays, many researchers' focus has been shifted towards metal oxides because of their properties like magnetic, electrical, catalytic, etc.<sup>9-18</sup>. Complex oxides like cobaltites, ferrites, cuprites, chromites and manganites arouse interest due to its fascinating properties such as magnetism<sup>19-21</sup>, ferroelectricity<sup>22-24</sup>, superconductivity<sup>25-28</sup> and magnetoresistance<sup>29-32</sup>. Thus metal and mixed metal hydrazine complexes head into nano world.

## REVIEWS

**Mono-metal hydrazine complexes:** Metal hydrazine dicarboxylates of Co, Ni, Zn and Cd with pimelic, suberic, azelaic and sebacic acids prepared by S. Yasodhai *et al.*<sup>33</sup>. IR data confirmed the bridging behaviour of both the hydrazine and the long chain dicarboxylatedianion except in the case of the cadmium pimelate compound. The most probable stereochemistry of the polymeric compounds fixed on the basis of the spectral and thermal data. TG-DTA showed all of the complexes decompose to give their metal oxides. T. Premkumar *et al.*<sup>34</sup> worked on the metal complexes of the type  $M(\text{imdc})0.5\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , where  $M=\text{Mn, Co or Cd}$  and  $M(\text{imdc})\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , where  $M=\text{Ni or Zn}$ . They suggested that the Co and Ni complexes are of spin-free type with octahedral geometry by electronic spectral data. From IR spectral data they confirmed the bidentate bridging nature of  $\text{N}_2\text{H}_4$  ligand and the unidentate coordination behaviour of carboxylate groups of the imidazole dicarboxylatedianion. TG-DTA revealed that all the complexes undergo two step decomposition to yield metal oxide as a final product.

S. Yasodhai *et al.*<sup>35</sup> report edhydraziniumoxydiacetates and oxydiacetatedianion complexes of some divalent metals with hydrazine. IR data revealed the existence of  $\text{N}_2\text{H}_5^+$  ion in the simple salts and the bidentate coordination of both hydrazine and dianion in the complexes. From TG data cobalt and nickel complexes decompose in a single step, whereas Zn and Cd complex decomposes through hydrazinate intermediates. And all the metal complexes yield metal oxide as the final residue. K. Saravanan *et al.*<sup>36</sup> investigated metal hydrazine pyridine-2, n-dicarboxylate hydrates  $[\text{M}(\text{L})\text{N}_2\text{H}_4\cdot x\text{H}_2\text{O}]$ , where  $M=\text{Co, Ni, Zn and Cd}$ . B. N. Sivasankar *et al.*<sup>37</sup> prepared bis-hydrazine metal glycolates and chloroacetates,  $[\text{MX}_2(\text{N}_2\text{H}_4)_2]_n$ , where  $M=\text{Co, Ni, or Zn}$  for  $X=\text{HOCH}_2\text{COO}$  and  $M=\text{Mn, Co, Ni, Zn, or Cd}$  for  $X=\text{ClCH}_2\text{COO}$ . Electronic spectra indicated that all the complexes are high-spin octahedral in nature. The IR data revealed the existence of bidentate bridging hydrazine and tridentate pyridine dicarboxylates in all the complexes. TG-DTA showed that the anhydrous compounds undergo exothermic dehydrazination followed by decomposition of the organic component to give either the corresponding metal oxide or a mixture of metal oxide and metal carbonate as the final residue.

B. N. Sivasankar<sup>38</sup> synthesized Co, Ni and Zn dicarboxylate complexes of the type  $\text{MX}(\text{N}_2\text{H}_4)_n$  where  $n=1$  for  $X=\text{OOCCH}_2\text{COO}$  and  $n=2$  for  $X=\text{OOCCH}_2\text{COO, OOCCH}_2\text{CH}_2\text{COO}$  and  $\text{OOC}(\text{CH}_2)\text{CH}_2\text{COO}$  by aqueous reactions. T. Premkumar *et al.*<sup>39</sup> reported new divalent Co, Ni, Zn and Cd pyrazinecarboxylate hydrazinates of the formulae  $\text{M}(\text{pyzCOO})_2\cdot n\text{N}_2\text{H}_4\cdot x\text{H}_2\text{O}$  and  $\text{Mpyz}(\text{COO})_2\cdot \text{N}_2\text{H}_4\cdot x\text{H}_2\text{O}$ . R. Manimekalai *et al.*<sup>40</sup> found some bis- and tris- hydrazine complexes of metal phenoxyacetates by aqueous reactions. The electronic spectra of the complexes suggested that are of high-spin variety with octahedral geometry. IR data showed the bridging bidentate nature of hydrazine moieties present in both mono-hydrazine and bis-hydrazine complexes. TG-DTA curves of all the complexes revealed the formation of respective metal oxide as final residue.

Metal hydrazine complexes of the type  $\text{Mpz}(\text{COO})_2\text{N}_2\text{H}_4$  where  $M=\text{Co, Zn or Cd}$  and  $\text{Mpz}(\text{COO})_2\cdot n\text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$ , where  $n=1$  for  $M=\text{Ni}$  and  $n=0.5$  for  $M=\text{Cu}$  studied by T. Premkumar *et al.*<sup>41</sup>.

Electronic spectroscopic data suggested that Co and Ni complexes adopt an octahedral geometry. The IR spectra confirmed the presence of bidentate bridging hydrazine in the metal hydrazine complexes. The TG-DTA showed the formation of metal oxides as the end products except manganese pyrazoledicarboxylate hydrate. L. Vikram *et al.*<sup>42</sup> synthesized some new hydrazinium transition metal sulfite dihydrate complexes of the formula  $(\text{N}_2\text{H}_5)_2\text{M}(\text{SO}_3)_2(\text{H}_2\text{O})_2$  where  $\text{M}=\text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$  and  $\text{Zn}$ . The electronic spectra indicated their high spin octahedral nature. From the IR data they reported that both the hydrazinium ions are coordinated to the metal ions, the sulfite ions are present as bidentate ligand. In air, the TG-DTA of cobalt, nickel and zinc complexes gave respective metal sulfate as the final residue while Fe and Cu complexes gave the mixture of respective metal oxide and sulfate as the decomposition product. In nitrogen atmosphere respective metal sulfites are formed as the end residue.

S. Yasodha *et al.*<sup>43</sup> synthesized uranium complexes of composition,  $\text{UO}_2\text{X} \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  ( $\text{X}=\text{succinate}$  or  $\text{glutarate}$ ),  $\text{UO}_2\text{X}_2 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  ( $\text{X}=\text{adipate}, \text{pimelate}, \text{suberate}, \text{azelate}$  and  $\text{sebacate}$ ) and  $\text{UO}_2\text{X} \cdot \text{N}_2\text{H}_4$  ( $\text{X}=\text{malate}$  and  $\text{oxydiacetate}$ ). IR spectra revealed that hydrazine acts as a monodentate ligand in uranyl succinate, glutarate, malate and oxydiacetate hydrazinates and bidentate in uranyl adipate, pimelate, suberate, azelate and sebacate hydrazinate hydrate complexes. TG-DTA showed all the complexes decompose to give  $\text{U}_3\text{O}_8$  as the end product. The preparation of hydrazinium metal(II) ethylenediaminetetraacetates,  $(\text{N}_2\text{H}_5)_2[\text{M}(\text{EDTA})]$  ( $\text{M}=\text{Co}, \text{Ni}, \text{Cu}$  or  $\text{Zn}$ ),  $(\text{N}_2\text{H}_5)_3[\text{M}(\text{EDTA})(\text{H}_2\text{O})](\text{NO}_3)(\text{H}_2\text{O})$  and nine co-ordinated hydrazinium lanthanide ethylenediaminetetraacetate hydrates  $\text{N}_2\text{H}_5[\text{Ln}(\text{EDTA})(\text{H}_2\text{O})_3](\text{H}_2\text{O})_5$  where  $\text{Ln}=\text{Eu}, \text{Gd}, \text{Tb}$  or  $\text{Dy}$  carried out by L. Vikram *et al.*<sup>44,45</sup>. The ionic nature of hydrazinium cation found from the IR spectral data. Electronic spectral data showed the octahedral geometry around the metal ions with EDTA serving as a hexadentate ligand. From TG-DTA they observed that these complexes undergo multi-step decomposition to give the respective metal oxides as a final residue.

B. Raju *et al.*<sup>47</sup> prepared bis-hydrazine metal pyruvates of transition metal ions of the formula  $\text{M}[\text{CH}_3\text{COCOO}]_2[\text{N}_2\text{H}_4]_2$  ( $\text{M}=\text{Co}, \text{Ni}, \text{Zn}$  or  $\text{Cd}$ ), tris-hydrazine metal pyruvates of the formula  $\text{M}[\text{CH}_3\text{COCOO}]_2[\text{N}_2\text{H}_4]_3$  ( $\text{M}=\text{Co}, \text{Ni}, \text{Zn}$  or  $\text{Cd}$ ) and hydrazinium metal pyruvates  $[\text{N}_2\text{H}_5]_2\text{M}[\text{CH}_3\text{COCOO}]_4$  ( $\text{M}=\text{Co}$  or  $\text{Ni}$ ). The electronic spectra of the complexes suggested a high-spin octahedral geometry for them. Infrared spectral data of bis-hydrazine complexes revealed the bidentate bridging mode shown by hydrazine molecules and monodentate coordination by pyruvate ions. In hydrazinium complexes two hydrazinium ions and four pyruvate ions showed unidentate coordination mode resulting in six coordination around metal ions. From TG-DTA they confirmed that the hydrazinium complexes yield  $\text{Co}_2\text{O}_3$  and  $\text{NiO}$  as the final residue.

S. Vairam *et al.*<sup>48</sup> reported dihydrazinium divalent transition metal trimellitate hydrates of empirical formula  $(\text{N}_2\text{H}_5)_2\text{M}(\text{Html})_2 \cdot n\text{H}_2\text{O}$ , where  $n=1$  for  $\text{M}=\text{Co}$  or  $\text{Ni}$ , and  $n=2$  for  $\text{M}=\text{Mn}, \text{Zn}$ , or  $\text{Cd}$  ( $\text{H}_3\text{tml}=\text{trimellitic acid}$ ), and monohydrazinium cadmium trimellitate,  $[(\text{N}_2\text{H}_5)\text{Cd}(\text{Html})_{1.5} \cdot 2\text{H}_2\text{O}]$ . Electronic spectra suggested that Co and Ni complexes adopt an octahedral geometry. The IR spectra confirmed the presence of monodentate carboxylate anion and coordinated  $\text{N}_2\text{H}_5^+$  ion in all the complexes. TG-DTA showed all the complexes undergo endothermic decomposition followed by exothermic decomposition to give the respective metal carbonate as the end products except Ni and Co complexes, which yield respective metal oxides.

K. S. Rane *et al.*<sup>49</sup> found Iron(II) carboxylato-hydrazinates: ferrous fumarato-hydrazinate,  $\text{FeC}_4\text{H}_2\text{O}_4 \cdot 2\text{N}_2\text{H}_4$ ; ferrous succinato-hydrazinate,  $\text{FeC}_4\text{H}_4\text{O}_4 \cdot 2\text{N}_2\text{H}_4$ ; ferrous maleato-hydrazinate,  $\text{FeC}_4\text{H}_2\text{O}_4 \cdot 2\text{N}_2\text{H}_4$ ; ferrous malato-hydrazinate,  $\text{FeC}_4\text{H}_4\text{O}_5 \cdot 2\text{N}_2\text{H}_4$ ; ferrous malonato-hydrazinate,  $\text{FeC}_3\text{H}_2\text{O}_4 \cdot 1.5\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ; ferrous tartrato-hydrazinate,  $\text{FeC}_4\text{H}_4\text{O}_6 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and S. Vairam *et al.*<sup>50</sup> stated that hydrazine forms two different types of complexes with divalent metal ions and

pyromellitic acid ( $H_4pml$ ) in aqueous medium. From IR the N–N stretching frequency indicated the nature of hydrazine present in the complexes. TG-DTA data showed that hydrazinium complexes decompose to give the respective metal oxides.

R. Manimekalai<sup>51,52</sup> investigated  $M(cin)_2N_2H_4$  ( $M=Co$  or  $Zn$ ),  $M(cin)_2(N_2H_4)_2$  ( $M=Co, Ni, Zn$  or  $Cd$ ),  $M(crot)_2(N_2H_4)_2$  ( $M=Co$  or  $Ni$ ),  $Ni(crot)_2.N_2H_4.H_2O$ ,  $Cd(crot)_2(N_2H_4)_2.H_2O$  and transition metal hydrazine carboxylates of the type  $Co(PhAc)_2(N_2H_4)_2$  ( $M=Co, Ni, Cd$  and  $Mn$ ),  $M(Di-PhAc)_2.1.5N_2H_4.H_2O$  ( $M=Co, Ni$  and  $Cd$ ),  $M(2,4\text{-}di-ClPhAc)_2.1.5N_2H_4.H_2O$  ( $M=Co, Ni$  and  $Cd$ ) respectively and L. Vikramet *al.*<sup>53</sup> prepared bis-hydrazine complexes of metal glyoxylates  $M(OOCCHO)_2(N_2H_4)_2$  ( $M=Mg, Mn, Co, Ni, Cu, Zn$  or  $Cd$ ). Electronic spectral data suggested that the octahedral environment around the central metal ion. The IR data confirmed the bridging bidentate coordination of hydrazine molecules. TG-DTA showed that all the complexes undergo multi step decomposition to give respective metal oxides. K. Kalpanadevi *et al.*<sup>54</sup> reported transition metal hydrazine complexes with cinnamic acid, R. Manimekalai *et al.*<sup>55</sup> synthesized metal hydrazine pyridine-2-carboxylate hydrates, pyridine-3-carboxylate hydrates and P. Kanchana *et al.*<sup>56</sup> worked on  $[M(Pyc)_2(N_2H_4)_2]$  where  $M=Ni, Co, Cd$  &  $Zn$  and  $pyc=pyridine-4\text{-carboxylic acid}$ . The bidentate bridging nature of hydrazine ligand confirmed from IR analysis. They assigned chemical formula to the precursor complexes, based on the observed and calculated percentage values of hydrazine and the metal. The simultaneous TG-DTA curves for the precursors showed the formation of respective metal oxides.

Hydrazine complexes of 3-d transition metal with 2, 4-Dichlorophenoxy acetates synthesized by R. Manimekalai *et al.*<sup>57</sup>, the precursor  $Co(Di-PhAc)_2(N_2H_4).1.5H_2O$  reported by C. R. Sinduja *et al.*<sup>58</sup> and D. Santhosh Shantha kumar *et al.*<sup>59</sup> prepared Bis-hydrazine metal(II) p-nitrobenzoates,  $[M(p-NO_2C_6H_4COO)_2(N_2H_4)_2]$  ( $M=Co, Ni, Zn$  or  $Cd$ ). IR data indicated the bidentate bridging nature of hydrazine. The simultaneous TG-DTA curves indicated the formation of respective metal oxides as an end product. Thathan Prem kumar *et al.*<sup>60</sup> synthesized the hydrazinium lanthanide metal complexes of 2-pyrazinecarboxylic acid ( $HpyzCOO$ ) of the formulae  $(N_2H_5)_2[Ln(pyzoCOO)_5].2H_2O$  ( $Ln=La$  or  $Ce$ ),  $(N_2H_5)_3[Ln(pyzoCOO)_4(H_2O)].2NO_3$  ( $Ln=Pr, Nd, Sm$  or  $Dy$ ) and Lucie De Almeida *et al.*<sup>61</sup> found new hydrazinium lanthanide oxalates  $N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$  where  $Ln=Ce(Ce-HyOx), Nd(Nd-HyOx)$  by hydrothermal reaction. The IR band confirmed the coordination of  $N_2H_5^+$  to the metal and the N–N stretching frequencies revealed the presence of both non-coordinated and coordinated  $N_2H_5^+$  ions in the compounds. The thermal decomposition of the compounds revealed the formation of the respective metal oxides.

R. Ragulet *al.*<sup>62</sup> prepared  $[(N_2H_5)_2M(HCOO)_4].H_2O$  ( $M=Co, Ni$  or  $Zn$ ), acetate and glycinate complexes  $[(N_2H_5)_2M(CH_3COO)_4]$  and  $[(N_2H_5)_2M(NH_2CH_2COO)_4]$  ( $M=Co, Ni$  or  $Zn$ ), E. Helen Pricilla Baiet *al.*<sup>63</sup> investigated the metal complexes of isomeric acetamido benzoic acids with  $Co, Ni, Zn$  and  $Cd$  and N. Arunadevi *et al.*<sup>3</sup> carried out the reaction of hydrazine and 3-hydroxy-2 naphthoic acid with some transition metal ions. From IR spectra they revealed the bridging bidentate coordination of hydrazine. From chemical analyses they confirmed the composition of the complexes. The electronic spectra indicated the octahedral coordination around the metal ions. TG-DTA revealed the formation of respective metal oxides as an end product.

**Mixed metal hydrazine complexes:** B. N. Sivasankar<sup>64</sup> prepared  $M_{1/3}Co_{2/3}(N_2H_3COO)_2$  where  $M=Mg, Mn, Fe, Ni$  or  $Zn$  and  $M_{1/3}Fe_{2/3}(N_2H_3COO)_2$  where  $M=Mg, Mn, Co, Ni$  or  $Zn$ . Reema A. Porobetal.<sup>8</sup> synthesized Nickel manganese succinato-hydrazinate ( $NiMn_2(C_4H_4O_4)_3.6N_2H_4$ ) by a novel precursor technique, L. Vikramet *al.*<sup>53</sup> prepared mixed metal glyoxylates of 3d-metal ions of the formula  $M_{1/3}Co_{2/3}(OOCCHO)_2(N_2H_4)_2$  ( $M=Mg, Mn, Ni, Zn$  or  $Cd$ ). From IR they revealed that the

bidentate bridging nature of hydrazine. From thermal decomposition they showed that the formation of respective metal oxide as an end products.

The preparation of nickel manganese fumarato-hydrazinate ( $\text{NiMn}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ) reported by S. Y. Sawant *et al.*<sup>65</sup> and R. Manimekala *et al.*<sup>66</sup> reported  $\text{Co}_2\text{NiN}_2\text{H}_4\text{L}_2 \cdot \text{H}_2\text{O}$  (L=Diphenyl acetate). They fixed chemical formula of the precursor based on the percentage of hydrazine and metals which closely matches with the calculated one. The IR data showed N–N stretching frequency at  $965\text{cm}^{-1}$ , which confirmed the bidentate bridging nature of hydrazine. From TG-DTA the precursor showed the formation of mixed metal oxides as a final residue. A. More *et al.*<sup>67</sup> carried out the preparation of  $\text{NiFe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ . In 2012, R. Manimekala *et al.*<sup>68</sup> prepared  $\text{NiFe}_2(\text{L})_2 \cdot (\text{N}_2\text{H}_4)_2$  (L= $\text{C}_6\text{H}_5\text{OCH}_2\text{COO}^-$ ) and R. Manimekala *et al.*<sup>69</sup> synthesized  $\text{NiFe}_2(\text{L})_2 \cdot (\text{N}_2\text{H}_4)_2$  (L= $\text{C}_8\text{H}_7\text{O}_3\text{Cl}_2$ ). They fixed chemical formula of the precursors based on the total percentage mass loss and percentage of hydrazine, nickel and iron which matches closely with the calculated ones. They confirmed the bidentate bridging nature of hydrazine ligand from IR spectral data. The TG-DTA curves showed three step decomposition and the formation of  $\text{NiFe}_2\text{O}_4$  confirmed.

Manimekalai Rakkiyasamy *et al.*<sup>70</sup> synthesized  $\text{NiCo}_2(\text{Cinn})_2(\text{N}_2\text{H}_4)_2$ . The mixed metal complexes,  $[\text{M}_{1/3}\text{Co}_{2/3}(\text{p-NO}_2\text{C}_6\text{H}_4\text{COO})_2(\text{N}_2\text{H}_4)_2]$  (M=Ni, Zn and Cd) prepared by D. Santhosh Shantha kumar *et al.*<sup>59</sup> and Rakkiyasamy Manimekalai *et al.*<sup>71</sup> reported  $\text{NiCo}_2(\text{PhAc})_2(\text{N}_2\text{H}_4)_2$  by co-precipitation method. The formation of complexes confirmed by the chemical analysis, total weight loss and infrared spectra analysis. The IR spectra indicated two absorption bands in the region  $662\text{cm}^{-1}$  and  $560\text{cm}^{-1}$  corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are characteristics of cobaltite. From TG-DTA they revealed that the precursors decompose exothermically to yield  $\text{NiCo}_2\text{O}_4$  as the final product.

Kalpanadevi Kalimuthu *et al.*<sup>72</sup> stated that  $\text{ZnFe}_2(\text{cin})_3(\text{N}_2\text{H}_4)_3$  prepared by co-precipitation method. They determined chemical formula of the precursor by elemental and EDX analysis. From IR spectrum they proved the bidentate bridging nature of hydrazine ligand. The TG-DSC showed the decomposition in two particular steps and revealed the formation  $\text{ZnFe}_2\text{O}_4$ . New mixed metal complexes of 2, 4 dichlorophenoxy acetic acid with hydrazine were synthesized by Manimekalai Rakkiyasamy *et al.*<sup>73</sup>. Agatheeshwaren Arumugam<sup>74</sup> reported  $\text{NiCo}_2\text{L}_2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and  $\text{MnCo}_2\text{L}(\text{N}_2\text{H}_4)_2$  (L=diphenylacetate) and Manimekalai Rakkiyasamy *et al.*<sup>75</sup> prepared  $\text{NiCo}_2(\text{N}_2\text{H}_4)_{1.5}(\text{crot})_2 \cdot \text{H}_2\text{O}$  and  $\text{CdCo}_2(\text{N}_2\text{H}_4)(\text{crot})_2 \cdot \text{H}_2\text{O}$  by co-precipitation method. The IR spectra showed bridging bidentate nature of hydrazine ligand. From TG-DTA they revealed that the complexes indicated their facile decomposition at relatively low temperature range to give the corresponding stable mixed metal oxides.

K. S. Rane *et al.*<sup>76</sup> reported the hydroxide, oxalate and citrate precursors of the metal oxides such as  $(\text{MnZn})\text{Fe}_2\text{O}_4$ ,  $\text{Cu}(\text{K})\text{Fe}_2\text{O}_4$ ,  $\text{BaTiO}_3$ ,  $\text{La}(\text{Sr})\text{MnO}_3$ ,  $\text{La}(\text{Sr})\text{AlO}_3$  and  $\text{La}/\text{Gd}(\text{Ca}/\text{Ba}/\text{Sr})\text{CoO}_3$ . Chemical formulas of citrate and their hydrazinates confirmed by elemental, IR and isothermal total mass loss studies. The N–N stretching frequency showed the bidentate bridging nature of hydrazine. TG-DSC revealed that all the precursors yield respective metal oxide as a final residue. L. R. Gonsalves *et al.*<sup>77-79</sup> prepared cobalt zinc ferrous fumarato-hydrazinate with various compositions  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ,  $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$  and  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$  (x = 0, 0.1, 0.3, and 0.4). Sinduja C. R. *et al.*<sup>80</sup> in 2013 reported the preparation of  $\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2(\text{PhAc})_3(\text{N}_2\text{H}_4)_5$ . IR data indicated the monodentate linkage of both carboxylate groups in the dianion and the bidentate bridging nature of the hydrazine ligand. The chemical formula of the complexes fixed based on the observed percentage of hydrazine and metals which matches closely with the calculated one. TG-DSC confirmed the formation of respective mixed metal oxides as an end product.



U. B. Gawas *et al.*<sup>81-83</sup> reported  $\text{Ni}_{0.5}\text{Mn}_{0.1}\text{Zn}_{0.4}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ ,  $\text{Mn}_{0.3}\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$  and  $\text{Ni}_{0.5-x}\text{Mn}_x\text{Zn}_{0.5}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$  ( $x=0.0-0.5$ ) with various compositions. The chemical formula of the precursors fixed based on the total percentage mass loss, percentages of hydrazine, nickel, manganese, zinc and iron which match closely with the calculated values. IR spectra of these complexes showed that the bidentate bridging nature of hydrazine ligand while fumarate anion showed monodentate behavior. From TG-DTA they revealed the mixed metal oxide as a final residue.

## CONCLUSION

Hydrazine complexes with transition metals<sup>8,33-42,44,46-59,62-83</sup>, lanthanides<sup>45,60,61,76</sup>, actinides<sup>43,76</sup> and carboxylic acids<sup>33-83</sup> are discussed in this review. Large number of mono-metal hydrazine complexes<sup>33-63</sup>, bi-metal complexes<sup>8,53,59,64-75</sup>, tri-metal complexes<sup>76-80</sup> and tetra-metal complexes<sup>81-83</sup> are reported by various researchers. Some complexes suggested high-spin octahedral geometry<sup>33,35-42,44-48,50,51,53,55,56,63</sup> and spin-free type octahedral geometry<sup>34</sup> from electronic spectra. IR data showed bidentate bridging nature of hydrazine ligand<sup>8,33-42,47,51-59,62-83</sup> in most of the complexes. There were some cases indicated monodentate nature of  $\text{N}_2\text{H}_4$  ligand<sup>43</sup> and the existence of  $\text{N}_2\text{H}_5^+$  ion<sup>35,48</sup> in which some were coordinated and non-coordinated  $\text{N}_2\text{H}_5^+$  ion<sup>60,61</sup>. Unidentate coordination of carboxylate groups are also reported<sup>34,47,48</sup>. From TG data most of the complexes revealed the formation of metal oxides<sup>8,33-41,43-47,49-83</sup>, metal carbonates<sup>37,48</sup> and metal sulfates<sup>42</sup>. The thermal decomposition takes place in single step<sup>34,35,38,47,56,75</sup>, two steps<sup>33,34,37-39</sup> and multi steps<sup>36,44,45,49,51,52,60,64,67-69,77,78,81-83</sup> to give an end product.

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