Thermal behaviour of metal(II) isonicotinate tetrahydrates

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Received 15 February 2010; revised and accepted 2 June 2010

Metal isonicotinate tetrahydrates with M = Mn, Fe, Co, Ni, Cu, Zn are analogous hexacoordinate complexes of the type trans-[M(NC$_2$H$_3$-p-CO$_2$)$_2$(OH$_2$)$_4$], which form a robust 3-D supramolecular network in the solid state. Hydrogen bonds formed between OH$_2$ donors and CO$_2$- acceptors strongly hold the water molecules and the isonicotinato ligands together with the metal ions to make these compounds quite stable in air at room temperature. Thermogravimetric analysis shows that these complexes lose weight in two well defined steps occurring in the 50-600 °C range. Thermogravimetric data on the compounds are found to follow metal-dependence close to expectations based on the Irving-Williams order for bivalent metal ions.

**Keywords:** Coordination chemistry, Hydrogen bonded network, Thermogravimetry, Thermal stability, Irving-Williams order, Metal isonicotinate tetrahydrates

Stability of metal complexes depends both on the metal ion as well as a given set of ligands. It was concluded earlier that thermal analysis techniques may play an important role in studying the relative stabilities of metal complexes. Systematic thermogravimetric (TG) studies on a given series of closely related complexes may be used to examine whether or not thermal decomposition behaviour of the complexes in the solid state complies with principles of coordination chemistry regarding the stability of complexes, estimated primarily from studies in the solution phase. Since thermal behaviour of molecular solids is influenced by intermolecular forces, such studies may also provide important information regarding the strength of supramolecular interactions which play an important role in determining crystal structures.

In the above context it may be pointed out that the metal(II) isonicotinate tetrahydrates, formulated as trans-[M(NC$_2$H$_3$-p-CO$_2$)$_2$(OH$_2$)$_4$], constitute a series of analogous complexes which are air-stable, non-hygroscopic and poorly soluble in water. In view of this, it is instructive to examine if their thermal behaviour follows metal dependence suggested by earlier work of Donia et al. on other complexes of transition metal ions containing amines, Schiff’s bases and carboxylates as ligands. These authors have suggested a relationship between the room temperature structures of transition metal complexes and their thermal stabilities by studying groups of related complexes. Such studies may be of help in clarifying the different factors affecting the thermal stability of metal complexes.

In addition to establishing the relationship between structure and thermal decomposition behaviour, TG studies may also indicate the temperature window in which a given thermal decomposition product may remain stable. Through such studies it may be possible to design temperature induced synthetic procedures to be used for preparing nanostructured materials via thermal decomposition. Furthermore, studies on the closely related coordination complexes having the general formula, trans-[M(NC$_2$H$_3$-p-CO$_2$)$_2$(OH$_2$)$_4$], are also likely to enable us to probe whether their thermal stabilities follow the well known Irving-Williams order for bivalent metal ions.

Thermal decomposition behaviour of trans-[Cu(NC$_2$H$_3$-p-CO$_2$)$_2$(OH$_2$)$_4$] has been described earlier by Sileo et al. We have also discussed the TG behaviour of the same species in the context of its use in the gravimetric determination of copper. Herein we report the TG behaviour of six complexes of type trans-[M(NC$_2$H$_3$-p-CO$_2$)$_2$(OH$_2$)$_4$] or M(C$_6$H$_5$O$_2$N)$_2$(H$_2$O)$_4$ [M = Mn (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6)] to evaluate their relative thermal stabilities.
Materials and Methods

The metal isonicotinate tetrahydrates, $\text{M(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_4$ with $\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn}$ have been prepared by following a general method described by us earlier\(^2\). The TG studies were carried out using a Shimadzu TGA-50 thermal analyser in the 50-600 °C range. Samples were ground to the fine powder state prior to loading into the quartz cup used as the sample holder. Sample weight used was ~20 mg. Thermal decomposition behaviour was determined by increasing sample temperature at the rate of 10°/min in an atmosphere of dry nitrogen gas flowing at the rate of 20 mL/min. Origin 8.0 was used to draw the DTG curves from the TG data\(^9\).

Results and Discussion

The tetraaquabis(isonicotinato)metal(II) species, $\text{M(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_4$ ($\text{M} = \text{Mn (1), Fe (2), Co (3), Ni (4), Cu (5), Zn (6)}$), constitute a series of well-defined complexes which may be easily prepared in excellent yield by a simple procedure. All the complexes have been characterized by a variety of physicochemical techniques including single crystal X-ray diffraction\(^10\). The TG curves obtained for the compounds are plotted together in Fig. 1. It can be clearly seen that although there are differences in the temperature ranges in which weight loss occurs for the various species, by and large the curves are similar. The weight loss up to 600 °C occurs in two major steps. While the first step in the curves is due to dehydration of the samples used, the second one is an outcome of irreversible decomposition of the dehydrated products. This thermal decomposition behaviour is also clearly shown in Fig. 2, where a comparison of the DTG curves of complexes 1-6 is shown.

Step I: Dehydration

The first step corresponding to a mass loss of ca. 19 % is due to the complete dehydration of the metal(II) isonicotinate tetrahydrates. The initial and final dehydration temperatures for the six compounds are listed in Table 1. It is observed from the tabulated data that weight loss due to dehydration occurs over the widest range of temperatures in the case of Ni(C$_6$H$_4$O$_2$N)$_2$(H$_2$O)$_4$ (4) for which the (isolated) product appearance is distinctly different from the other compounds. During its preparation this particular compound is obtained as a finely divided light blue powder. No well-defined crystals are visible in a sample of this compound even under microscopic examination. Other samples of M(C$_6$H$_4$O$_2$N)$_2$(H$_2$O)$_4$ are visibly microcrystalline in nature. The lowest onset as well as final ($T_i$ and $T_f$) values for thermal dehydration is noted for the Zn compound. This may be attributed to the fact that zinc, unlike the other metals under study, is a non-transition metal, and hence not subject to crystal field stabilization effects. According to the well-known Irving-Williams series the general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is given in (1), but it is modified to

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**Fig. 1** – TG curves of M(C$_6$H$_4$O$_2$N)$_2$(H$_2$O)$_4$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn; 1-6}$) in the 50-600 °C range.

**Fig. 2** – DTG traces of 1-6 showing the rates of mass loss during thermal decomposition in the 50-600 °C range.
Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)

invariably distorted due to Jahn-Teller effect.

concede that six-coordinate copper(II) complexes are

(2) after taking account of crystal field effects to
concede that six-coordinate copper(II) complexes are
invariably distorted due to Jahn-Teller effect.

Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)

...(1)

Mn(II) < Fe(II) < Co(II) < Ni(II) > Cu(II) > Zn(II)

...(2)

On account of the above reason, all six-coordinate 

Cu²⁺ centres in metal complexes are generally characterized by two long and four short M–L bonds in the coordination sphere. In the crystal structure of 

Cu(C₆H₄O₂N)₂(H₂O)₄, the Cu–L bonds along the direction of the C₄ axis are over 2.4 Å, while the other four are ca. 2.0 Å. Since the two long bonds are Cu–O bonds, the observed structural distortion also affects the strength of the intermolecular hydrogen bonds.

It is observed that Ni(C₆H₄O₂N)₂(H₂O)₄ starts losing water molecules at a temperature below what is expected from the Irving-Williams series. On the other hand, the trends of T_{deh,max} and T_{deh,f} follow stability series (2). This immediately suggests that the thermal stabilities of the M(C₆H₄O₂N)₂(H₂O)₄ type compounds against dehydration are largely determined by the strengths of the M–O and M–N bonds present in the coordination complexes. However, formation of intermolecular hydrogen bonds is also a striking aspect of the solid state structure of metal(II) isonicotinate tetrahydrates. Since the strengths of M–OH bonds in these complexes are likely to influence the ability of O–H functionalities to serve as hydrogen bond donors, the above facts derived from TGA analysis of the compounds are consistent with the crystal structures determined by single crystal X-ray diffraction (Fig. 3). The <(D–H⋯A) values for 

Cu(C₆H₄O₂N)₂(H₂O)₄ for two of the crystallographically independent hydrogen bonds lie near 165 °C, while the other two are found to have values near 175 °C to indicate that the hydrogen bonds with lower O–H⋯O angles are weaker. Consequently, loss of water molecules could ensue at a lower temperature for this compound. The low onset temperature observed for Ni(C₆H₄O₂N)₂(H₂O)₄ (4) is believed to be related to the apparently smaller particles in the sample which may allow for the release of water molecules from surface regions at a relatively low temperature because intermolecular hydrogen bonds are expected to be fewer in this product due to its finely divided state. The last stage of thermally induced dehydration may be attributed to the loss of water from the complex molecules present in the interior regions of the small crystallites that constitute the sample under study.

**Step II: Thermal decomposition of M(C₆H₄O₂N)₂**

It may be mentioned here that the anhydrous species M(C₆H₄O₂N)₂ obtained by application of heat to M(C₆H₄O₂N)₂(H₂O)₄ (M = Mn, Fe, Co, Ni, 

Table 1 – The first step of the thermal decomposition of M(C₆H₄O₂N)₂(H₂O)₄ due to dehydration as monitored by TG

<table>
<thead>
<tr>
<th>Complexes</th>
<th>T_{deh,f} (ºC)</th>
<th>T_{deh,max} (ºC)</th>
<th>ΔT (ºC)</th>
<th>Dehydrated product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(C₆H₄O₂N)₂(H₂O)₄ (I)</td>
<td>84</td>
<td>143</td>
<td>84</td>
<td>Mn(C₆H₄O₂N)₂</td>
</tr>
<tr>
<td>Fe(C₆H₄O₂N)₂(H₂O)₄ (2)</td>
<td>100</td>
<td>165</td>
<td>88</td>
<td>Fe(C₆H₄O₂N)₂</td>
</tr>
<tr>
<td>Co(C₆H₄O₂N)₂(H₂O)₄ (3)</td>
<td>106</td>
<td>176</td>
<td>106</td>
<td>Co(C₆H₄O₂N)₂</td>
</tr>
<tr>
<td>Ni(C₆H₄O₂N)₂(H₂O)₄ (4)</td>
<td>81</td>
<td>186</td>
<td>148</td>
<td>Ni(C₆H₄O₂N)₂</td>
</tr>
<tr>
<td>Cu(C₆H₄O₂N)₂(H₂O)₄ (5)</td>
<td>83</td>
<td>156</td>
<td>104</td>
<td>Cu(C₆H₄O₂N)₂</td>
</tr>
<tr>
<td>Zn(C₆H₄O₂N)₂(H₂O)₄ (6)</td>
<td>57</td>
<td>93</td>
<td>84</td>
<td>Zn(C₆H₄O₂N)₂</td>
</tr>
</tbody>
</table>

Fig. 3 – Hydrogen bond network (viewed along a) in the crystal structure of Cu(C₆H₄O₂N)₂(H₂O)₄ (5). The other compounds in the series also show analogous supramolecular 3-D networks in the solid state.
Cu, Zn; 1-6) are hygroscopic. The dehydrated species Cu(C₆H₄O₂N₂)₂ may be obtained by heating Cu(C₆H₄O₂N₂)₂(H₂O)₄ at 220 °C. The green anhydrous product rapidly converts to blue Cu(C₆H₄O₂N₂)₂(H₂O)₄ by absorbing moisture from air. On the other hand, the hydrothermally synthesized polymeric compound Cu(C₆H₄O₂N₂)₂2H₂O (7) was earlier shown to be convertible to Cu(C₆H₄O₂N₂)₂(H₂O)₄ (5) and vice versa.\(^{36}\) Let us now discuss the thermal behaviour of Cu(C₆H₄O₂N₂)₂ and its analogues.

As described above, the first step of the thermal decomposition of M(C₆H₄O₂N₂)₂(H₂O)₄ involves removal of water molecules from species 1-6. The second step is more complicated compared to the dehydration step. Thermal data for this decomposition step are listed in Table 2. The \(T_i\) temperatures for the complexes do not appear to show decomposition behaviour of the complexes as expected on the basis of the Irving-Williams order primarily due to the anomalous behaviour observed for the Co complex. Amongst the six complexes studied herein, the \(T_{max}\) and the \(T_i\) the values for the Cu complex appear at the minima. But for slight deviations, the trends of \(T_{max}\) and \(T_i\) to be noted is Mn(II) > Fe(II) > Co(II) > Ni(II) > Cu(II) < Zn(II), which is the reverse of the Irving-Williams order. The observed deviations may perhaps be rationalized by stating that the metal ions in the dehydrated complexes, M(C₆H₄O₂N₂)₂, may not be six-coordinate. In fact, a hydrated form of Cu(C₆H₄O₂N₂)₂ was earlier reported\(^{36}\) to be a 3-D polymer of 5-coordinate Cu(II) complexes. Moreover, at the estimated \(T_i\) values noted for 1-6 the observed mass loss values are also widely different perhaps due to the different end products which may form at higher temperatures, depending on the metal. Clearly, the decompositions of 1-6 do not proceed analogously in Step II. The anomalous behaviour noted for 3 in is believed to be due to the structural difference of Co(C₆H₄O₂N₂)₂ from the rest of the dehydrated species.

**Thermal stabilities of M(C₆H₄O₂N₂)₂(H₂O)₄ and M(C₆H₄O₂N₂)₂**

We have commented above upon the thermal stabilities of metal isonicotinate tetrahydrates on the basis of TG data. In view of our interest on the use of these compounds for analytical purposes by the gravimetric method, it is important to learn about the form of the precipitate to be weighed for analytical determination. Thermal stability of M(C₆H₄O₂N₂)₂(H₂O)₄ against dehydration may allow us to determine the conditions to be applied for drying the precipitates without decomposition. The temperatures up to which M(C₆H₄O₂N₂)₂(H₂O)₄ complexes do not lose water and the temperature ranges in which the M(C₆H₄O₂N₂)₂ complexes remain thermally stable are listed in Table 3.

The data presented in Table 3 show that the dehydrated products, M(C₆H₄O₂N₂)₂, from the Mn and Zn compounds (1 and 6) remain stable over the widest ranges of temperatures, while the Ni and Cu compounds (4 and 5) are stable over the narrowest ranges. Since any weight loss at this stage is likely to involve the breaking of M–L bonds, the thermal stability of M(C₆H₄O₂N₂)₂ is controlled by the strengths of the M–N or M–O bonds. In view of the comparable strengths of the M–N(pyridyl) and M–O(carboxyl) bonds, it is difficult to say which one is likely to break, in spite of the fact that under the temperature conditions decarboxylation is a near certainty. It must be stated that TG curves for the

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**Table 2** - Step II of the TG decomposition of M(C₆H₄O₂N₂)₂(H₂O)₄ (1-6)

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(T_i) (TG) (°C)</th>
<th>(T_{max}) (DTG) (°C)</th>
<th>(T_i) (TG) (°C)</th>
<th>Total mass loss (%) at (T_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(C₆H₄O₂N₂)₂(H₂O)₄ (1)</td>
<td>380</td>
<td>451</td>
<td>498</td>
<td>69.5</td>
</tr>
<tr>
<td>Fe(C₆H₄O₂N₂)₂(H₂O)₄ (2)</td>
<td>315</td>
<td>458</td>
<td>486</td>
<td>61.5</td>
</tr>
<tr>
<td>Co(C₆H₄O₂N₂)₂(H₂O)₄ (3)</td>
<td>386</td>
<td>453</td>
<td>491</td>
<td>68.9</td>
</tr>
<tr>
<td>Ni(C₆H₄O₂N₂)₂(H₂O)₄ (4)</td>
<td>286</td>
<td>380</td>
<td>456</td>
<td>70.3</td>
</tr>
<tr>
<td>Cu(C₆H₄O₂N₂)₂(H₂O)₄ (5)</td>
<td>266</td>
<td>293</td>
<td>316</td>
<td>67.2</td>
</tr>
<tr>
<td>Zn(C₆H₄O₂N₂)₂(H₂O)₄ (6)</td>
<td>350</td>
<td>456</td>
<td>533</td>
<td>56.4</td>
</tr>
</tbody>
</table>

**Table 3** - The second step of the thermal decomposition of M(C₆H₄O₂N₂)₂(H₂O)₄ as monitored by TG

<table>
<thead>
<tr>
<th>Complexes</th>
<th>(T_{d(is)}) (TG) (°C)</th>
<th>Dehydrated product</th>
<th>Stability range (°C)</th>
<th>(ΔT) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(C₆H₄O₂N₂)₂(H₂O)₄ (1)</td>
<td>84</td>
<td>Mn(C₆H₄O₂N₂)₂</td>
<td>168-380</td>
<td>212</td>
</tr>
<tr>
<td>Fe(C₆H₄O₂N₂)₂(H₂O)₄ (2)</td>
<td>100</td>
<td>Fe(C₆H₄O₂N₂)₂</td>
<td>188-315</td>
<td>127</td>
</tr>
<tr>
<td>Co(C₆H₄O₂N₂)₂(H₂O)₄ (3)</td>
<td>106</td>
<td>Co(C₆H₄O₂N₂)₂</td>
<td>212-386</td>
<td>174</td>
</tr>
<tr>
<td>Ni(C₆H₄O₂N₂)₂(H₂O)₄ (4)</td>
<td>81</td>
<td>Ni(C₆H₄O₂N₂)₂</td>
<td>229-286</td>
<td>57</td>
</tr>
<tr>
<td>Cu(C₆H₄O₂N₂)₂(H₂O)₄ (5)</td>
<td>83</td>
<td>Cu(C₆H₄O₂N₂)₂</td>
<td>182-266</td>
<td>79</td>
</tr>
<tr>
<td>Zn(C₆H₄O₂N₂)₂(H₂O)₄ (6)</td>
<td>57</td>
<td>Zn(C₆H₄O₂N₂)₂</td>
<td>141-350</td>
<td>209</td>
</tr>
</tbody>
</table>
compounds are not definitive enough to say the final words in this regard. The TG data however suggest that for complex 5 the M–L bond strength is the lowest. On the other hand, the \( T_{\text{deh,i}} \) is the lowest for the Zn compound (6). Nevertheless, one obvious observation for all six compounds is that the onset temperature for dehydration is either slightly over 100 °C or somewhat lower than 100 °C. In view of the above results it may be stated that since any thermal decomposition may depend on the sample consistency, a few degrees of temperature may not be of much significance in bringing forth decisive results. However, it may be stated clearly that all the compounds may be dried without any change in stoichiometry at temperatures up to 50 °C. This underlines the compositional stability of compounds 1-6 under ordinary conditions.

**Mechanism of thermal decomposition of \( \text{M(C}_6\text{H}_4\text{O}_2\text{N)}_2 \)**

As in the case of the thermal analysis of many other compounds, it is rather hazardous to make decisive comments on the nature of thermal decomposition as observed by TG studies on the metal isonicotinate tetrahydrates, \( \text{M(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_4 \) (M = Mn, Fe, Co, Ni, Cu, Zn; 1-6), particularly at high temperatures. It also needs to be emphasized that analyses of the evolved gases as well as solid residues obtained via thermal decomposition are highly important for drawing useful conclusions regarding thermal decomposition behaviour on the basis of TG results. Primarily based on chemically expected decomposition routes we summarize overall possibilities on the thermal decomposition of \( \text{M(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_4 \) in Scheme 1. Assuming thermal decomposition according to steps (i) and (ii) of Scheme 1, we expect a combined weight loss of ca. 67.5 % for the complexes. For the copper complex these two reactions appear to be certainly involved because, as shown in Fig. 4, there is no appreciable weight loss in the temperature range of 316-333 °C (observed weight loss = 67.18 %). Above 333 °C, the weight loss for this compound is rather gradual and the total mass loss may be expected to be on the basis of step (iii) in Scheme 1. However, for \( \text{Cu(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_4 \) the oxide forming at the end of the thermal decomposition may as well be \( \text{Cu}_2\text{O} \) or even metallic Cu, during the formation of which competing reactions involving other likely products such as C, \( \text{CO}_2 \) could be taking place simultaneously. In view of the above, it is obvious that in order to establish the mechanism of Step II, TG behaviour of the complexes needs to be studied up to an even higher temperature and at the same time the decomposition products need to be identified unambiguously using complementary experimental techniques\(^{12} \).

It may be mentioned here that Sileo et al. had previously described the thermal behaviour of \( \text{Cu(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_4 \). Although these authors studied the thermal decomposition products using techniques such as X-ray diffraction and scanning electron microscopy, the findings regarding the second step of thermal decomposition remained inconclusive. The

\[
\begin{align*}
\text{[M(NH}_4\text{C}_5\text{p-CO}_2\text{)]_2(OH}_2\text{)]_4} & \xrightarrow{-4\text{H}_2\text{O}} \text{[M(NH}_4\text{C}_5\text{p-CO}_2\text{)]_2} \quad (i) \\
\text{[M(NH}_4\text{C}_5\text{p-CO}_2\text{)]_2} & \xrightarrow{-\text{CO + NH}_4\text{C}_5\text{p-C}_2\text{H}_4\text{N}} \text{MCO}_3 \quad (ii) \\
\text{MCO}_3 & \xrightarrow{-\text{CO}_2} \text{MO} \quad (iii) \\
\text{CoCO}_3 & \xrightarrow{-\text{CO}} \text{CoO}_2 \quad (iv) \\
3\text{CoO}_2 & \xrightarrow{-2\text{O}_2} \text{Co}_3\text{O}_4 \quad (v) \\
\text{[Cu(NH}_4\text{C}_5\text{p-CO}_2\text{)]_2(OH}_2\text{)]_4} & \xrightarrow{-4\text{H}_2\text{O}, 18.97\%} \quad (vi) \\
& xrightarrow{-\text{CO + NH}_4\text{C}_5\text{p-C}_2\text{H}_4\text{N}, 48.49\%} (vii) \\
& xrightarrow{-\text{CO}_2, 11.59\%} \quad (viii) \\
\text{NH}_4\text{C}_5\text{p-CO}_2\text{N} & \xrightarrow{\text{N}} \text{NH}_4\text{C}_5\text{p-C}_2\text{H}_4\text{N} + \text{N} \\
\end{align*}
\]

\[
\text{Total weight loss expected: 79.05\%} \\
\text{Total weight observed: 76.21\% at 800°C}
\]

**Scheme 1**
Table 4 – Thermal decomposition of $\text{M}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ as expected from the scheme proposed by Sileo et al.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Thermal decomposition according to:</th>
<th>Expected weight loss (%) due to removal of volatile products</th>
<th>Max. observed weight loss (%) at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ (1)</td>
<td>$5 \text{M}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4 = 5\text{M}(s) + 10\text{CO}_2(g) + 8\text{N}_2\text{H}_3(g) + \text{N}_2(g) + 10\text{C}(s)$</td>
<td>78.73</td>
<td>63.28</td>
</tr>
<tr>
<td>$\text{Fe}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ (2)</td>
<td></td>
<td>78.53</td>
<td>65.43</td>
</tr>
<tr>
<td>$\text{Co}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ (3)</td>
<td></td>
<td>77.89</td>
<td>74.58</td>
</tr>
<tr>
<td>$\text{Ni}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ (4)</td>
<td></td>
<td>77.94</td>
<td>73.39</td>
</tr>
<tr>
<td>$\text{Cu}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ (5)</td>
<td></td>
<td>76.94</td>
<td>71.89</td>
</tr>
<tr>
<td>$\text{Zn}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ (6)</td>
<td></td>
<td>76.58</td>
<td>57.25</td>
</tr>
</tbody>
</table>

Scheme 2

stoichiometry for the thermal decomposition proposed by Sileo et al. is as given in Scheme 2.

The above equations appear to account for the results obtained for 5 on an empirical basis. Expected weight loss values for compounds 1-6 on the basis of Scheme 2 are given in Table 4.

In view of the above results obtained by us, it is not clear if the same equation may be applied to explain the thermal decomposition of the other complexes. In any case, the samples must be studied in more detail to find out how the final mass losses relate to the expected values according to Scheme 2. It is also notable that in the thermal decomposition of sodium isonicotinate hydrate, Sileo et al. observed the formation of Na$_2$CO$_3$ at 495 °C, but the authors refrained from giving the overall stoichiometry of the thermal decomposition of sodium isonicotinate based on their TG and DTA studies.

Conclusions

Thermal decomposition behaviour of $\text{Mn}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn}$) is primarily dependent on the nature of the metal atom and also that complete decomposition pathways are difficult to establish. All six compounds are stable under ordinary conditions against mass loss due to dehydration. The thermally induced dehydration of the compounds follows the Irving-Williams order of stabilities for bivalent metal ions. The dehydrated products have broad stability windows, but at higher temperatures they undergo further decomposition via complicated pathways.

Acknowledgement

The authors thank Department of Science & Technology, Govt. of India, and University Grants Commission, India, for financial support.

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