

Cobalt (II), Nickel (II), Zinc (II) and Manganese (II) Complexes of Pyridine-n-Carboxylic Acids with Hydrazine as a Ligand

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Abstract

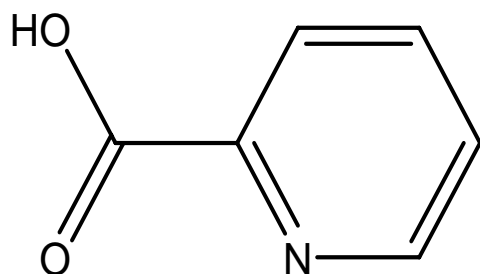
Metal hydrazine, pyridine-2-carboxylate hydrates, pyridine-3-carboxylate hydrates, $[ML(N_2H_4)_{0.5}.H_2O]$ where L = pyridine-2-carboxylic acid, pyridine-3-carboxylic acid and M = Co, Ni, Mn and Zn have been prepared and characterized by analytical, IR, UV-Vis and XRD Studies. Thermal decomposition of the compounds is studied from room temperature to 1200^oC by TG-DTA analysis. The compounds were found to decompose auto catalytically, once ignited. UV spectra measurements indicate that all the Co and Ni complexes are high- spin octahedral in nature. The IR studies show that N-N stretching frequency at 971 – 985 cm⁻¹ suggesting a bidentate bridging structure of hydrazine molecules to the central metal ion in all the complexes. $\gamma_{sym} - \gamma_{asym}$ separation of 194 – 180 cm⁻¹ indicating monodentate linkage of carboxylate groups.

Keywords: Hydrazine, pyridine-2-carboxylate, pyridine-3-carboxylate, IR spectra, Thermal decomposition.

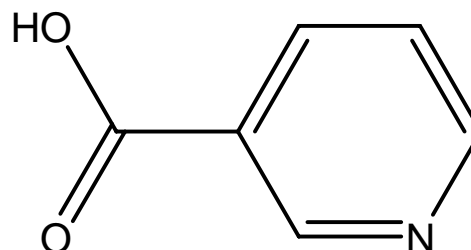
Introduction

Preparation, characterization and thermal reactivity of divalent transition metal complexes of hydrazine with dinitrogen heterocyclic dicarboxylic acids [1] namely 2-pyrazinecarboxylic acid, 3,5-pyrazinecarboxylic acid [2] and 3,5-dicarboxylic acid, 4,5-imidazole dicarboxylic acid [3] are reported. But there is no report on transition metal complexes of hydrazine with pyridine-2-carboxylic acid namely picolinic acid and pyridine-3-carboxylic acid namely nicotinic acid. pyridine-3-carboxylic acid

forms chelating complex with chromium, zinc, manganese, copper, iron and molybdenum in the human body. This gives us to the idea to prepare transition metal complexes using these carboxylic acids.



pyridine-2-carboxylic acid



pyridine-3-carboxylic acid

Experimental

Preparation of the complexes

Preparation of $ML_2 \cdot 0.5N_2H_4 \cdot H_2O$ Where $M = Co, Ni, Mn$ or Zn $L =$ pyridine-2-carboxylate or pyridine-3-carboxylate

In 50 mL of warm water pyridine-n-carboxylic acid (1.190 g 0.009 mol) is dissolved. The solution is heated on a water bath for about 1 hr and respective carbonate of metals is added until no more carbon dioxide is evolved. The excess carbonate is removed by filtration and to this filtrate hydrazinehydrate (0.2 mL, 0.003 mol) is added drop by drop with constant stirring. The content of the beaker is concentrated on water bath. Then it is kept aside for complexation. After 24 hrs cobalt, nickel and zinc complexes are separated in the form of semi solid where as manganese complexes are also separated as semi solid after 7 days. The semi solids are washed with ether. During ether washing complexes are separated as amorphous powder. The complexes so obtained are highly hygroscopic.

Results and Discussion

The analytical data of the complexes are compatible with the proposed composition for the complexes (Table 1)

Table 1: Analytical data.

| S. No. | Compound | Hydrazine % | | Metal % | |
|--------|--|-------------|------------|---------|------------|
| | | Found | Calculated | Found | Calculated |
| 1. | $Co(Pic)_2 \cdot 0.5N_2H_4 \cdot H_2O$ M. Wt. : 335.22 | 4.2 | 4.77 | 17.95 | 17.39 |
| 2. | $Ni(Pic)_2 \cdot 0.5 N_2H_4 \cdot H_2O$ M. Wt. : 334.22 | 4.8 | 4.7 | 16.91 | 17.33 |

| | | | | | |
|----|--|------|------|-------|-------|
| 3. | Mn(Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O M. Wt. : 335.13 | 5.4 | 4.8 | 15.00 | 16.37 |
| 4. | Zn(Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O M. Wt. : 345.63 | 3.9 | 4.6 | 19.00 | 18.92 |
| 5. | Co(nic) ₂ 0.5N ₂ H ₄ . H ₂ O M. Wt. : 339.23 | 3.40 | 4.40 | 15.90 | 16.06 |
| 6. | Ni(nic) ₂ 0.5 N ₂ H ₄ . H ₂ O M. Wt. : 328.94 | 3.60 | 4.70 | 16.00 | 17.53 |
| 7. | Mn(nic) ₂ 0.5 N ₂ H ₄ . H ₂ O M. Wt. : 335.13 | 4.00 | 4.84 | 14.94 | 16.30 |
| 8. | Zn(nic) ₂ 0.5 N ₂ H ₄ . H ₂ O M. Wt. : 345.63 | 3.36 | 4.60 | 18.20 | 19.17 |

Magnetic moments and Electronic spectra

The effective magnetic moments of cobalt and nickel complexes lie in the range 5.10 – 5.68 BM and 2.79 – 3.28 B.M. respectively, suggesting a high-spin octahedral environment for the metal atoms. As expected the zinc, cadmium complexes are diamagnetic. The cobalt complexes show band in the range 17,800 – 18,600 cm⁻¹ which usually splits into two bands due to spin-orbit coupling in the ⁴T_{1g} state and which is assigned to ⁴Tig(F) → ⁴Tig(p) transition of typical six – coordinated Co(II) complexes [4]. The nickel complexes show two bands in the regions 10,800–13,700 and 16,770- 18,980cm⁻¹ which are due to ³A_{2g} → ³T_{2g} and ³A_{2g} → ³T_{1g} (F) transition.

Infrared spectra

Infrared spectra of the prepared complexes are given in table 2. These exhibit broad bands centered at 3326 cm⁻¹ due to O-H stretching, confirming the presence of water molecules in the compound. The absence of sharp band for OH stretching is due to the H₂O involved in intramolecular hydrogen bonding in the complex structure. The peak due to N-H stretching overlaps with the peak corresponds to O-H stretching. The band in the region 1624 – 1604 cm⁻¹ corresponds to the ring vibration. The increase in the value of the ring vibration (about 2 cm⁻¹) relative to the free ligand value shows the coordination of the ring nitrogen to the metal [5]. The asymmetric and symmetric stretching frequencies of carboxylate ions are seen at 1582 – 1520 cm⁻¹ and 1394 – 1326 cm⁻¹ respectively with a $\gamma_{\text{asym}} - \gamma_{\text{sym}}$ separation of 194 – 180 cm⁻¹ indicating the monodentate linkage of both carboxylate group. The N-N stretching frequencies of these complexes appear at 985 – 971 cm⁻¹ respectively, indicating bidentate bridging N₂H₄ molecule. The Infrared spectra of Co(Pic)₂ 0.5N₂H₄ . H₂O and Zn(Pic)₂ 0.5N₂H₄ . H₂O are given as representative examples.

Table 2: IR Spectral data (cm⁻¹).

| S.No | Compound | γ_{OH} of water | γ_{N-H} | Ring vibration | γ_{asym} | γ_{sym} | $\gamma_{asym} - \gamma_{sym}$ | γ_{N-N} |
|------|---|------------------------|----------------|----------------|-----------------|----------------|--------------------------------|----------------|
| 1 | Co(Pic) ₂ 0.5N ₂ H ₄ . H ₂ O | 3326(b) | - | 1618 | 1560 | 1375 | 185 | 981 |
| 2 | Ni(Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O | 3326(b) | - | 1618 | 1560 | 1375 | 185 | 981 |
| 3 | Mn(Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O | 3326(b) | - | 1624 | 1574 | 1385 | 189 | 981 |
| 4 | Zn(Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O | 3326(b) | - | 1616 | 1566 | 1382 | 184 | 981 |
| 5 | Co(nic) ₂ 0.5N ₂ H ₄ . H ₂ O | 3326(b) | - | 1620 | 1565 | 1385 | 180 | 985 |
| 6 | Ni(nic) ₂ 0.5 N ₂ H ₄ . H ₂ O | 3326(b) | - | 1618 | 1565 | 1380 | 185 | 982 |
| 7 | Mn(nic) ₂ 0.5 N ₂ H ₄ . H ₂ O | 3326(b) | - | 1604 | 1520 | 1326 | 194 | 971 |
| 8 | Zn(nic) ₂ 0.5 N ₂ H ₄ . H ₂ O | 3326(b) | - | 1612 | 1582 | 1394 | 180 | 985 |

Thermal studies

All complexes undergo two steps of decomposition except Ni(pic)₂0.5N₂H₄.H₂O. The first step corresponds to dehydration and dehydrazination with endothermic or exothermic peak in the range of 102 – 305°C confirming the coordination of the water in these complexes. The anhydrous intermediate decomposes into mixture of metal oxide and metal carbonate as the end product. Similar to that of transition metal complexes of pyridine-2, n-dicarboxylates (n = 3, 4, 5 and 6) [6]. TG – DTA pattern of Co(Pic)₂0.5N₂H₄.H₂O and Ni(Pic)₂0.5N₂H₄.H₂O are given in Fig. 3 and 4.

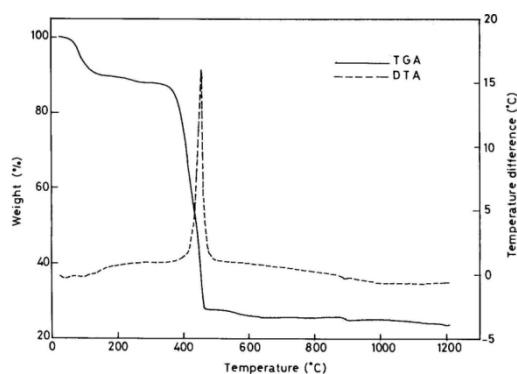


Figure 3: TG – DTA pattern of Co(Pic)₂ 0.5N₂H₄ . H₂O

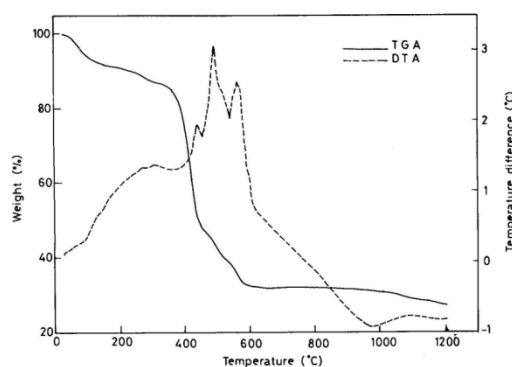


Figure 4: TG – DTA pattern of Ni(Pic)₂ 0.5N₂H₄ . H₂O

Table 3: TG – DTA Analysis

| S. No. | Compound | Thermo gravimetry | % weight loss | | DTA peak | Product |
|--------|--|------------------------------|-------------------------|-------------------------|------------------------------|---|
| | | | Cal | Obs | | |
| 1 | Co(Pic) ₂ 0.5N ₂ H ₄ . H ₂ O M.Wt. : 339.23 | 50-125 125-465 | 10.02 71.75 | 9.12 69.50 | 123(+) 460 (-) | CoL ₂ Co O + CoCO ₃ |
| 2 | Ni(Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O M.Wt. : 338.74 | 86-320 258-450 450-581 | 10.03 54.00 66.72 | 11.00 56.09 64.95 | 305(+) 443 (-) 497 (-) | NiL ₂ Ni (HCOO) ₂ NiCO ₃ |
| 3 | Mn (Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O M.Wt. : 335.19 | 70-149 149-482 | 10.15 71.98 | 9.80 70.20 | 102(+) 478 (-) | MnL ₂ MnO + MnCO ₃ |
| 4 | Zn (Pic) ₂ 0.5 N ₂ H ₄ . H ₂ O M.Wt. : 345.63 | 60-169 169-500 | 9.84 70.22 | 10.20 70.00 | 150(-) 414 (-) | ZnL ₂ ZnO + ZnCO ₃ |
| 5 | Co (nic) ₂ 0.5N ₂ H ₄ . H ₂ O M.Wt. : 339.23 | 50-126 126-485 | 10.02 71.75 | 9.58 72.00 | 125(+) 462 (-) | CoL ₂ CoO + CoCO ₃ |
| 6 | Ni (nic) ₂ 0.5 N ₂ H ₄ . H ₂ O M.Wt. : 338.74 | 80-248 248-570 | 10.03 71.74 | 11.00 70.72 | 305(-) 478 (-) | NiL ₂ NiO + NiCO ₃ |
| 7 | Mn (nic) ₂ 0.5 N ₂ H ₄ . H ₂ O M.Wt. : 335.19 | 65-150 150-472 | 10.15 71.98 | 10.00 69.20 | 120(-) 471 (-) | MnL ₂ MnO + MnCO ₃ |
| 8 | Zn (nic) ₂ 0.5 N ₂ H ₄ . H ₂ O M.Wt. : 345.63 | 62-159 159-492 | 9.84 71.98 | 10.21 69.29 | 150(-) 484 (-) | ZnL ₂ ZnO + 2NCO ₃ |

Conclusion

It is found that the reaction of metal carbonates with hydrazine in the presence of pyridine-2-carboxylic acid, pyridine-3-carboxylic acid yields neutral hydrazine complexes.

Two isomeric acids form complexes of similar composition with Co, Ni, Mn and Zn. The positional change of the carboxyl groups seems to have no effect on complexation and may be due to their similar binding atoms. During heating, all complexes undergo similar types of decomposition through their metal carboxylate intermediates.

Based on the physical nature of the complexes formed, which are powdery and insoluble in any medium, polymeric six coordination nature of the complexes are proposed as under. Hydrazine acts as the bridging bidentate ligand, H₂O as monocoordinated and the pyridine carboxylates acts as bridging bidentate with carboxylate on one side and N on the other side. The following structures (fig 5,6) may be proposed for these complexes.

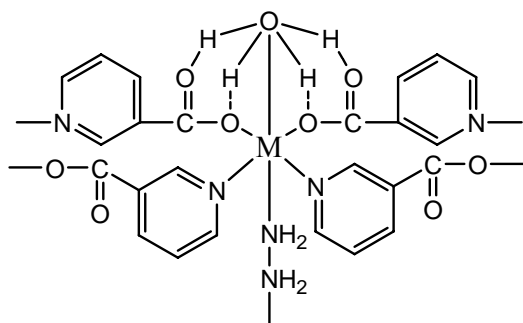


Figure 5: Proposed structure of $M(\text{nic})_2 \cdot 0.5 \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$

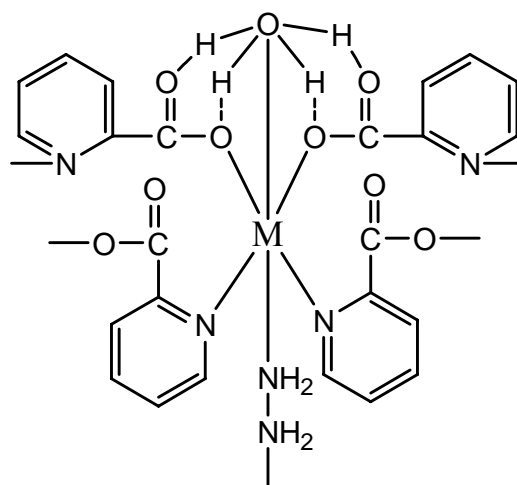


Figure 6: Proposed structure of $M(\text{pic})_2 \cdot 0.5 \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$

References

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