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TRANSITION METAL COMPLEXES OF PYRAZINECARBOXYLIC ACIDS WITH NEUTRAL HYDRAZINE AS A LIGAND

Synthesis, spectroscopic, thermal and XRD studies

*T. Premkumar and S. Govindarajan**

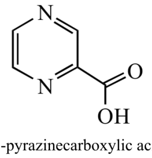
Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

New divalent Co, Ni, Zn and Cd pyrazinecarboxylate hydrazinates of the formulae $M(pyzCOO)_2 \cdot nN_2H_4 \cdot xH_2O$ and $Mpyz(COO)_2 \cdot N_2H_4 \cdot xH_2O$ obtained by the reaction of respective metal nitrate hydrates with 2-pyrazinecarboxylic (HpyzCOO)/2,3-pyrazinedicarboxylic ($H_2pyz(COO)_2$) acid and hydrazine hydrate have been characterized on the basis of analytical, spectroscopic (electronic and infrared), thermal and X-ray powder diffraction studies. The electronic spectroscopic data suggest that the cobalt and nickel complexes are of spin-free (high-spin) type with octahedral geometry. The IR absorption bands of N–N stretching in the range 980–972 cm^{-1} unambiguously prove the bidentate bridging nature of the N_2H_4 ligand. The hydrazinate complexes of 2,3-pyrazinedicarboxylate lose hydrazine molecule exothermally, whereas 2-pyrazinecarboxylate compounds lose the same endothermally. Further, all the complexes undergo endothermic (dehydration and/or dehydrazination) followed by exothermic decomposition except the Zn and Cd complexes of 2,3-pyrazinedicarboxylate, which show only exothermic decomposition. In order to know the isomorphic nature among the complexes, the X-ray powder patterns have been compared.

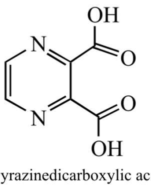
Keywords: *hydrazine, IR spectra, 2-pyrazinecarboxylic acid, 2,3-pyrazinedicarboxylic acid, thermal decomposition*

Introduction

Our current interest in transition metal chemistry began with the preparation and characterization of hydrazine complexes of some dinitrogen containing heterocyclic, both mono- and dicarboxylic acids. We recently reported the coordinating ability and thermal property of 4,5-imidazoledicarboxylic acid complexes of transition metals with hydrazine [1, 2]. We turned our attention to related six-membered ring dinitrogen containing carboxylic acids particularly, pyrazine derivatives, 2-pyrazinecarboxylic and 2,3-pyrazinedicarboxylic acids, due to their versatile coordination towards metals. While 2-pyrazinecarboxylic acid, HpyzCOO, acts as a bidentate ligand via their (N, O) moieties consisting of a heteroring nitrogen atom and an oxygen atom belonging to the nearest unidentate carboxylic group [3–6], 2,3-pyrazinedicarboxylic acid, $H_2pyz(COO)_2$, has six sites for potential coordination to a metal atom but without severe distortion it can serve as a mono- or bidentate chelating (tetradentate) ligand [7–10].



2-pyrazinecarboxylic acid
(HpyzCOO)



2,3-pyrazinedicarboxylic acid
($H_2pyz(COO)_2$)

Earlier studies carried out on bivalent metal dicarboxylates [11–14] have revealed some interesting results, such as the ability of hydrazine to behave as either a neutral or protonated ligand, and the coordinating behaviour of the dicarboxylate anions. Though, a variety of simple metal complexes of pyrazinecarboxylic acids are known with their crystal structures [4–10], there appears to be no report on transition metal hydrazine compounds of pyrazinecarboxylic acids and their thermal properties. Therefore, this paper describes the coordinating properties of the acids and thermal characterisation of their metal complexes.

Experimental

Preparation of metal 2-pyrazinecarboxylate hydrazinates

Either of the following methods has been employed for the preparation of the compounds.

- In 50 mL of warm water, 0.6205 g (0.005 mol) of 2-pyrazinecarboxylic acid was dissolved. The solution was heated on a waterbath for about 1 h, and 0.0025 mol (e.g., 0.2973 g of $CoCO_3$) of respective carbonates of the metal was added until no more carbon dioxide was evolved. The excess carbonate was removed by filtration and to this filtrate, 99–100% hydrazine hy-

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* Author for correspondence: drsgovind@yahoo.co.in

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

drate of 0.75 mL, (0.015 mol) was added drop by drop with constant stirring. The cobalt complex was obtained after 10 min at room temperature whereas nickel and zinc complexes formed only after a couple of days. The powdered crystalline complexes formed were isolated and washed successively with ice-cold water–alcohol (1:1) mixture, and diethyl ether and dried under vacuo over P_2O_5 in desiccator. In the case of cadmium, white crystalline product was isolated from the filtrate that was obtained after the removal of the insoluble cadmium 2-pyrazinecarboxylate formed initially.

- These compounds were also prepared by adding an aqueous solution (25 mL) of respective metal nitrate hydrates (e.g., 0.7712 g of $Cd(NO_3)_2\cdot 4H_2O$, 0.0025 mol; in the case of Mn, manganese(II) acetate tetrahydrate 0.6125 g, 0.0025 mol was used) to an aqueous solution (25 mL) containing a mixture of 2-pyrazinecarboxylic acid (0.6205 g, 0.005 mol) and hydrazine hydrate (1 mL, 0.02 mol), with constant stirring. The resulting solution was concentrated to ~30 mL and kept for crystallization. While the white crystalline powdered product of Cd complex was formed after 1 h, brownish green nickel compound formed after a couple of days. These complexes were isolated and dried as before. The other metals viz., Mn, Co and Zn did not yield the desired hydrazinates, instead only the insoluble metal 2-pyrazinecarboxylates were obtained in the case of manganese and cobalt, whereas the zinc gave its nitrate hydrazinate.

Preparation of metal 2,3-pyrazinedicarboxylate hydrazinates

To the hot aqueous ligand solution (100 mL) containing 2,3-pyrazinedicarboxylic acid (1.68 g, 0.01 mol) and hydrazine hydrate (2.0 mL, 0.04 mol) was added corresponding hot aqueous solution (100 mL) of metal nitrate hydrates (e.g., 2.91 g of $Co(NO_3)_2\cdot 6H_2O$, 0.01 mol; in the case of Mn, manganese(II) acetate tetrahydrate 2.45 g, 0.01 mol was used) with constant stirring. While the Co complexes precipitated after an hour, the other complexes were formed after few minutes of mixing the ligand solution. The solid products were digested over a waterbath for about 1 h and were isolated and washed as above. Our effort to isolate the Mn complex was unsuccessful due to its formation of stable $Mnpyz(COO)_2\cdot 3H_2O$ [15].

Physico-chemical techniques

All the chemicals used were pure commercial grade and the solvents were distilled before use. The hydrazine content of the complexes was determined volumetrically using a standard (0.025 M) KIO_3 solution under Andrews' condition [16]. The metals, after destroying the organic part and hydrazine by treatment with concentrated HNO_3 and evaporating the excess acid, were determined volumetrically by EDTA titration [16]. Instrumental details for elemental analysis, IR and UV-Vis spectra, TG-DTA and XRD are the same as described earlier [2].

Result and discussions

The results of chemical analysis of the complexes are given in Table 1 and are best fit with the proposed compositions viz., $M(pyzCOO)_2\cdot nN_2H_4\cdot xH_2O$, where M=Co, n=0.5 and x=1; Ni, n=1 and x=4; Zn, n=2 and x=0; Cd, n=1 or 2 , x=0, and $Mpyz(COO)_2\cdot N_2H_4\cdot xH_2O$ where for M=Co and Ni, x=3; M=Zn and Cd, x=0. The complexes are powdered solids, air stable and are insensitive to light. The Zn and Cd complexes of 2-pyrazinecarboxylate are soluble in water whereas all other complexes are insoluble in water and most of the organic solvents like alcohol, chloroform and acetone. While Co and Ni complexes are hydrated, Zn and Cd complexes are anhydrous. Cadmium gives two different products with 2-pyrazinecarboxylic acid in the same ratio, but with different starting materials and experimental condition. The monohydrazinate compound of cadmium was obtained when using the metal carbonate as a starting material, whereas dihydazinate compound isolated from the nitrate solutions.

Quite a different decomposition behaviour has been observed with each 2-pyrazinecarboxylate complex. Cobalt complex shows a two-step decomposition to give cobalt carbonate, $CoCO_3$, as the final product whereas the nickel complex undergoes an endothermic followed by exothermic decomposition in three steps to leave nickel metal as the final residue. In the case of cobalt, the first stage mass loss occurs in the range 175–320°C, is attributed to the loss of a water molecule and half a molecule of hydrazine. In DTA, this decomposition was observed as successive endotherms at 243 and 305°C, such high temperature dehydration supports the presence of a coordinated water molecule in the complexes [17]. In the second stage, the cobalt pyrazinecarboxylate intermediate undergoes exothermic decomposition to give the final products. In the case of nickel, the DTA shows an endothermic peak at 113°C, corresponding to the loss of four water molecules and this low temperature endothermic dehydration indicates that the water molecules are hydrated. The anhydrous nickel complex undergoes endothermic (215°C) followed by exothermic doublet at 425 and 518°C to give final residue via the nickel pyrazinecarboxylate intermediate.

The TG-DTA of zinc and both the mono- and dihydrazinate cadmium complexes exhibit a two-step decomposition to give the respective metal oxides as

Table 1 Analytical and IR data of the complexes

Compound	Yield/%	Colour	Found (Calculated)/%					IR spectral data/cm^{-1}			
			hydrazine	metal	C	N	H	Ring vibr.	ν_{asyCOO}	ν_{syCOO}	ν_{N-N}
$Co(pyzCOO)_2\cdot 0.5N_2H_4\cdot H_2O$	87	orange	4.59 (4.72)	16.93 (17.38)	35.08 (35.38)	20.53 (20.64)	2.81 (2.95)	1470m	1627	1365	972
$Ni(pyzCOO)_2\cdot N_2H_4\cdot 4H_2O$	88	brownish green	7.74 (7.83)	14.02 (14.36)	29.12 (29.34)	23.57 (23.96)	3.28 (3.47)	1473m	1636	1364	979
$Zn(pyzCOO)_2\cdot 2N_2H_4$	85	light yellow	16.91 (17.04)	16.98 (17.41)	31.78 (31.95)	29.47 (29.82)	3.68 (3.73)	1471m	1615	1383	974
$Cd(pyzCOO)_2\cdot 2N_2H_4$	82	white	15.21 (15.14)	25.81 (26.59)	27.95 (28.39)	26.62 (26.50)	3.12 (3.32)	1471m	1617	1384	973
$Cd(pyzCOO)_2\cdot N_2H_4$	55	white	8.01 (8.19)	28.07 (28.78)	30.81 (30.72)	20.97 (21.50)	2.41 (2.56)	1468m	1618	1380	980
$Copyz(COO)_2\cdot N_2H_4\cdot 3H_2O$	97	peach	10.19 (10.28)	18.13 (18.94)	22.63 (23.14)	17.59 (18.00)	3.75 (3.85)	1455m	1637	1387	973
$Nipyz(COO)_2\cdot N_2H_4\cdot 3H_2O$	95	light green	10.12 (10.29)	18.61 (18.88)	22.97 (23.16)	17.78 (18.02)	3.79 (3.86)	1452m	1638	1385	979
$Znpyz(COO)_2\cdot N_2H_4$	92	white	12.34 (12.14)	24.17 (24.81)	27.02 (27.33)	21.13 (21.25)	2.19 (2.28)	1458m	1619	1363	972
$Cdpyz(COO)_2\cdot N_2H_4$	93	white	10.11 (10.30)	35.87 (36.19)	22.36 (22.67)	17.19 (17.58)	2.44 (2.51)	1460m	1621	1358	976

m – medium

the end product. The hydrazine molecules are lost endothermically in the first step to leave the respective metal carboxylate as the intermediate. The intermediate formed is not thermally stable but undergo gradual decomposition in the temperature range 215–530°C to respective metal oxides. Although the anion is the same in all the complexes, the thermal decomposition modes and the temperatures of the individual complexes differ depending upon the composition, the metal ion and the nature of hydrazine.

The TG of the cobalt and nickel 2,3-pyrazinedicarboxylate complexes show two-step mass loss accordance with DTA showing a broad endotherm followed by sharp exotherm(s). The first stage mass loss (17.00%), which occurs in the range 45–150°C, is attributed to the loss of three water molecules. Such a low temperature of dehydration supports the presence of three-lattice water in these compounds. The observed mass loss (17.00%) for this step agrees well with the theoretical value (17.36%). The anhydrous hydrazinate complexes of Co and Ni show a continuous decomposition in the range 150–400°C to give the respective metal oxide as the end products. This is seen as a sharp exotherm at 340°C for cobalt compound and two successive exotherms at 259°C (broad) and 398°C (sharp) for nickel compound. The TG of the cadmium complex also shows two-step decomposition whereas the zinc compound shows a distinct single step continuous decomposition to give the respective metal oxide as the end products. The cadmium compound loses a molecule of hydrazine exothermically at 313°C in its first step to give the cadmium pyrazinedicarboxylate intermediate, which further undergoes continuous exothermic decomposition to give cadmium oxide. Though TG of the zinc compound shows continuous single step decomposition, the DTA exhibits an exothermic multiplets (Fig. 8). From the thermoanalytical curves, it is observed that both zinc and cadmium complexes are stable upto 150°C and the decomposition starts at above 150°C and completes with in 560°C.

The simultaneous TG-DTA of the metal pyrazinecarboxylate hydrazinates are shown in Figs 1–9. Our effort to isolate the intermediates was unsuccessful due to their continuous decomposition as evident from the TG. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses, which are in agreement with the calculated mass losses.

The electronic spectra of the cobalt complexes of pyrazine mono- and dicarboxylates register a broad band in the range 22.222–22.730 cm^{-1} which is assigned to $^4T_{1g}(F)\rightarrow{}^4T_{1g}$ (P) transition of typical six-coordinated cobalt(II) complex [18]. The corresponding nickel complexes exhibit two bands in the region 13.513–16.345

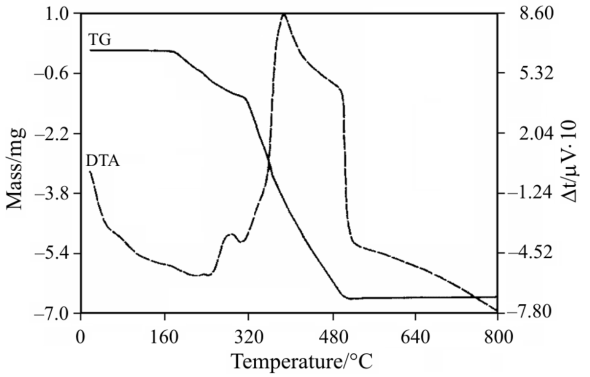

Fig. 1 Simultaneous TG-DTA of Co(pyzCOO)$_2$·0.5N$_2$H$_4$·H$_2$O

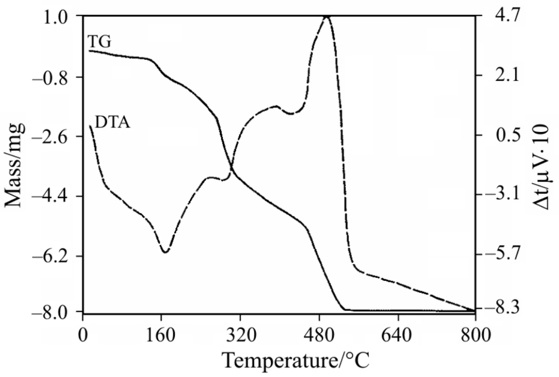

Fig. 3 Simultaneous TG-DTA of Zn(pyzCOO)$_2$·2N$_2$H$_4$

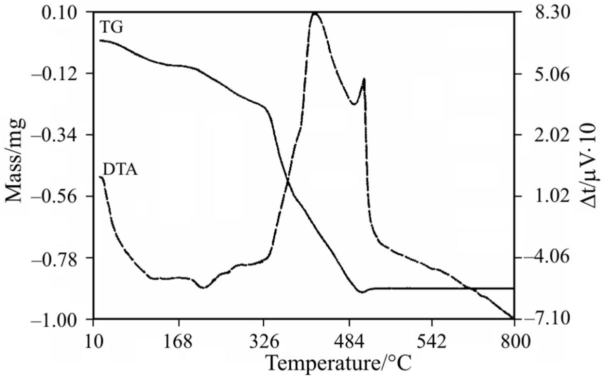

Fig. 2 Simultaneous TG-DTA of Ni(pyzCOO)$_2$·N$_2$H$_4$·4H$_2$O

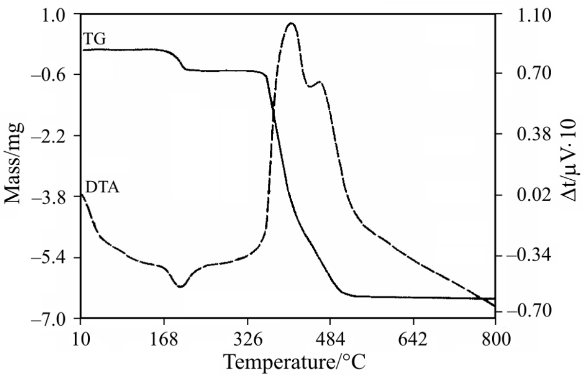

Fig. 4 Simultaneous TG-DTA of Cd(pyzCOO)$_2$·N$_2$H$_4$

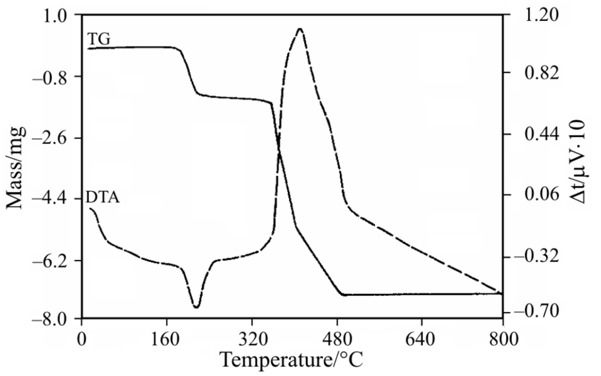

Fig. 5 Simultaneous TG-DTA of $Cd(pyzCOO)_2{\cdot}2N_2H_4$

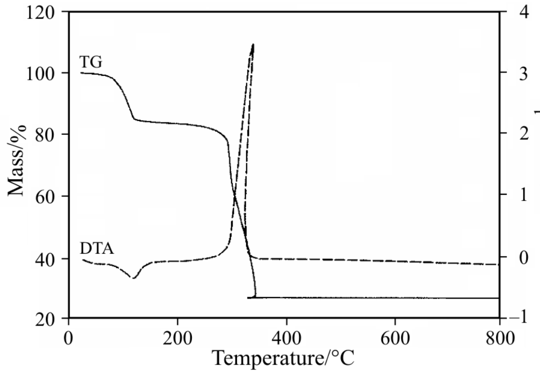

Fig. 6 Simultaneous TG-DTA of $Copyz(COO)_2N_2H_4{\cdot}3H_2O$

and 24.038–26.316 cm^{-1}, which are ascribable to $^3A_{2g}\to{}^3T_{1g}(F)$ and $^3A_{2g}\to{}^3T_{1g}(P)$ transitions, respectively, characteristic of octahedral geometry [18].

The IR absorption frequencies of importance are given in Table 1 and are assigned on the basis of earlier studies [19]. The infrared spectra of both pyrazine mono- and dicarboxylate complexes of Co and Ni show a broad band centered in the region 3437–3405 cm^{-1} due to O–H stretching frequency of water molecules which is totally absent in the Zn and Cd complexes indicating their anhydrous nature. The peaks in the range 1640–1615 and 1390–1358 cm^{-1} correspond to the asymmetric and symmetric ν(COO) frequencies of the metal bound carboxylate. The large difference in ν(COO) frequencies (Δν>230 cm^{-1}) is indicative of a monodentate coordination of the carboxylate ions to the metal. The bidentate bound hydrazines [20] of these complexes display a N–N stretching frequency in the range 979–967 cm^{-1}. The IR band centered at 1725 cm^{-1} in the spectrum of the free acid, assigned to stretching vibration of the non-ionized carboxyl group, is absent in the spectra of the $Mpyz(COO)_2{\cdot}N_2H_4{\cdot}xH_2O$ complexes, confirming that the $H_2pyz(COO)_2$ ligand is doubly ionized. The bands due to the ring vibrations of the pyrazine molecule [21] are found to move to higher frequency and the band due to the carboxyl group moves to a lower frequency in the compounds, suggesting that the nitrogen atoms in the aromatic ring and the oxygen of the carboxyl groups are coordinated to the metal atom [22, 23].

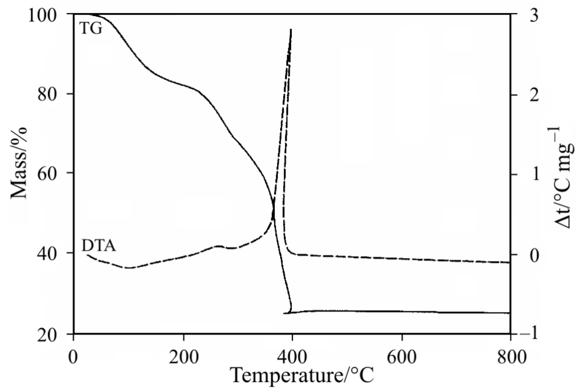

Fig. 7 Simultaneous TG-DTA of $Nipyz(COO)_2N_2H_4{\cdot}3H_2O$

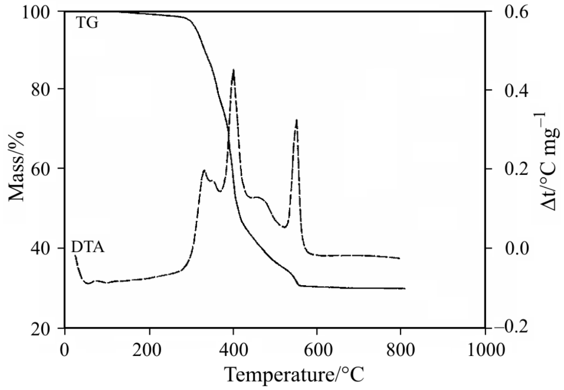

Fig. 8 Simultaneous TG-DTA of $Znpyz(COO)_2{\cdot}N_2H_4$

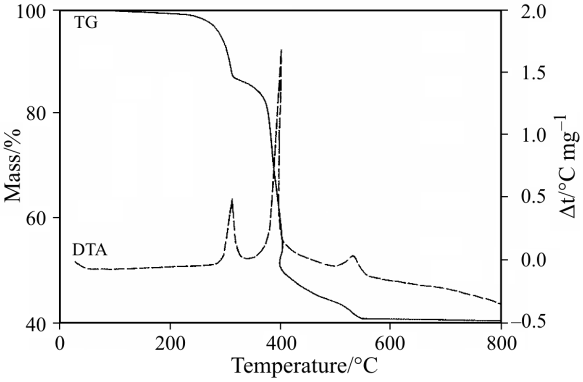

Fig. 9 Simultaneous TG-DTA of $Cdpyz(COO)_2{\cdot}N_2H_4$

The close examination of the X-ray powder patterns (Fig. 10) of the zinc and cadmium complexes of 2,3-pyrazinedicarboxylate seems to reveal isomorphism between them. X-ray diffraction pattern of the Co compound differ from that of Zn and Cd compounds suggesting that it is not isomorphic with zinc and cadmium, may be due to the presence of three lattice water molecules in the former. The diffraction pattern of the nickel compound does not show any

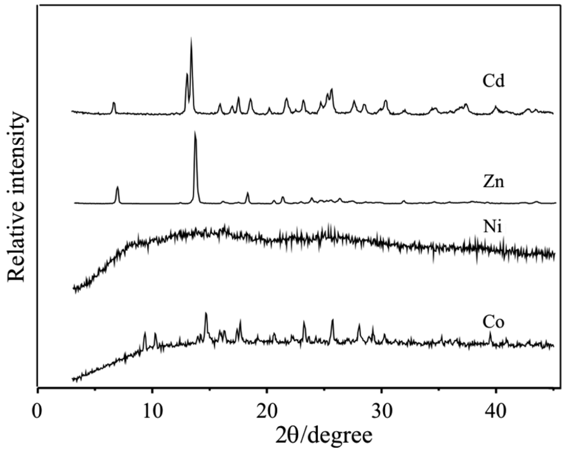

Fig. 10 X-ray powder diffraction patterns of 2,3-pyrazinedicarboxylate compounds

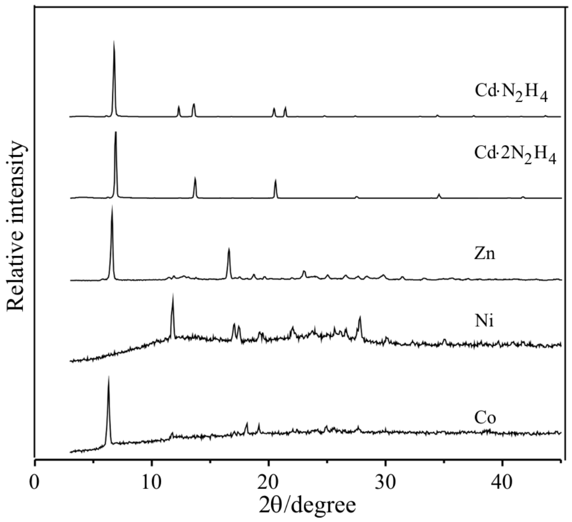

Fig. 11 X-ray powder diffraction patterns of 2-pyrazinecarboxylate compounds

peak, indicating that it is amorphous. The X-ray powder patterns of the 2-pyrazinecarboxylate (Fig. 11) compounds differ from one another, suggesting that the structures of the compounds are not same as their composition themselves is different.

Conclusions

- The cobalt and nickel complexes are hydrated whereas zinc and cadmium complexes are anhydrous.
- The fact that the compounds were obtained as polycrystalline powders and not as single crystals means that no complete structure determination could be carried out. However, IR, electronic spectroscopic and thermal data enable us to suggest the environment of the metal ion in each of the complexes. Six-coordination has been proposed for the central divalent transition metals with octahedral geometry for all the newly prepared complexes except for the Zn and Cd 2-pyrazinecarboxylate dihydrazinates, which have four coordination, probably tetrahedral geometry as reported in the metal pimalate complexes [24].
- From simultaneous TG-DTA, it is observed that hydrazinate complexes of pyz(COO)$_2$ lose hydrazine molecule exothermally, whereas pyz(COO) compounds lose the same endothermally. Further, all the complexes undergo endothermic followed by exothermic decomposition except the Zn and Cd complexes of pyz(COO)$_2$, which show only exothermic decomposition.
- It is interesting to note that, the cobalt and nickel complexes of pyz(COO)$_2$ undergo thermal decomposition comparatively at lower temperature (~370–400°C) to leave the respective metal oxide as the end products, whereas the pyzCOO compounds of the cobalt and nickel metals undergo at higher temperature (~520°C) to give cobalt carbonate and nickel metal, respectively, as the final residue. However, the zinc and cadmium complexes of both the acids undergo pyrolysis (~570°C) to give the respective metal oxide as the final products. The relatively low temperature decomposition behaviour of cobalt and nickel complexes may be attributed due to their catalytic activity [24].

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