DIVALENT TRANSITION METAL COMPLEXES OF 3,5-PYRAZOLEDICARBOXYLATE

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New divalent transition metal 3,5-pyrazoledicarboxylate hydrates of empirical formula $Mpz(COO)_2(H_2O)_2$, where M=Mn, Co, Ni, Cu, Zn and Cd ($pz(COO)_2$=3,5-pyrazoledicarboxylate), metal hydrazine complexes of the type $Mpz(COO)_2N_2H_4$ where M=Co, Zn or Cd and $Mpz(COO)_2nN_2H_4 \cdot H_2O$, where n=1 for M=Ni and n=0.5 for M=Cu have been prepared and characterized by physico-chemical methods. Electronic spectroscopic data suggest that Co and Ni complexes adopt an octahedral geometry. The IR spectra confirm the presence of unidentate carboxylate anion ($\Delta v = v_{asy}(COO^-) - v_{sym}(COO^-) > 215$ cm^{-1}) in all the complexes and bidentate bridging hydrazine (v_{N-N}=985–950 cm^{-1}) in the metal hydrazine complexes. Both metal carboxylate and metal hydrazine carboxylate complexes undergo endothermic dehydration and/or dehydrazination followed by exothermic decomposition of organic moiety to give the respective metal oxides as the end products except manganese pyrazoledicarboxylate hydrate, which leaves manganese carbonate. X-ray powder diffraction patterns reveal that the metal carboxylate hydrates are isomorphous as are those of metal hydrazine complexes of cobalt, zinc and cadmium.

Introduction

Hydrazine is a versatile ligand and it offers the possibility of different modes of coordination towards transition metal ions [1, 2]. It can function as a monodentate [3] or bridging bidentate [4, 5] ligand. Thermal reactivity of metal carboxylates with hydrazine is of increasing interest, since they serve as precursors to fine-particle oxide materials [6, 7]. Our recent interest in hydrazine chemistry began with the preparation and characterisation of metal complexes of nitrogen containing heterocyclic dicarboxylic acids [8]. Hetero-aromatic dicarboxylates have been extensively used in coordination chemistry; most reports are on pyrazines, some of which have been reviewed [9]. Among hetero-aromatic dicarboxylic acids, 3,5-pyrazoledicarboxylic acid, $pz(COOH)_2$, and 4,5-imidazoledicarboxylic acid, (H_2imdc), are particularly of interest as they have a number of attractive features. They are sterically compact, planar and have multi-donor coordination sites [10, 11]. In the five-membered diaza ring

system we have recently shown that the imidazoledicarboxylic acid can form both mono- and dianionic planar chelates with divalent transition metals under appropriate experimental conditions and the nature of decomposition of its complexes [12, 13].

Now $pz(COOH)_2$ has been chosen in order to compare the coordinating ability of carboxyl groups to that of H_2imdc, with respect to their position in the ring, with divalent transition metal under same experimental conditions. Although various metal complexes have been synthesized by using $pz(COOH)_2$ and other species as a secondary ligand viz., tetrabutylammine [10, 14], acetylacetone [15] and ethylenediamine-N,N'-di-acetic and -propionic acids [16], the simple reaction between the divalent transition metal ions and $pz(COOH)_2$ has not yet been carried out. Also, the interaction of $pz(COOH)_2$ and transition metals with hydrazine has not been studied to date. In this paper we report for the first time the preparation, spectroscopic and thermal studies on divalent transition metal complexes of 3,5-pyrazoledicarboxylate and their hydrazine adducts.
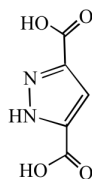
3,5-pyrazoledicarboxylic acid
($pz(COOH)_2$)
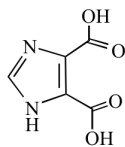
4,5-imidazoledicarboxylic acid
(H_2imdc)

Experimental

Preparation of $Mpz(COO)_2(H_2O)_2$ (M=Mn, Co, Ni, Cu, Zn and Cd)

Hot aqueous solution (50 cm^3) containing 3,5-pyrazoledicarboxylic acid (1.74 g, 0.01 mol) was added

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respective metal nitrate hydrates (e.g., 2.91 g of $Co(NO_3)_2 \cdot 6H_2O$, 0.01 mol and manganese(II) acetate tetrahydrate 2.45 g, 0.01 mol) in 25 cm^3 of distilled water. The micro-crystalline complexes deposited after 30 min were filtered off after standing overnight. The compounds were washed with cold water and ethanol, and air-dried.

Preparation of $Mpz(COO)_2N_2H_4 \cdot nH_2O$ (M=Ni, Co, Zn and Cd)

To a hot aqueous solution (50 cm^3) containing 3,5-pyrazoledicarboxylic acid monohydrate (1.741 g, 0.01 mol) and hydrazine hydrate (4 cm^3, 0.08 mol), aqueous solution (50 cm^3) of the respective metal nitrate hexahydrates (e.g., 2.97 g of $Zn(NO_3)_2 \cdot 6H_2O$; 0.01 mol) was added slowly with constant stirring. The resulting micro-crystalline product formed was digested over a water bath for about 1 h and isolated as above.

Preparation of $Cupz(COO)_20.5N_2H_4 \cdot H_2O$

The title compound was prepared by the addition of an aqueous solution (50 cm^3) of copper nitrate trihydrate (2.42 g, 0.01 mol) to an aqueous solution (50 cm^3) containing 3,5-pyrazoledicarboxylic acid monohydrate (1.741 g, 0.01 mol) and hydrazine hydrate (1.5 cm^3, 0.03 mol). A blue product, precipitated rapidly, was filtered off and washed successively with

water, alcohol and ether, and air-dried. Excess addition of hydrazine hydrate, that is more than 0.03 mol reduced the Cu(II) to metallic copper.

Materials and measurements

All the chemicals were of commercial grade. Solvents were distilled before use. The hydrazine content of the complexes was determined volumetrically using a standard KIO_3 solution (0.025 M) under Andrews' condition [17]. The metals after destroying the organic part and hydrazine by treatment with concentrated HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration [17]. Instrumental details for elemental analysis, IR and UV-Vis spectra, TG-DTA and XRD are the same as described earlier [12, 13].

Results and discussion

Compounds of empirical formula $Mpz(COO)_2(H_2O)_2$ (*M*=Mn, Co, Ni, Cu, Zn and Cd) and metal hydrazine complexes of the type $Mpz(COO)_2N_2H_4$ (*M*=Co, Zn or Cd) and $Mpz(COO)_2nN_2H_4 \cdot H_2O$ (*n*=1 for *M*=Ni and *n*=0.5 for *M*=Cu) have been prepared for which the results of the analyses are given in Table 1. All the complexes obtained are micro-crystalline, which are stable in air and insensitive to light. They are insolu-

Table 1 Analytical data

Compound	D.pt./°C	Yield/%	Colour	Found (calculated)/%				
				hydrazine	metal	carbon	hydrogen	nitrogen
$Mnpz(COO)_2(H_2O)_2$	140	87	white	–	22.00 (22.42)	23.98 (24.49)	2.42 (2.45)	11.03 (11.42)
$Copz(COO)_2(H_2O)_2$	209	95	peach	–	23.70 (23.66)	23.76 (24.09)	2.35 (2.41)	10.92 (11.24)
$Nipz(COO)_2(H_2O)_2$	187	95	light green	–	23.20 (23.59)	23.79 (24.11)	2.50 (2.41)	11.01 (11.25)
$Cupz(COO)_2(H_2O)_2$	119	93	light blue	–	24.80 (25.05)	22.99 (23.65)	2.28 (2.37)	11.21 (11.03)
$Znpz(COO)_2(H_2O)_2$	135	95	white	–	24.90 (25.59)	22.89 (23.48)	2.28 (2.35)	10.28 (10.96)
$Cdpz(COO)_2(H_2O)_2$	137	85	white	–	36.80 (37.16)	19.07 (19.83)	2.02 (1.98)	8.94 (9.26)
$Copz(COO)_2N_2H_4$	198	95	pink	13.60 (13.06)	23.80 (24.05)	23.95 (24.48)	2.37 (2.45)	22.83 (22.85)
$Nipz(COO)_2N_2H_4 \cdot H_2O$	116	97	dark blue	12.30 (12.18)	21.90 (22.34)	22.47 (22.83)	2.95 (3.04)	19.97 (21.31)
$Cupz(COO)_20.5N_2H_4 \cdot H_2O$	138	79	blue	6.20 (6.36)	26.00 (25.25)	23.42 (23.84)	1.62 (1.59)	16.09 (16.69)
$Znpz(COO)_2N_2H_4$	205	85	white	12.10 (12.72)	25.90 (25.99)	23.27 (23.86)	2.19 (2.39)	21.86 (22.26)
$Cdpz(COO)_2N_2H_4$	186	80	white	10.50 (10.72)	36.90 (37.65)	19.76 (20.09)	1.99 (2.01)	18.29 (18.76)

ble in water and in most of the organic solvents. It is observed that only the 1:1:8 mole-ratio of metal salt, 3,5-pyrazoledicarboxylic acid and hydrazine hydrate, respectively, yielded the hydrazine compounds. The hydrazine content below eight mole-ratio always resulted simple metal 3,5-pyrazoledicarboxylates, probably due to strong acidic nature [18] of the parent acid which maintains the resulting solution pH<7.

The electronic spectra of cobalt carboxylate hydrate and its hydrazine complexes show a broad band centered at 20,600 cm^{-1}. This has been attributed to $^4T_{1g}(F) \rightarrow ^4T_{1g}$ (P) transition, which is characteristic of octahedral geometry around the metal ion [19]. The electronic spectra of nickel complexes exhibited maxima around 17,000 and 27,000 cm^{-1} corresponding to $^3A_{2g} \rightarrow ^3T_{1g}$ (F) and $^3A_{2g} \rightarrow ^3T_{1g}$ (P) d-d transitions, which are characteristic of octahedral geometry [14]. The copper complex shows a single band at 12,890 cm^{-1}, which is assigned to $^2E_g \rightarrow ^2T_{2g}$ transition, as expected for a six-coordinate d^9 species. These transitions are characteristics of octahedral geometry of the metal atoms [19].

The IR spectra of all the metal carboxylate hydrates, copper and nickel hydrazine complexes show strong bands in 3551–3370 cm^{-1} range assignable to ν_{OH} stretching vibrations of coordinated and/or lattice water molecules [20]. In this region the difference in O–H absorption of these complexes is consistent with the different water content and this is further substantiated by the results of elemental and thermal analyses. The N–H stretching vibrations of complexes appear in the region of 3333–2923 cm^{-1}. The absorptions in the range of 1640–1560 and 1394–1352 cm^{-1} correspond to the asymmetric and symmetric ν_{COO} frequencies of the metal bound carboxylates. The large difference in ν_{COO} frequencies ($\Delta\nu$>200 cm^{-1}) is indicative of monodentate coordination of both the carboxylate groups of the 3,5-pyrazoledicarboxylate ion. The bidentate bound hydrazines of metal hydrazine complexes display a N–N stretching frequency [4] in the range 982–951 cm^{-1}. The IR band centered at 1697 cm^{-1} in the spectrum of the free dicarboxylic acid, assigned to stretching vibrations of the non-ionized carboxyl group, is absent in the spectra of both metal carboxylates and their hydrazine complexes, confirming that the ligand is doubly ionized in both the cases.

Though the simultaneous TG-DTA curves of metal 3,5-pyrazoledicarboxylate dihydrates appear rather complex, there are two major steps of decomposition except zinc compound that shows three distinct steps. In the first step of the TG, two water molecules are lost in the temperature range 85–230ºC. In DTA, this decomposition is observed as a sharp endotherm above 140ºC with a shoulder (except for cobalt and

nickel complexes) around 125°C. Such high temperature dehydration suggests the presence of two metal bounded water molecules [21]. In the second step, the isomeric anhydrous intermediate, (Mpz(COO)$_2$), undergoes a continuous decomposition to give the respective metal oxide as the end product except manganese complex, which leaves MnCO$_3$ as the final residue probably due to the partial ionic character of the manganese compound [13]. This is seen as an exothermic multiplets with subtle differences. It is noteworthy that the manganese 4,5-imidazoledicarboxylate dihydrate also leaves MnCO$_3$ as the end product, unlike others giving metal oxides [13]. Close observation of the TG results shows that the metal carbonates are formed as intermediates but the decomposition is continuous so that this cannot be quantified. However, the TG of the zinc compound shows a distinct step for the formation of ZnCO$_3$ intermediate. The simultaneous TG-DTA of the manganese and copper compounds are shown in Figs 1 and 2, respectively, as representative examples.

The simultaneous TG-DTA of metal 3,5-pyrazoledicarboxylate hydrazine adducts show that all the complexes yield metal oxide as the final residue via the iso-
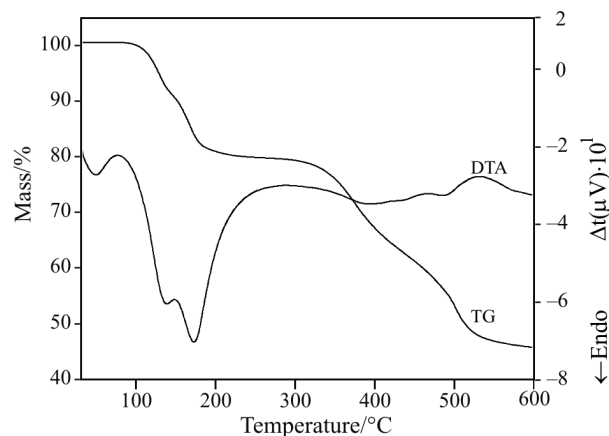

Fig. 1 Simultaneous TG-DTA of Mnpz(COO)$_2$(H$_2$O)$_2$

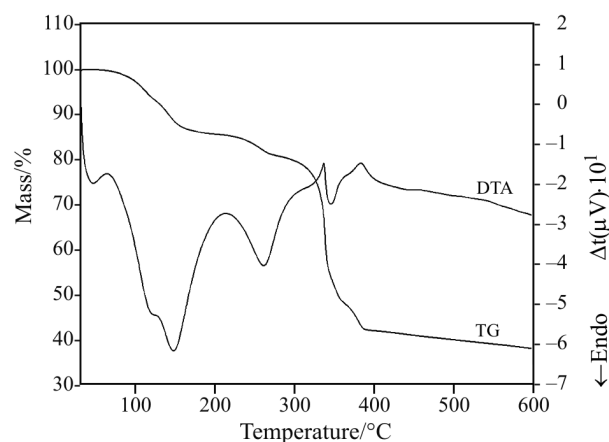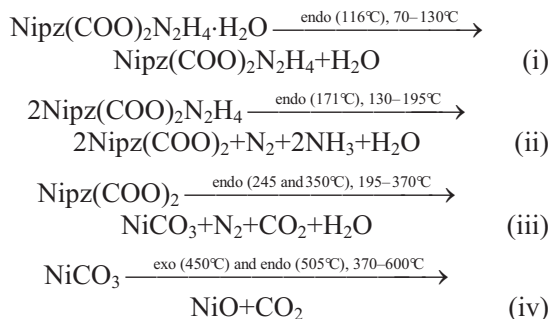**Fig. 2** Simultaneous TG-DTA of Cupz(COO)$_2$(H$_2$O)$_2$

meric metal pyrazoledicarboxylate intermediate as observed in the metal hydrazine 4,5-imidazoledicarboxylates [12]. All of them show endothermic dehydrazination followed by endo- and exothermic decomposition of the metal organic moieties in multiple steps. However, between nickel and copper complexes, the former undergoes endothermic dehydration at 116°C, whereas the latter at 140°C indicating the presence of a lattice and a coordinated water molecule, respectively. As a representative example, the decomposition pattern of nickel complex, in air, is given below on the basis of mass losses in the TG curve.

$$Nipz(COO)_2N_2H_4 \cdot H_2O \xrightarrow{\text{endo (116°C), 70–130°C}} Nipz(COO)_2N_2H_4 + H_2O \quad (i)$$

$$2Nipz(COO)_2N_2H_4 \xrightarrow{\text{endo (171°C), 130–195°C}} 2Nipz(COO)_2 + N_2 + 2NH_3 + H_2O \quad (ii)$$

$$Nipz(COO)_2 \xrightarrow{\text{endo (245 and 350°C), 195–370°C}} NiCO_3 + N_2 + CO_2 + H_2O \quad (iii)$$

$$NiCO_3 \xrightarrow{\text{exo (450°C) and endo (505°C), 370–600°C}} NiO + CO_2 \quad (iv)$$

The simultaneous TG-DTA of the nickel and copper hydrazine complexes is shown in Figs 3 and 4, respectively, as examples. 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.

X-ray powder diffractogram of metal 3,5-pyrazoledicarboxylate hydrates and their hydrazine adducts has been recorded in order to know the isomorphism among the set of complexes. Except with variation in peak intensity, the patterns (Fig. 5) of the former compounds are convincingly comparable suggesting them to be isomorphous. Similarly, the latter hydrazine complexes of cobalt, zinc and cadmium (Fig. 6) seem to reveal isomorphism among them. However, the nickel and
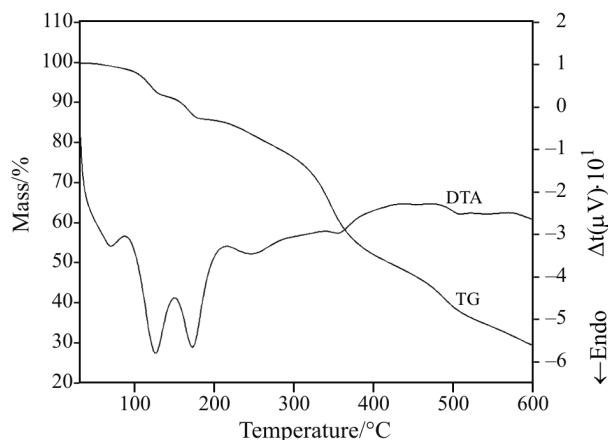

Fig. 4 Simultaneous TG-DTA of Cupz(COO)$_2$·0.5N$_2$H$_4$·H$_2$O
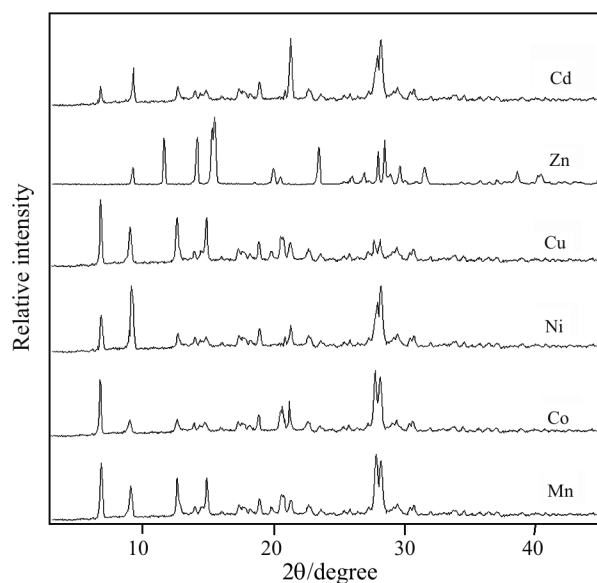
Fig. 5 X-ray powder diffraction patterns of Mpz(COO)$_2$(H$_2$O)$_2$

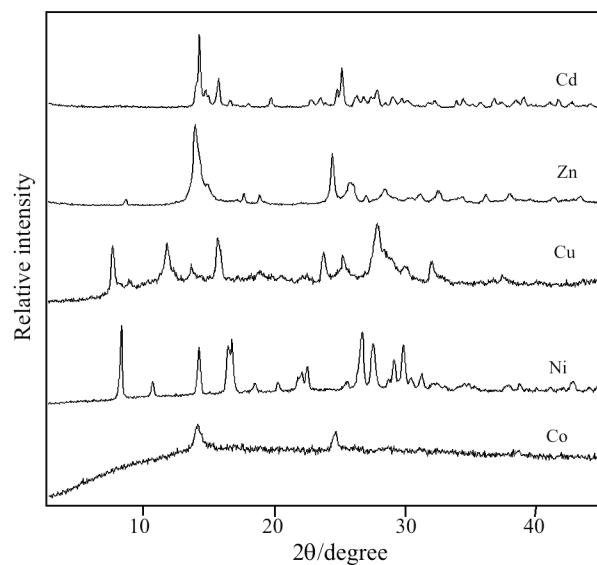**Fig. 3** Simultaneous TG-DTA of Nipz(COO)$_2$N$_2$H$_4$·H$_2$O

Fig. 6 X-ray powder diffraction patterns of metal hydrazine complexes

copper hydrazine compounds are not isomorphous with the above complexes indicating the structural differences between them as their composition themselves is different. The fact that these compounds were isolated as powders and not as single crystals prevented X-ray structure determination.

Conclusions

- Based on the physico-chemical results it is observed that pz(COOH)$_2$ is present as a dianion in both the set of complexes. On the other hand, H$_2$imdc is behaving as a monoanion in the M(Himdc)$_2\cdot n$H$_2$O [13] complexes and dianion in the hydrazine complexes as reported earlier [12]. The reason for the dianionic behaviour of the former acid, in both set of complexes, may be due to its easy solubility and also the lack of internal hydrogen bonding between the carboxylic groups [18] as against the latter.
- Six coordination has been proposed for all the metal complexes considering tetradentate coordination of pyrazoledicarboxylate dianion and bidentate coordination of neutral hydrazine moiety in the case of hydrazine adduct complexes and monodentate coordination of water molecules in metal pyrazoledicarboxylate dihydrates.

Acknowledgements

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