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PREPARATION AND THERMAL BEHAVIOUR OF TRANSITION METAL COMPLEXES OF 4,5-IMIDAZOLEDICARBOXYLIC ACID

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Abstract

Some new transition metal imidazolehydrogendicarboxylate hydrates of empirical formula $M(Himdc)_2 \cdot nH_2O$ (*H_2imdc*=4,5-imidazoledicarboxylic acid), where n=2 for M=Mn, Ni, Zn, Cd and n=3 for M=Co, have been prepared in aqueous solution. The compounds have been characterized by analytical, electronic and IR spectroscopic, thermal analysis and X-ray powder diffraction studies. Electronic spectroscopic data suggest that the Co and Ni compounds are of spin free (high spin) type with octahedral geometry. For these compounds, the IR bands in the region 1750–1710 cm^{-1} has been assigned to stretching vibrations of the non-ionized carboxylic group, confirming that the ligand is monoionized. IR spectra also suggest the unidentate co-ordination behaviour of carboxylate (ν_{asy}=1570 and ν_{sym}=1390 cm^{-1}) groups of the imidazoledicarboxylate monoanion. The thermal behaviour of these compounds has been studied by simultaneous TG-DTA techniques. All of these compounds are dihydrates except cobalt which is a trihydrate. Thermal decomposition studies show that they lose two water molecules endothermally in the range 200–270°C to give their anhydrous compounds, indicating that these water molecules are coordinated to the metal. The anhydrous compounds further decompose exothermally in the range 300–620°C to leave the respective metal oxides via the metal oxalate intermediates. Whereas the manganese compound undergoes pyrolytic cleavage in a single step to give the manganese carbonate as the final residue. Isomorphic nature of these compounds is evident from XRD data. Six-coordination for the metal atoms has been proposed based on the thermal analysis, visible and IR spectroscopic results.

Keywords: 4,5-imidazoledicarboxylic acid, IR spectra, metal carboxylate, thermal decomposition

Introduction

Heteroaromatic dicarboxylates have been extensively used for investigation in coordination chemistry; most reports are on pyrazine, some of which has been reviewed [1–5]. We have become particularly interested in the chemistry of 4,5-imidazoledicarboxylic acid, H_2imdc, (**1**), since it has a number of attractive features. It is sterically compact, planar and has multi-donor coordination sites. Imidazoledicarboxylic acid is a simple model suitable for testing the ability of the N (azole), COO^- donor set to bind with transition

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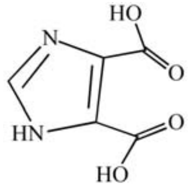
metal systems. H_2imdc containing aromatic N and carboxylate donor sets are potentially capable of yielding mononuclear and polynuclear complexes with oxovanadium(IV) in aqueous solution [6]. H_2imdc has been reported to act also as dinucleating ligand with Rh^I and Ir^I [7, 8]. In the five-membered diaza ring system we have recently reported that the imidazoledicarboxylate can form dianionic planar chelates with bivalent transition metals under appropriate experimental conditions [9]. Carboxylate-type compounds of transition metals generate great interest as potential precursors for the preparation of finely divided metal or metal oxide-type solid compounds [10–16]. Although a number of complexes have been synthesized with H_2imdc [6–8], the interaction between the bivalent transition metals and the afore-mentioned ligand has not yet been investigated much, in aqueous solution. Further, the thermal stability of the transition metal 4,5-imidazoledicarboxylates has not been studied. Therefore, the present work was undertaken to prepare and study the thermal behaviour of bivalent transition metal imidazoledicarboxylates and the results are presented herein.

Experimental



(1)

Scheme 1 4,5-imidazoledicarboxylic acid

Preparation of the metal complexes, $M(Himdc)_2 \cdot nH_2O$

The complexes were prepared by adding the solid 4,5-imidazoledicarboxylic acid (3.122 g, 0.02 mol) to a hot aqueous solution (50 cm^3) of the respective 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) in 2:1 mole ratio with constant stirring. Thus the powdered polycrystalline compound obtained was digested over a steam bath for about 1 h and filtered off, and washed with cold water and diethyl ether, and air-dried. The same product was also obtained with 1:1 mole ratio of H_2imdc and metal salts.

Physico-chemical techniques

All the chemicals used were pure commercial grade and the solvents were distilled before use. The metals after destroying the organic part by treatment with concentrated HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration [17]. The reflectance spectra of the powdered complexes were recorded on a Shimadzu 240-A UV-Vis spectrophotometer in the range 300–800 nm. IR spectra were recorded as KBr pellets with a Perkin Elmer 597-model spectrophotometer in the 4000–400 cm^{-1} ranges. Elemental analyses were performed on Perkin Elmer 240 B CHN analyser. X-ray diffraction patterns of the compounds were recorded on a Jeol JDX 8P X-ray diffractometer using CuK_α radiation except, the cobalt compound for which CoK_α radiation was used. Simultaneous TG-DTA measurements were carried out using a universal V2.5H TA instruments. The experiments were carried out in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10°C min^{-1}.

Results and discussion

Compounds of empirical formula $M(Himdc)_2 \cdot nH_2O$, where n=2 for M=Mn, Ni, Zn, Cd and n=3 for M=Co, have been prepared for which the results of the analyses are given in Table 1. The metal complexes are insoluble in water and other common organic solvents such as alcohol, acetone and chloroform. All of them are hydrated and stable in air.

The electronic spectrum of the cobalt complex shows a broad band centring around 20.325 cm^{-1} and is assigned to spin allowed transition $^4T_{1g}(F)\to{}^4T_{1g}$ (P) there by suggesting octahedral geometry around cobalt(II) complex [18]. The nickel complex exhibits broad electronic spectral maxima centring around 16.339 and 26.882 cm^{-1} corresponding to $^3A_{2g}\to{}^3T_{1g}$ and $^3A_{2g}\to{}^3T_{1g}$ (P) *d-d* transitions, respectively, which are characteristic of octahedral geometry [18].

Table 1 gives the main bands in the infrared spectra of the metal complexes and are assigned on the basis of earlier studies [19]. The infrared spectra of these complexes show a sharp band in the region 3444–3211 cm^{-1}, due to O–H stretching of the free COOH group. Further, the absorption band observed in the region 1750–1710 cm^{-1} has been assigned to carbonyl stretching vibration of the non-ionised carboxylic group, confirming that the acid is existing as a monoanion. The broad band observed in the range 3532–3334 cm^{-1}, is indicative of hydrogen bonding probably involving the water molecules. In these complexes, the asymmetric and symmetric stretching frequencies of the carboxylate ion are seen in the range 1625–1570 and 1391–1328 cm^{-1}, respectively, with an average separation $\Delta\nu$ (ν_{asy}–ν_{sy}) of 235 cm^{-1}, revealing the monodentate coordination of carboxylate group [19] in the monoanion.

The thermoanalytical curves of manganese, cobalt, nickel, zinc and cadmium are shown in Figs 1–5, respectively. Among the compounds, the simultaneous TG-DTA curves of the cobalt compound shows a different pattern of decomposition in the initial stage due to the presence of an additional water molecule. The DTA of this compound shows four peaks corresponding to TG mass loss. The first endotherm at 79°C is assigned to the loss of a water molecule as supported by the mass loss in the TG (found: 4.5%; calcd: 4.25%). This low temperature decomposition indicates that the water is present as lattice water. The second endotherm at 203°C corresponds to the loss of remaining two water molecules. This endotherm at elevated temperature reveals that the two water molecules are coordinated to the central metal ion. Then, the anhydrous cobalt compound undergoes endothermic followed by sharp exothermic decompositions to give the metal oxide as the final residue possibly via the cobalt

Table 1 Analytical and IR data

Compound	Yield/ %	D.pt./ °C	Colour	Found (Calculated)/%				IR data/cm^{-1}		
				Metal	Carbon	Hydrogen	Nitrogen	$\nu_{(C=O)}$ of COOH	$\nu_{asy(OCO)}$	$\nu_{sy(OCO)}$
Mn(Himdc)$_2$(H$_2$O)$_2$	92	211	dull white	13.58 (13.69)	29.95 (29.91)	2.42 (2.48)	14.03 (13.96)	1738	1625	1388
[Co(Himdc)$_2$(H$_2$O)$_2$]·H$_2$O	95	79	peach	13.88 (13.93)	28.27 (28.36)	2.87 (2.83)	13.19 (13.23)	1710	1570	1388
Ni(Himdc)$_2$(H$_2$O)$_2$	98	272	light green	14.63 (14.49)	29.59 (29.63)	2.50 (2.47)	13.91 (13.83)	1749	1582	1391
Zn(Himdc)$_2$(H$_2$O)$_2$	94	221	dull white	16.02 (15.89)	28.99 (29.16)	2.50 (2.45)	14.01 (13.83)	1748	1579	1389
Cd(Himdc)$_2$(H$_2$O)$_2$	93	203	light yellow	24.45 (24.51)	26.02 (26.17)	2.28 (2.18)	12.28 (12.21)	1733	1580	1328

H$_2$imdc=4,5-imidazoledicarboxylic acid; (s): sharp; D.pt.=decomposition point

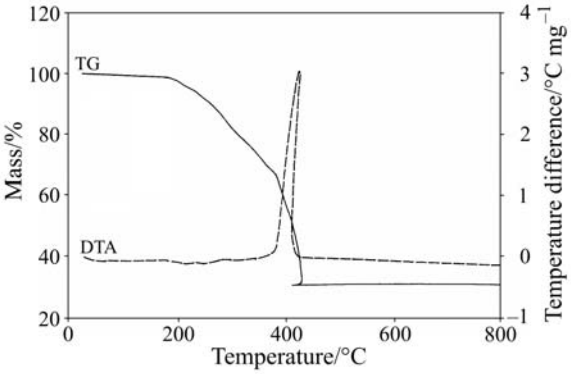


Fig. 1 Simultaneous TG-DTA of $Mn(Himdc)_2(H_2O)_2$

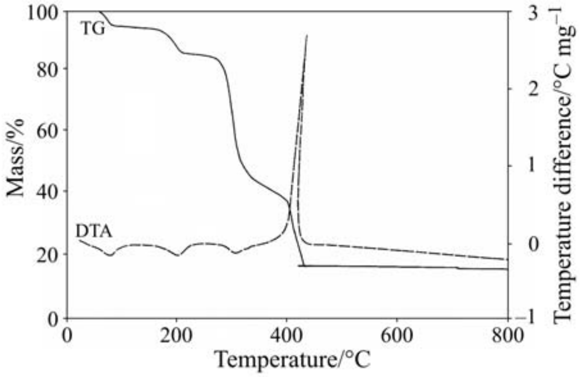


Fig. 2 Simultaneous TG-DTA of $[Co(Himdc)_2(H_2O)_2]\cdot H_2O$

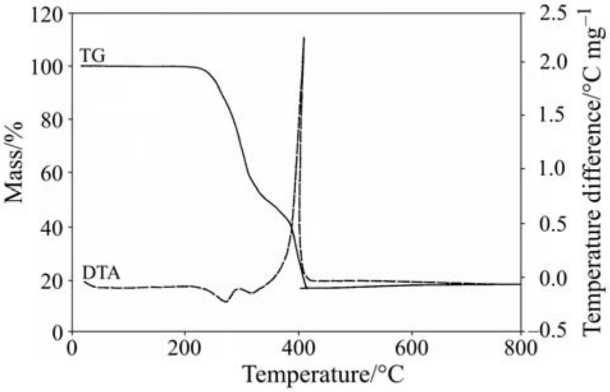


Fig. 3 Simultaneous TG-DTA of $Ni(Himdc)_2(H_2O)_2$

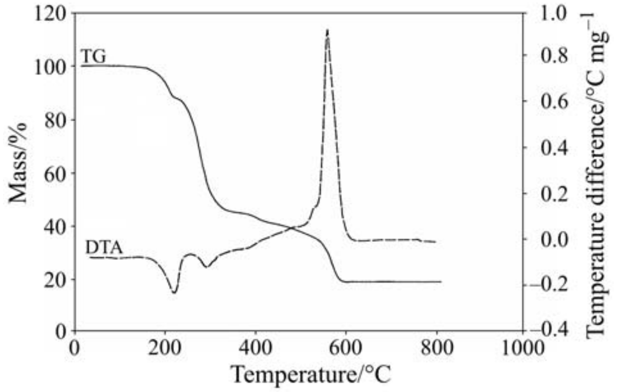


Fig. 4 Simultaneous TG-DTA of Zn(Himdc)$_2$(H$_2$O)$_2$

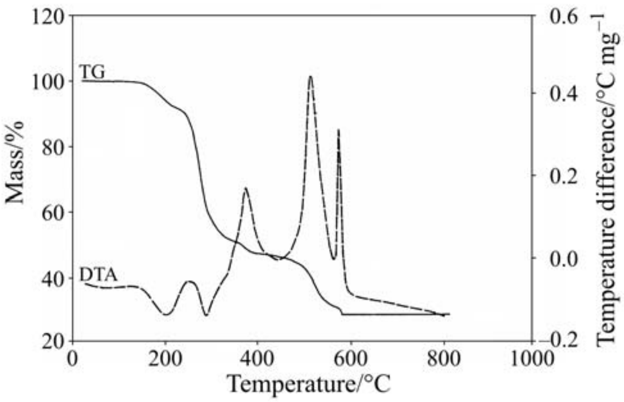


Fig. 5 Simultaneous TG-DTA of Cd(Himdc)$_2$(H$_2$O)$_2$

oxalate intermediate. Such a kind of oxalate intermediate has been observed in the earlier studies [20, 21]. The TG-DTA curves of the nickel, zinc and cadmium compounds show almost similar modes of decomposition as that of the cobalt compound except the first endotherm (79°C) seen in the latter. In contrast to the above, manganese compound undergoes distinct single step (exothermic) decomposition between 180 and 450ºC to give manganese carbonate as the final product probably due to the partial ionic character of the manganese compound.

Our effort to isolate the intermediates was unsuccessful due to their continuous degradation. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses which are well consistent with the calculated mass losses.

In order to know the isomorphic nature among the complexes, the X-ray powder patterns have been compared. Except with variation in peak intensity, the pattern as well as 2θ and *d*-spacings (Table 2) of all the compounds are convincingly comparable to be isomorphous.

Table 2 XRD data of the complexes (*d*-spacing value Å)

Mn	Co	Ni	Zn	Cd
–	–	–	–	12.11
11.78	11.68	11.63	11.63	11.71
6.37	6.39	–	–	–
6.01	5.97	6.03	6.00	6.08
–	5.75	5.78	5.68	5.88
5.47	5.45	5.44	5.47	5.34
5.37	–	–	–	–
5.09	5.03	–	–	–
4.87	4.81	–	–	4.89
4.64	4.65	4.68	4.71	4.66
–	4.36	4.38	4.39	4.34
3.80	3.99	4.02	–	4.06
3.66	3.66	3.66	3.67	3.72
3.52	3.54	–	–	–
3.33	3.45	–	–	3.33
3.23	3.28	3.27	3.27	3.21
3.19	3.19	3.21	3.22	3.18
–	3.11	3.12	3.12	3.13
2.96	2.96	2.97	2.97	2.99
2.89	2.88	2.88	2.86	2.94
–	2.80	–	2.83	2.84
2.69	2.54	2.60	2.60	2.65
–	–	2.55	–	2.49
2.30	–	2.30	–	2.37
–	2.28	2.26	2.26	2.33
–	2.22	2.21	2.22	2.27
2.07	2.12	2.12	2.13	2.12

The analytical data, infrared spectral and thermal analysis results reveal that the H_2imdc is present as a monoanion in these compounds. It is worth to mention that, our attempt to prepare the dianionic complexes of H_2imdc with 1:1 mole ratio of ligand (assuming that the acid could act as a dianion) and metal was unsuccessful and it resulted in the formation of the 2:1 mole ratio product, which unambiguously prove that the acid is acting only as a monoanion. The reason for this could be the poor solubility of the neutral acid and also a strong hydrogen bonding between the COOH and COO^- groups [6] of the bicarboxylate anion.

While manganese, cobalt and nickel complexes decompose comparatively at a lower temperature (around 450°C), zinc and cadmium complexes show a higher temperature of decomposition (around 620°C) to give the end products. The same trend has been observed earlier in the case of cobalt (495°C) and zinc (550°C) 2,3-pyrazinedicarboxylate dihydrate compounds [22].

Based on the physicochemical studies, octahedral coordination has been proposed for the metal atoms in the complexes considering that a ring nitrogen atom and an oxygen atom of the 4-carboxylate group (N, COO^-) for each Himdc moiety, and the two water molecules to a single metal atom. The similar (N, COO^-) type of chelation involving the 4-carboxylate group has been reported [6] on the system containing $V^{IV}O$ and H_2imdc, in which the 5-carboxylic group is not involved in the metal coordination. Further, in the present set of complexes, the polymeric network may extend through hydrogen bonding between the hydrogen atom of the water molecules and the uncoordinated oxygen atoms of the carboxyl groups in a neighbouring unit. This type of extensive hydrogen bonding which leads to the polymeric structure has been observed and proved crystallographically in the related systems of heteroaromatic dinitrogen containing ligand viz., 2-pyrazinecarboxylic acid [23, 24] compounds. The insolubility of the compounds in both polar and non-polar solvents implies that the compounds have polymeric structure [25].

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