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Preparation and thermal behaviour of divalent transition metal complexes of pyromellitic acid with hydrazine

S. Vairam · T. Premkumar · S. Govindarajan

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Abstract Hydrazine forms two different types of complexes with divalent metal ions and pyromellitic acid (H_4pml) in aqueous medium: (i) hydrazinium complexes of formulae, $(N_2H_5)_2M(pml)\cdot xH_2O$, where $x = 3$ for M=Ni and $x = 4$ for M=Co or Zn, and $(N_2H_5)_2Mn(H_2pml)_2$, at pH 4.5, (ii) neutral hydrazine complexes with formulae, $M_2(pml)(N_2H_4)_n\cdot xH_2O$ where M=Co or Ni when $n = 4$ and $x = 5$ or 4 and M=Zn or Cd when $n = 2$, and $x = 4$ or 3 at pH 7, and $M(H_2pml)(N_2H_4)\cdot xH_2O$ where $x = 4$; M=Cu and $x = 0$; M=Hg, at pH 3, 7.5, respectively. All the complexes are insoluble in water, alcohol and ether. The N–N stretching frequency (990–1,007 cm^{-1} for coordinated hydrazinium ion and 956–985 cm^{-1} for bridged neutral hydrazine) indicates the nature of hydrazine present in the complexes. Simultaneously TG-DTA analysis indicates that hydrazinium complexes undergo dehydration and dehydrazination in a single step endothermally in the range of 289–300 °C whereas neutral hydrazine complexes undergo endothermic dehydration (~100 °C) followed by exothermic dehydrazination in the temperature range, 253–332 °C. The anhydrous metal carboxylates further decompose exothermally to leave the respective metal oxides or metal carbonates except zinc, which gives its oxalate as the end product. X-ray powder patterns indicate that even the complexes with the same formulation possess no isomorphism.

Keywords Hydrazine · Hydrazinium ligand · IR spectra · Pyromellitic acid · Thermal analysis

Introduction

A survey of literature indicates that the chemistry of pyromellitic acid (1,2,4,5-benzene tetracarboxylic acid denoted as H_4pml), one of the major products of oxidation of coal, has been extensively studied [1]. The crystal structure of its dihydrate was investigated by Takusagawa et al. [2]. Owing to the various ways of its coordination through carboxylate ions, its use as a ligand is of recent interest [3]. Despite the versatility in ligation of its anion, in some cases, for instance in hexaaquacobaltate(II) dihydrogen pyromellitate, it behaves so indifferently that it does not involve in coordination [4]. This is because of the hydrogen bonding held between the carboxylate anions with water, which prevents it in the participation of coordination. The salts of the acid with monovalent ions such as Na^+, K^+, and $NH_4{}^+$, divalent ions viz., Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and $UO_2{}^{2+}$ ions, and trivalent ions, Al^{3+} and Tl^{3+} have been reported and characterised by IR and Raman spectroscopy studies [5]. The study reveals that it behaves as mono-, di-, tri-, and tetra-anions in their compounds. Lanthanide complexes with pyromellitic acid have also been reported along with their complexation thermodynamics [6, 7]. The luminescence studies and absorption methods indicate that the pyromellitate forms 1:1 lanthanide complexes with carboxylates in the ortho position, in bidentate fashion. Recently a study of thermochemical properties of lanthanide complexes with pyromellitic acid has also been reported [8].

Hydrazine, N_2H_4, a base with a lone pair of electrons each on their nitrogen atoms act as a mono- or bi-dentate bridging ligand, and its protonated ($N_2H_5{}^+$) form serves as a monodentate ligand. Several hydrazinium and hydrazine complexes with transition/lanthanide metal carboxylates are found in the literature [9–15]. Our research group has long been involved in the study of coordination ability and

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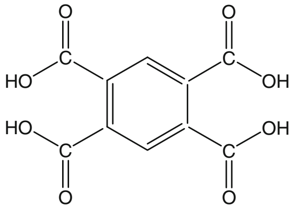
S. Vairam · T. Premkumar · S. Govindarajan (✉)
Department of Chemistry, Bharathiar University,
Coimbatore 641 046, India
e-mail: drsgovind@yahoo.co.in

thermal stability of hydrazine in the presence of various carboxylic acids with metals (complexation). We have recently reported the thermal behaviour of various hydrazinium salts and metal hydrazine complexes of nitrogen containing heterocyclic carboxylic acids such as 2-pyrazinecarboxylic acid, 2,3-pyrazinedicarboxylic acid [16], 4,5-imidazoledicarboxylic acid [17] and 3,5-pyrazoledicarboxylic acid [18]. In earlier reports, we have also reported the preparation and thermal reactivity of hydrazinium 2,*n*-pyridinedicarboxylates ($n = 3$, 4, 5 and 6) [19] and metal dipicolinate complexes of hydrazine [20]. Encouraged by these results obtained in our laboratory in association with our extensive knowledge in thermal behaviour of other metal carboxylate and/or metal hydrazine carboxylate system [21–25], we thought of extending this study to understand the coordination ability and thermal reactivity of hydrazine in the presence of aromatic carboxylic acids, which contain higher number of carboxylic acid groups, with divalent transition metals and also to understand the thermal behaviour of these complexes. In this study, we selected pyromellitic acid (1,2,4,5-benzene tetracarboxylic acid), which has four carboxylic groups and eight sites for potential coordination to a metal atom. Though, a range of simple metal complexes of pyromellitic acid have been reported [4–7], there appears to be no report on transition metal hydrazine compounds of pyromellitic acid and their thermal properties. Therefore, in this article we report the coordinating properties of the acids and thermal characterisation of their metal complexes.



1,2,4,5-benzene tetracarboxylic acid or Pyromellitic acid (H_4pml)

Experimental

Preparation of hydrazinium complexes

$(N_2H_5)_2Mpml\cdot xH_2O$ where M=Co, Ni or Zn and $x = 3$ or 4

These complexes were prepared by adding the ligand solution, which was obtained by mixing an aqueous solution of pyromellitic acid (0.508 g, 2 mmol in 40 mL of distilled water) and 99–100% hydrazine hydrate (0.3 g, 6 mmol) to a metal nitrate solution (e.g. 0.291 g of $Co(NO_3)_2\cdot 6H_2O$, 1 mmol in 10 mL of distilled water) in a beaker. A clear solution of pH 4.5 obtained was heated over a waterbath at 80 °C for about 45 min. A microcrystalline solid product formed was allowed to stand for about 1 h. The product was filtered, washed with ethyl alcohol and diethyl ether, and dried over anhydrous $CaCl_2$ in a desiccator.

$(N_2H_5)_2Mn(H_2pml)_2$

The above procedure was followed with manganous acetate, pyromellitic acid and hydrazine hydrate in the same molar ratio to prepare the title compound which formed only after 6 days.

Preparation of hydrazine complexes

$M_2pml(N_2H_4)_n\cdot xH_2O$ where M=Co, Ni, Zn or Cd; $n = 2$ or 4; $x = 3$, 4 or 5

These complexes were prepared by adding metal nitrate (e.g. 0.291 g of $Co(NO_3)_2\cdot 6H_2O$ in 10 mL of distilled water), to an aqueous solution (50 mL) containing pyromellitic acid (0.254 g) and 99–100% hydrazine hydrate (3 g) in the molar ratio 1:1:6 at room temperature. A solid product formed immediately in the reaction mixture at pH 7, was digested over waterbath at 80 °C for 10 min and the resulting product was filtered, washed with distilled water, ethyl alcohol and diethyl ether. The compound was dried over $CaCl_2$ in a desiccator.

$CuH_2pmlN_2H_4\cdot 4H_2O$

Similar synthetic procedure was followed to prepare this complex by using metal nitrate, pyromellitic acid and hydrazine hydrate with the molar ratio 1:1:3. On vigorous stirring, a clear solution became turbid and a dark blue solid appeared slowly. The solid products were digested over a waterbath for about 10 min and were isolated and washed as above.

$HgH_2pmlN_2H_4$

An aqueous solution (80 mL) of the ligand containing pyromellitic acid (0.508 g, 2 mmol) and hydrazine hydrate (1 g, 2 mmol) was added carefully to an aqueous solution (10 mL) of mercuric nitrate (0.333 g, 1 mmol) with vigorous stirring (so as to avoid reduction to mercury). A dull white precipitate formed immediately was digested for about 2 h on a waterbath. The resulting solid products were filtered, washed with absolute alcohol followed by diethyl ether and dried over anhydrous $CaCl_2$ in a desiccator.

Physicochemical techniques

The stoichiometry of the complexes was fixed by chemical analysis. Hydrazine content was determined by titrating against standard KIO_3 (0.025 M) under Andrews conditions [26]. Metal contents were determined by titrating with 0.01 M EDTA [26], after decomposing the complexes with concentrated HNO_3. Mercury was estimated gravimetrically by precipitating HgS. IR spectral data of the complexes were recorded as KBr pellets using a Perkin Elmer 597 spectrometer. Electronic spectra in the UV–visible region were obtained using a Hitachi Perkin Elmer 20/200 recording spectrophotometer by dispersing the solid samples in Nujol. The magnetic susceptibility of the complexes was measured (298 K) using a vibrating sample magnetometer (VSM E.G&G model 155) in the magnetic field from 2 to 10 KG and appropriate corrections were also made. ESR spectrum was recorded at room temperature using a Jeol 100 TES spectrometer. The simultaneous TG-DTA experiments were carried out in air using STA 1500 thermal analyser and NETZSCH-Geratebeau GmbH thermal analyser at the heating rate of 10 °C/min. Platinum cups were employed as sample holders and alumina as reference. The temperature was ambient to 700 °C.

Results and discussion

All the complexes obtained are polycrystalline solids, which are stable in air and insensitive to light. They are insoluble in water and in organic solvents like ethanol, acetone and chloroform. The analytical data of the complexes are compatible with the proposed compositions (Table 1).

Electronic and ESR spectra

The cobalt complexes of pyromellitic acid register a band in the range of 19,800–20,835 cm^{-1}, due to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions of typical six coordinated Co(II) complexes [27]. The corresponding nickel complexes show two bands in the regions 10,560–10,822 and 17,212–17,730 cm^{-1} which are ascribable to $^4A_{2g} \rightarrow {}^3T_{1g}$, $^3T_{1g}(p)$ transitions, respectively, of octahedral Ni(II) complexes. The Cu complex shows absorptions at 21,354 (intense), 17,721(weak) and 12,136 (weak) cm^{-1} corresponding to the excitation of electrons, $zx \rightarrow x^2 - y^2$, $zx \rightarrow xy$ and $zx \rightarrow z^2$ orbitals, respectively, implying the complex in square planar geometry. The magnetic moments of Ni and Co complexes lie in the range of 3.2–3.3 and 4.9–5.1 BM, respectively.

Table 1 Analytical and IR data

Compound/colour	D. pt. /°C	Found (calculated)/%					IR absorptions/cm^{-1}				
		Carbon	Hydrogen	Nitrogen	Hydrazine	Metal	ν_{OH}	ν_{NH}	$\nu_{C=Osym}$	$\nu_{C=Oasym}$	ν_{N-N}
$(N_2H_5)_2Co(pml)\cdot 4H_2O$ (pink)	290	26.72 (26.84)	4.60 (4.47)	12.40 (12.52)	14.3 (14.3)	13.4 (13.2)	3,276	3,162	1,323	1,578	999
$(N_2H_5)_2Ni(pml)\cdot 3H_2O$ (green)	>300	28.12 (27.99)	4.26 (4.20)	12.96 (13.06)	15.0 (14.9)	13.6 (13.7)	3,240	3,167	1,324	1,572	1,007
$(N_2H_5)_2Zn(pml)\cdot 4H_2O$ (dull white)	>300	26.40 (26.47)	4.20 (4.41)	12.49 (12.35)	14.1 (14.1)	14.3 (14.4)	3,270	3,153	1,322	1,578	1,005
$(N_2H_5)_2Mn(H_2pml)_2$ (dull white)	252	37.90 (38.40)	2.61 (2.89)	9.02 (8.96)	10.3 (10.2)	8.7 (8.8)	3,280	3,160	1,370	1,586	991 and 973
$Co_2(pml)(N_2H_{4)4}\cdot 5H_2O$ (pale pink)	>300	20.46 (20.50)	4.81 (4.78)	19.28 (19.12)	21.4 (21.8)	19.7 (20.1)	3,400–3,600	3,200	1,371	1,578	982
$Ni_2(pml)(N_2H_4)_4\cdot 4H_2O$ (pale blue)	>300	21.25 (21.15)	4.69 (4.58)	19.64 (19.73)	22.5 (22.5)	20.4 (20.7)	3,400–3,600	3,200	1,369	1,560	980
$Zn_2(pml)(N_2H_{4)2}\cdot 4H_2O$ (white)	>300	23.42 (23.22)	3.60 (3.48)	10.78 (10.84)	12.4 (12.3)	25.4 (25.3)	3,400–3,600	3,277	1,332	1,583	981
$Cd_2(pml)(N_2H_4)_2\cdot 3H_2O$ (white)	>300	20.20 (20.24)	2.68 (2.69)	9.52 (9.45)	10.7 (10.8)	37.5 (37.9)	3,331	3,234	1,328	1,560	972
$Cu(H_2pml)(N_2H_4)\cdot 4H_2O$(dark blue)	>300	28.72 (28.60)	3.76 (3.81)	6.65 (6.67)	7.6 (7.9)	15.2 (15.1)	3,329	3,120	1,352	1,664	946
$Hg(H_2pml)(N_2H_4)$ (dirty white)	210	24.62 (24.76)	1.67 (1.65)	5.66 (5.78)	41.1 (41.4)	6.5 (6.6)	–	3,280	1,350	1,580	959

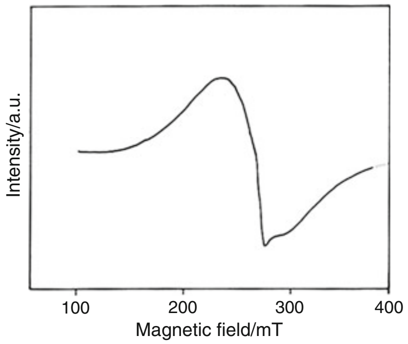


Fig. 1 ESR spectrum of Cu(H_2pml)(N_2H_4)·4H_2O

The axial ESR spectrum for copper complex shown in Fig. 1 has features at $g_{\parallel} = g_{\perp} = 2.11$ which clearly indicates that the Cu(II) ion is in isotropic environment.

IR spectra

The important IR absorption frequencies of the compounds are given in Table 1. The hydrazinium complexes of cobalt, nickel, manganese and zinc display a N–N stretching frequency [28] in the range of 1,008–991 cm^{-1} and the hydrazine complexes show in the range of 985–946 cm^{-1}, corroborating the presence of $N_2H_5^+$ and N_2H_4, respectively. All the hydrated complexes display a broad peak in the region of 3,600–3,400 cm^{-1} indicating the O–H stretching band of water. All the complexes show absorption in the range of 1,664–1,560 cm^{-1} corresponding to C=O asymmetric and 1,370–1,352 cm^{-1} corresponding to C=O symmetric, difference being >200 cm^{-1} unequivocally revealing monodental coordination of carboxylate group [29]. The complexes of manganese, copper and mercury show absorption at 1,680–1,707 cm^{-1} indicating the presence of free carboxyl group in them.

Thermal studies

The thermal data of the complexes are listed in Table 2. The compositions of the intermediates and the final products are those which best fit with the observed mass losses in the TG studies. Thermogravimetric results are in good agreement with the corresponding DTA data.

(N_2H_5)$_2$Mpml·xH_2O where M=Co, Ni or Zn and $x = 3$ or 4

These complexes are stable up to 260 °C and lose their water and N_2H_4 molecules after 270 °C. The high temperature dehydration may be due to strong hydrogen bonding between carboxylate groups and water. Exothermic dehydrazination and endothermic dehydration merge with each other in the range of 270–485 °C showing the resultant endotherm with low intensity around 300 °C, followed by a strong exothermic peak in the range of 475–535 °C (483 °C for Co, 474 °C for Ni and 535 °C for Zn). The intermediates formed during decomposition of all these complexes are anhydrous metal dihydrogencarboxylates (shown in Fig. 2a–c as representative examples). This is understood on comparison with the TG-DTA curve (Fig. 2a) of nickel hydrogencarboxylate. The final products are the corresponding metal carbonates except nickel and zinc, which leave mixture of carbonates and oxides and oxalate as the end products, respectively.

(N_2H_5)$_2$Mn(H_2pml)$_2$

This complex undergoes two-step decomposition. First step mass loss is dehydration from the carboxyl groups forming anhydride followed by a continuous dehydrazination between 250 and 311 °C showing successive endothermic peaks at 250 and 303 °C forming the manganese pyromellitate intermediate as in the previous case. In the second step, the remaining manganese pyromellitate intermediate undergoes sharp exothermic decomposition at 483 °C to give manganese carbonate as the final residue.

M_2pml(N_2H_4)$_n$·$x$$H_2O$ where M=Co, Ni, Zn or Cd; $n = 2$ or 4; $x = 3$, 4 or 5: the DTA curves show endothermic peaks in the range of 100–130 °C corresponding to the first stage mass loss as shown by TG curves. This mass loss is equivalent to the mass of corresponding water molecules present in the complexes. The values of observed mass loss are comparable with the calculated values (Table 2). The high temperature elimination of water molecules indicates that lattice water molecules are strongly held by hydrogen bonding.

The second stage of decomposition occurs in the range of 160–375 °C showing broad exothermic peaks in the range of 240–332 °C (240 °C for Co, 253 °C for Ni, 286 °C for Zn and 332 °C for Cd) due to the loss of hydrazine molecules. This exothermic elimination implies that hydrazine molecules are involved in bridging coordination [9–11]. The intermediates are the corresponding pyromellitate for cobalt, zinc and cadmium, and oxalate for nickel complex. Finally, all the complexes undergo complete exothermic decomposition in the range of 400–500 °C to form their stable oxides except cadmium which gives its carbonate as the final products.

CuH_2pmlN_2H_4·4H_2O

This complex shows two-step decomposition, where first step is dehydration of a molecule of water showing endothermic peak at 100 °C. The second step is the elimination of water and hydrazine molecule showing exothermic peak at 269 °C resulting in the formation of $CuCO_3$ as the residue.

Table 2 Thermal data

Complex	DTA	Thermogravimetry (TG)			Decomposition products
	Temp./°C	Temp. range/°C	Mass loss/%		
			Obs.	Calc.	
$(N_2H_5)_2Co(pml)\cdot4H_2O$	289(+)	270–370	23.5	23.3	$(N_2H_5)Co(Hpml)$
	483(−)	370–500	71.6	73.4	$CoCO_3$
$(N_2H_5)_2Ni(pml)\cdot3H_2O$	300(+)	284–380	27.5	27.5	$Ni(H_2pml)$
	474(−)	380–700	77.6	77.4	1/2 $NiCO_3$ + 1/2 NiO
$(N_2H_5)_2Zn(pml)\cdot4H_2O$	296(+)	262–484	22.5	22.9	$(N_2H_5)Zn(Hpml)$
	535(−)	484–700	66.0	66.2	ZnC_2O_4
$(N_2H_5)_2Mn(H_2pml)_2$	250(−)	250–311	16.0	16.1	$Mn(C_6H_2\ (COOH)(CO)_2O(COO))_2$
	303(−)				
	483(−)	311–500	81.0	81.5	$MnCO_3$
$Co_2(pml)(N_2H_4)_4\cdot5H_2O$	100(+)	60–175	15.2	15.4	$Co_2(pml)(N_2H_4)_4$
	150(+)				
	240(−)	175–375	35.0	37.2	$Co_2(pml)$
	399(−)	375–650	69.0	72.6	Co_3O_4
$Ni_2(pml)(N_2H_4)_4\cdot4H_2O$	113(+)	60–160	13.0	12.7	$Ni_2(pml)(N_2H_4)_4$
	253(−)	160–318	46.5	48.3	NiC_2O_4
	407(−)	318–600	74.7	73.7	NiO
$Zn_2(pml)(N_2H_4)_2\cdot4H_2O$	127(+)	60–208	14.0	13.9	$Zn_2(pml)(N_2H_4)_2$
	286(−)	208–347	26.0	26.3	Zn_2pml
	505(−)	347–600	68.0	68.5	ZnO
$Cd_2(pml)(N_2H_4)_2\cdot3H_2O$	110(+)	80–120	8.9	9.1	$Cd_2(pml)(N_2H_4)_2$
	332(−)	120–430	14.4	14.5	$Cd_2(pml)(N_2H_4)$
	471(−)	430–650	47.0	45.1	$CdCO_3$
$Cu(H_2pml)(N_2H_4)\cdot4H_2O$	100(+)	80–300	27.0	24.8	$Cu(H_2pml)$
	269(−)				
	312(−)	300–340	72.0	70.5	$CuCO_3$
$Hg(H_2pml)(N_2H_4)$	195(+)	200–350	58.5	58.2	Mercury
	242(−)				
	530(−)	350–600	85.0	–	Volatilisation and phase changes
	570(−)				
$Hg[Hgpml]\cdot H_2O$	79(+)	52–330	2.8	2.7	$Hg[Hgpml]$
	152(+)				
	383(−)	330–600	82.6	–	Volatilisation and phase changes
	560(−)				

$HgH_2pmlN_2H_4$

The curve of this complex reveals that it melts and decomposes to metallic mercury showing endothermic peaks at 195 and 242 °C in DTA. Subsequently it further volatilizes accompanying phase changes showing exotherms at 530 and 578 °C to give 15% residue. This is quite similar to the decomposition of oxalato complex of mercury [30]. Further, while comparing the thermal decomposition of the pyromellitate complex of mercury, $Hg[Hgpml]\cdot H_2O$, which decomposes exothermally at 383 °C after its dehydration. It is found that the hydrazine complex decomposes in the low temperature (242 °C) due to the presence of hydrazine (Fig. 2d, e).

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 diffraction studies

The X-ray powder patterns indicate that no isomorphism exists among the complexes. However, the hydrazinium

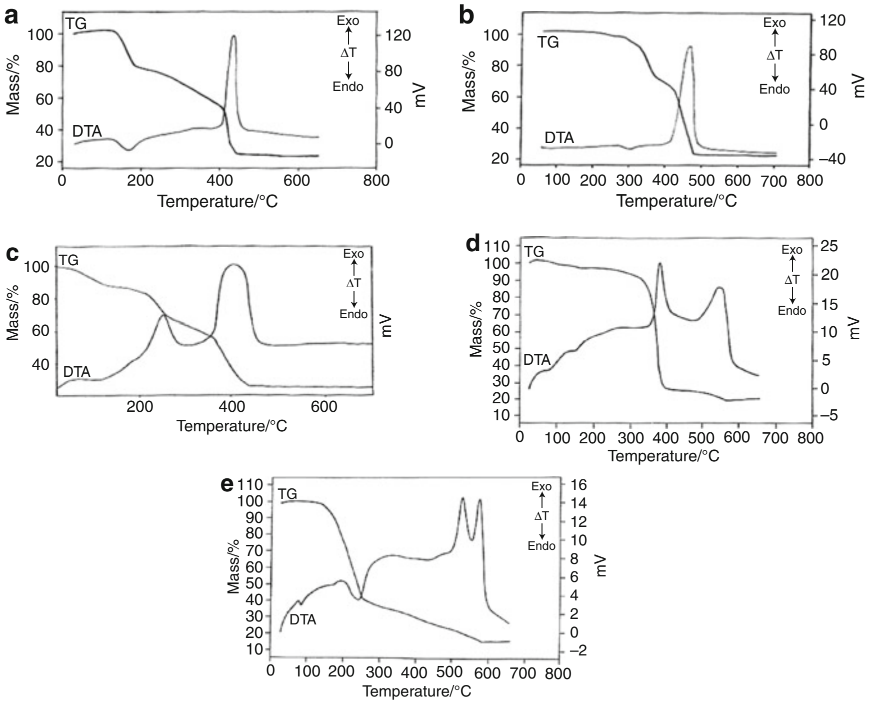


Fig. 2 Simultaneous TG-DTA of **a** $Ni(H_2pml)\cdot 12H_2O$, **b** $(N_2H_5)_2Nipml\cdot 3H_2O$, **c** $Ni_2pml(N_2H_4)_4\cdot 4H_2O$, **d** $Hg[Hgpml]\cdot H_2O$ and **e** $Hg(H_2pml)\cdot N_2H_4$

complexes having the similar formulation, $(N_2H_5)_2M(pml)\cdot xH_2O$, seem to possess similarity to some extent in their diffractograms.

Conclusions

The reaction of metal nitrate with hydrazine in the presence of pyromellitic acid form hydrazinium complexes at pH 4 and neutral hydrazine complexes at around 7. Pyromellitate behaves as tetra anion in the case of Co, Ni, Zn and Cd complexes as well as dianion in the case of Cu and Hg. In the hydrazine complexes, hydrazine acts as neutral, bridging ligand for zinc, cadmium and mercury, and mono dentate ligand for copper. The insoluble nature of all complexes suggests a polymeric structure via pyromellitate and hydrazine moieties.

The thermal behaviour of the complexes seems to be related to the nature of hydrazine present in the complex. Hydrazinium complexes undergo endothermic dehydration and exothermic dehydrazination in a single step while the neutral hydrazine complexes undergo endothermic dehydration and exothermic dehydrazination in two different stages. While bidentate bridging hydrazine complexes show strong exothermic decomposition, monodentate hydrazine complex shows weak exothermicity. Unlike other complexes, mercury complex has low thermal stability and decomposes completely in the range of 200–350 °C to metallic mercury, which further shows phase changes at higher temperatures. The results of electronic spectra, magnetic moment and thermal studies of the complexes suggest that the Mn, Co, Ni and Zn (hydrazinium) complexes are of octahedral geometry with coordination number 6, and Cu is of square planar geometry, and Zn (hydrazine), Cd and Hg of tetrahedral geometry with coordination number 4.

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