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Synthesis, spectral and thermal studies of some 3d-metal hydroxybenzoate hydrazinate complexes

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Abstract

Metal *o*- or *p*-hydroxybenzoate hydrazinate complexes of the types: $Mn(o\text{-}C_6H_4(OH)COO)_2N_2H_42H_2O$; $ML_2N_2H_4$, where M is Cu(II), L is *o*-hydroxybenzoate(salicylate) and M is Zn(II), L is *o*- or *p*-hydroxybenzoate; $ML_22N_2H_4$, where M is Co(II) and Ni (II) and L is *o*- or *p*-hydroxybenzoate, and bishydrazinium metal salicylates $(N_2H_5)_2M(o\text{-}C_6H_4(OH)COO)_4$, where *M* is Co(II) and Ni(II), have been prepared and characterised by magnetic, spectral, thermal and XRD studies. IR spectral data reveal the monodentate coordination of hydroxybenzoates through COO^-, coordination of $N_2H_5^+$, bidentate bridging of N_2H_4 and coordination of H_2O in the Mn complex. The magnetic and electronic spectral data indicate octahedral coordination around Mn, Co and Ni and square-planar coordination around Cu ions. The simultaneous TG-DTA data show that Ni and Cu salicylate hydrazinate complexes undergo complete exothermic decomposition, whereas other complexes decompose both by endothermic and exothermic modes to produce metal oxide as the residual product. Most of the complexes form metal hydroxybenzoates as intermediates. Co and Ni intermediates melt before decomposition. The XRD studies show isomorphism among $ML_22N_2H_4$, $ZnL_2N_2H_4$ and $(N_2H_5)_2M(o\text{-}C_6H_4(OH)COO)_4$ complexes but not between the series.

Keywords: Hydrazinate; Hydrazinium; Metal hydroxybenzoate; Thermal analysis; XRD

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1. Introduction

The salicylate ion has a variety of dentation modes in which both carboxylate and phenolic oxygen atoms participate. The crystal structures of $Cu(C_6H_4(OH)COO)_2\cdot$

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$4H_2O$ [1] and $Zn(C_6H_4(OH)COO)_2 \cdot 2H_2O$ [2] show that the salicylate ion is monodentate, coordinated to the metal through the carboxyl group. Salicylate bidentate coordination through the carboxylate groups has been reported for cis and trans isomers of bis(4-aminosalicylato)copper(II) [3] and $Cu(C_6H_4(OH)COO)_2H_2O$ [4]. For $Cu(C_6H_4(OH)COO)_2 \cdot 2H_2O$ [5], the coordinating modes of salicylate are of two types. One is analogous to that described for the previous compounds [1,2]. In the other mode, two salicylate ions are linked (bridging) to different metal ions by both the carboxylate and phenolic oxygen atoms. In addition to these three different dentation modes of salicylate ion, a fourth is bidentate chelation through carboxylate and phenolic oxygen atoms. All these modes were reported in the isostructural aquatris(salicylato)samarium(III), and aquatris(salicylato)americium(III) complexes [6]. Solution studies [7] of Nd(III) with salicylate (*o*-hydroxybenzoate) and *p*-hydroxybenzoate show differences in solubility which were attributed, respectively to cyclic and linear attachment of ligands. The properties and structure of these complexes are directly related to natural materials like superoxide dismutase and humic materials. We are interested in hydrazine complexes of carboxylates with metal ions. There are reports on metal hydrazinate complexes of formate [8], acetate [9], propionate [10] and glycolate [11]. We have already reported salicylate and *p*-hydroxybenzoate complexes with uranyl and hydrazine [12]. We now report the preparation of 3d metal *o*- and *p*-hydroxybenzoate hydrazinate complexes and their characterisation by magnetic, spectral, thermal and *x*-ray studies.

2. Experimental

2.1. Synthesis

The ligands hydrazinium, and *o*- and *p*-hydroxybenzoates used in the preparation of the complexes were prepared as reported elsewhere [13].

$Mn(o\text{-}C_6H_4(OH)COO)_2N_2H_4 2H_2O$

Manganese nitrate tetrahydrate (2.51 g; 0.01 mol) in 0.1 l distilled water was mixed with hydrazinium salicylate (3.40 g; 0.02 mol) in 0.1 l water containing hydrazine hydrate (3 ml; 0.06 mol) and stirred well. The mixture was kept at room temperature for a day for the completion of the complexation. The fine crystals formed were filtered, washed with alcohol and ether, and dried over P_4O_{10}.

$Cu(o\text{-}C_6H_4(OH)COO)_2N_2H_4$

Reduction of Cu(II) in the presence of hydrazinium salts must be prevented. Copper nitrate trihydrate (2.41 g; 0.01 mol) was dissolved in 0.1 l distilled water and to this was added an aqueous solution (0.1 l) containing hydrazinium salicylate (1.70 g; 0.01 mol) with constant stirring. A blue-coloured solid formed immediately; this was filtered, washed with alcohol and ether, and dried over P_4O_{10}.

$ZnL_2N_2H_4$: L is o-*or* p-*hydroxybenzoate*

Zinc nitrate hexahydrate (2.97 g; 0.01 mol) and hydrazinium *o*- or *p*-hydroxybenzoate (6.81 g; 0.04 mol) each in 0.1 l water were mixed and the resultant clear solution was concentrated slowly at 80 °C. A colourless precipitate formed which was filtered, washed with alcohol and ether, and air dried.

$Co(o\text{-}C_6H_4(OH)COO)_2 2N_2H_4$ *and* $(N_2H_5)_2Co(o\text{-}C_6H_4(OH)COO)_4$

Cobalt nitrate hexahydrate (2.91 g; 0.01 mol) was dissolved in 0.1 l water and to this was added hydrazinium salicylate (6.81 g; 0.04 mol) with stirring. After 5 min, a pink complex, $Co(o\text{-}C_6H_4(OH)COO)_2 2N_2H_4$, formed slowly. The solid was filtered off and processed as before. The filtrate was concentrated over a water bath to one fifth of the original volume and the solid formed filtered hot. The light pink complex, $(N_2H_5)_2Co(o\text{-}C_6H_4(OH)COO)_4$, was washed and dried as before.

The hydrazinate complex can also be prepared using 1:2 molar concentration of the metal salt and the ligand.

$Ni(o\text{-}C_6H_4(OH)COO)_2 2N_2H_4$ *and* $(N_2H_5)_2Ni(o\text{-}C_6H_4(OH)COO)_4$

Nickel nitrate hexahydrate (2.91 g; 0.01 mol) and hydrazinium salicylate (3.40 g; 0.02 mol), each in 0.1 l water, were mixed and stirred well. The blue complex, $Ni(o\text{-}C_6H_4(OH)COO)_2 2N_2H_4$, was formed soon after mixing. When the amount of the ligand was doubled the light blue $(N_2H_5)_2Ni(o\text{-}C_6H_4(OH)COO)_4$ complex was formed. The solid products were filtered off, washed with alcohol and ether, and dried.

$M(p\text{-}C_6H_4(OH)COO)_2 2N_2H_4$: *M is Co and Ni*

The corresponding metal nitrate hexahydrate (2.91 g; 0.01 mol) in 0.1 l water was mixed with an equal volume of aqueous solution containing hydrazinium *p*-hydroxybenzoate (3.40 g; 0.02 mol) and stirred well. The mixture was kept overnight at room temperature. The complexes formed were filtered, washed and dried as before.

2.2. *Physicochemical techniques*

The hydrazine content of the complexes was determined volumetrically using a standard KIO_3 solution (0.025 mol) under Andrews conditions [14]. The metals, after destroying the organic part and hydrazine by treatment with conc. HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration [14] using xylenol orange as indicator.

The magnetic susceptibility measurements were carried out using a Gouy balance and $Hg[Co(NCS)_4]$ as calibrant at room temperature.

The diffuse reflectance spectra of the powdered complexes in nujol mulls were recorded on a Shimadzu UV–VIS-160A recording spectrophotometer in the 200–1100 nm range.

The infrared spectra were recorded using the KBr disc technique and a Perkin Elmer 597 spectrophotometer. The *x*-ray powder diffraction pattern was obtained on a Philips *x*-ray diffractometer model PW 1050/70 using Cu Kα radiation and a Ni filter.

The simultaneous TG-DTA measurements were carried out using STA 1500 (Version, U.K.) and Shimadzu DT 40 thermal analysers. The experiments were carried out in air, using 5–10 mg samples and a heating rate of 10 °C min^{-1}. Platinum cups were used as sample holders with α-alumina as reference.

3. Results and discussion

The preparation of the complexes involves a judicious and careful mixing of the stoichiometric proportions of the metal salts and the ligands. The formulae proposed are in good agreement with the analytical data presented in Table 1. The complexes are not soluble in water or in common organic solvents and are stable at room temperature.

3.1. Magnetic moments

The magnetic moment values are given in Table 1. The zinc complexes are diamagnetic, whereas room-temperature magnetic moments of all other complexes are in good agreement with the Van Vleck values [15]. The effective magnetic moment values of Co(II) and Ni(II) are found to be in the range 4.90–5.10 and 3.20–3.40 BM respectively, which suggest an octahedral geometry [16]. The magnetic moment of Mn(II) is 5.90

Table 1
Analytical and magnetic data

Compound	Hydrazine (%)		Metal %		μ_{eff}/BM
	Found	Calcd.	Found	Calcd.	
$Mn(o\text{-}C_6H_4(OH)COO)_2N_2H_4\cdot 2H_2O$	8.00	8.07	14.30	13.83	5.90
$Cu(o\text{-}C_6H_4(OH)COO)_2N_2H_4$	8.50	8.67	17.20	17.18	1.90
$Zn(o\text{-}C_6H_4(OH)COO)_2N_2H_4$	9.00	8.62	17.40	17.59	–
$Zn(p\text{-}C_6H_4(OH)COO)_2N_2H_4$	9.10	8.62	16.80	17.59	–
$Co(o\text{-}C_6H_4(OH)COO)_22N_2H_4$	15.80	16.13	14.70	14.83	5.05
$Ni(o\text{-}C_6H_4(OH)COO)_22N_2H_4$	15.90	16.14	14.80	14.79	3.30
$Co(p\text{-}C_6H_4(OH)COO)_22N_2H_4$	15.70	16.13	14.85	14.83	5.00
$Ni(p\text{-}C_6H_4(OH)COO)_22N_2H_4$	16.00	16.14	14.50	14.79	3.35
$(N_2H_5)_2Co(o\text{-}C_6H_4(OH)COO)_4$	9.30	9.52	9.20	8.75	4.95
$(N_2H_5)_2Ni(o\text{-}C_6H_4(OH)COO)_4$	9.80	9.52	9.20	8.72	3.25

BM which is very close to the spin-only moment. This suggests high-spin octahedral coordination [16]. The copper complex has a magnetic moment of 1.90 BM, typical of the spin-only value for Cu(II) complexes [16].

3.2. Electronic spectra

The electronic spectra of the Mn(II) complex shows two bands at 24390 and 29410 cm^{-1} and these bands are assigned to the $^6A_{1g} \rightarrow {}^4A_{1g}(G)$, $^4E_g(G)$ and $^6A_{1g} \rightarrow {}^4E_g(D)$ transitions respectively which support octahedral geometry [16] around Mn(II).

The electronic spectra of Co(II) complexes show two medium bands around 18000 and 20000 cm^{-1} which are respectively assigned to spin-allowed transitions $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, thereby suggesting octahedral geometry around Co(II).

The Ni(II) complexes exhibit electronic spectral maxima around 17000 and 27000 cm^{-1} corresponding to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ d–d transitions respectively, which are characteristic of octahedral geometry.

The electronic spectrum of the Cu(II) complex shows two broad bands at 15700 and 19600 cm^{-1} which are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$, respectively, in a square-planar geometry having the CuO_2N_2 chromophore [17]. The zinc(II) complexes are diamagnetic with a tetrahedral geometry.

3.3. IR spectra

IR spectra of the complexes are presented in Table 2. The absorption bands for all complexes are similar, except the Mn(II) complex, which shows medium bands at 3550 and 3600 cm^{-1} due to coordinated water molecules [18,19]. Invariably all the compounds show bands around 3050 and 1250 cm^{-1} which are assigned respectively to the stretching frequencies of phenolic OH and that of phenolic C–O as observed [13] in the ligands. This confirms that phenolic OH is not involved in coordination [18, 19]. The large separation $\Delta\nu(\nu_{asym} - \nu_{sym} = 220\text{–}250\ \mathrm{cm}^{-1})$ between the asymmetric and symmetric stretching frequencies of the carboxylate groups is consistent with monodentate coordination [19]. The N–N stretching frequencies of hydrazine complexes in the range 960–980 cm^{-1} are in conformity with bidentate bridging [20] of N_2H_4 ligands. In bishydrazinium complexes, the N–N stretching frequencies at 1015 cm^{-1} confirm the coordination of $N_2H_5^+$ ion [21].

3.4. Thermal studies

Thermal data of the complexes are given in Table 3. Such data not only corroborate the stoichiometric formulae and number of included hydrazine and water molecules, but also reveal different intermediates and confirm metal oxide as the end products.

Table 2
Infrared data

$M(o\text{-}C_6H_4(OH)COO)_2\ N_2H_4nH_2O$		$ZnL_2N_2H_4$		$M(o\text{-}C_6H_4(OH)COO)_2\ 2N_2H_4$		$M(p\text{-}C_6H_4(OH)COO)_2\ 2N_2H_4$		$(N_2H_5)_2M(o\text{-}C_6H_4(OH)COO)_4$		Band assignments/cm^{-1}
Mn($n = 2$)	Cu($n = 0$)	$L =$ *o*-compd.	$L =$ *p*-compd.	Co	Ni	Co	Ni	Co	Ni	
3600	–	–	–	–	–	–	–	–	–	O–H stretching of H_2O
3500										
3050	3050	3045	3050	3050	3045	3050	3055	3045	3050	O–H stretching of phenolic group
3350	3350	–	3320	3320	3320	3350	3350	3320	3320	
3320	3310	3275	3275	3300	3300	3300	3300	3300	3300	N–H stretching
3250	3220	3220	–	3250	3250	3275	–	3250	3250	
3170	3160	3150	3150	3150	3170	3170	3175	3160	3160	
1620	1620	1630	1600	1640	1640	1600	1600	1620	1620	OOO^- asym. stretching
1390	1390	1400	1380	1400	1390	1380	1380	1380	1390	OOO^- asym. stretching
230	230	230	220	240	250	220	220	240	230	$\Delta\nu = (\nu_{asym} - \nu_{sym})$
1250	1240	1245	1250	1250	1245	1240	1250	1245	1240	C–O stretching of phenolic C–OH
965	965	960	970	980	980	975	980	1015	1015	N–N stretching

Table 3
Thermal data

Compound	DTA peak temp./°C	Thermogravimetry			Decomposition product
		Temperature range/°C	Mass loss % Found	Calcd.	
Mn(*o*-C_6H_4(OH)COO)$_2N_2H_4\cdot 2H_2O$	195(+)	170–220	28.60	29.24	Mn(*o*-C_6H_4(OH)COO)C_2O_4H
	330–455(−)	220–480	79.00	78.11	MnO_2
Cu(*o*-C_6H_4(OH)COO)$_2N_2H_4$	110(−)	100–145	8.90	8.67	Cu(*o*-C_6H_4(OH)COO)$_2$
	150(−)	140–210	45.50	46.00	Cu(*o*-C_6H_4(O)COO)
	300(−) 330(−)	260–350	78.60	78.49	CuO
Zn(*o*-C_6H_4(OH)COO)$_2N_2O_2$	240(+)	200–300	46.00	45.79	Zn(*o*-C_6H_4(O)COO)
	430(−)	300–470	77.90	78.11	ZnO
Zn(*p*-C_6H_4(OH)COO)$_2N_2H_4$	220(+)	100–400	45.60	45.79	Zn(*p*-C_6H_4(O)COO)
	345(+)				
	495(−)	400–510	78.00	78.11	ZnO
Co(*o*-C_6O_4(OH)COO)$_2$2N_2H_4	255(+)	200–300	50.00	50.90	Co(*o*-C_6H_4(O)COO)
	340(+)	–	–	–	Melting
	375(−)				
	400(−)	360–430	79.90	79.80	Co_3O_4
Ni(*o*-C_6H_4(OH)COO)$_2$2N_2H_4	275(−)	150–320	62.90	63.04	NiC_2O_4
	340(−)	320–400	82.00	81.18	NiO
Co(*p*-C_6H_4(OH)COO)$_2$2N_2H_4	155(+)	120–180	7.70	8.07	Co(*p*-C_6H_4(OH)COO)$_2N_2H_4$
	200(−)				
	270(+)	180–300	49.95	50.90	Co(*p*-C_6H_4(O)COO)
	340(+)	–	–	–	Melting
	385(−)	350–400	79.40	79.80	Co_3O_4

Table 3 *(Continued)*

Compound	DTA peak temp./°C	Thermogravimetry			Decomposition product
		Temperature range/°C	Mass loss % Found	Calcd.	
$Ni(p\text{-}C_6H_4(OH)COO)_2 2N_2H_4$	180(+)	150–250	8.10	8.07	$Ni(p\text{-}C_6H_4(OH)COO)_2N_2H_4$
	275(−)				
	290(+)	250–310	50.80	50.93	$Ni(p\text{-}C_6H_4(O)COO)$
	330(+)	–	–	–	Melting
	385(−)	350–410	81.10	81.18	NiO
$(N_2H_5)_2Co(o\text{-}C_6H_4(OH)COO)_4$	100(+)	80–120	5.00	4.76	$N_2H_5Co(o\text{-}C_6H_4(OH)COO)_3C_6H_4(OH)COOH$
	150(+)				
	250(+)	120–300	70.70	71.04	$Co(o\text{-}C_6H_4(O)COO)$
	340(+)	–	–	–	Melting
	375(−)	360–400	88.00	88.08	Co_3O_4
$(N_2H_5)_2Ni(o\text{-}C_6H_4(OH)COO)_4$	160(+)	140–200	26.00	25.27	$N_2H_5Ni(o\text{-}C_6H_4(OH)COO)_3$
	300(−)	200–320	70.80	71.06	$Ni(o\text{-}C_6H_4(O)COO)$
	330(+)	–	–	–	Melting
	375(−)	340–400	88.30	88.90	NiO

key: (+), endotherm; (−), exotherm; d, doublet.

Mn(o-$C_6H_4(OH)COO)_2N_2H_42H_2O$

The simultaneous TG-DTA curves (Fig. 1) of this complex show a two-step decomposition. In the first step, a molecule of hydrazine and two molecules of water are lost endothermically at 195 °C. Such a high-temperature dehydration confirms coordinated water molecules [22]. The intermediate formed is manganese salicylate oxalate, which undergoes exothermic decomposition in the range 330–455 °C to form MnO_2.

Cu(o-$C_6H_4(OH)COO)_2N_2H_4$

This complex undergoes complete exothermic decomposition in three steps to produce CuO as the final product. The first step is an exothermic dehydrazination at 110 °C to form copper disalicylate. The second step involves the sublimation of a molecule of salicylic acid in the temperature range 140–210 °C to yield copper salicylate. This is in accordance with the melting and sublimation temperature of the acid at 211 °C. Finally the intermediate undergoes exothermic decomposition at 300 and 330 °C (doublet) to form copper oxide.

$ZnL_2N_2H_4$: *L is* o-*or* p-*hydroxybenzoate*

The two isomeric complexes undergo the same type of two-step decomposition. The first-step endothermic decompositions, respectively at 240 °C, and 220 and 345 °C, produce $Zn(C_6H_4(O)COO)$ with the loss of a molecule each of N_2H_4 and salicylic acid. The intermediates then decompose exothermically at 430 °C and 495 °C respectively

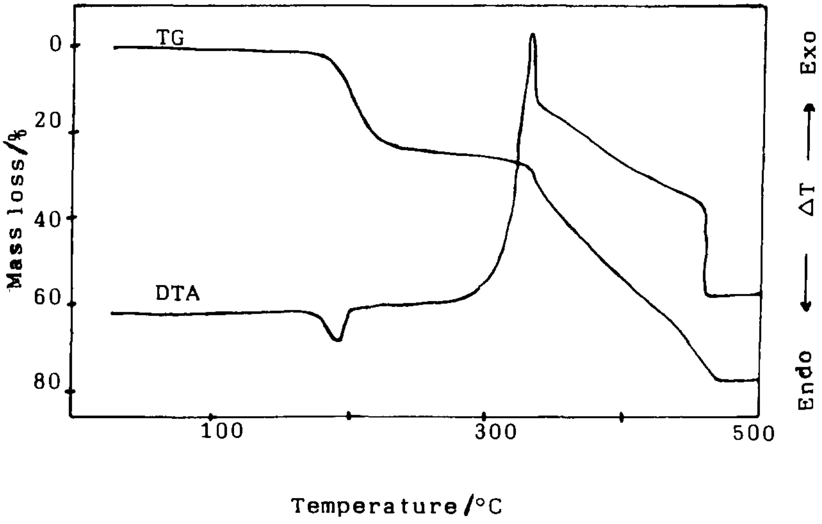

Fig. 1.

to form ZnO as the final product. The high decomposition temperature of the *p*-hydroxybenzoate complex may be due to the intermolecular H-bonding of phenolic OH in the solid lattice. The simultaneous TG-DTA curves of the salicylate complex are given in Fig. 2 as a representative example.

$Co(o\text{-}C_6H_4(OH)COO)_2 2N_2H_4$

The complex shows a two-step thermal decomposition; the first is endothermic and the second is exothermic. The endothermic decomposition at 255 °C produces the intermediate cobalt salicylate. This melts before decomposition as shown by a sharp endotherm at 340 °C in the DTA. The exothermic decomposition at 375 and 400 °C involves the decomoposition of the intermediate to form the metal oxide.

$N_i(o\text{-}C_6H_4(OH)COO)_2 2N_2H_4$

This follows an entirely different mode of decomposition compared to its coisomer: both decomposition steps are exothermic. The first at 275 °C produces nickel oxalate as intermediate which then decomposes at 340 °C to give NiO as the final product. Such a low decomposition temperature may be due to the catalytic action of trace Ni formed during decomposition.

$M(p\text{-}C_6H_4(OH)COO)_2 2N_2H_4$: *M is Co(II) and Ni(II)*

Both complexes undergo a three-step thermal decomposition. The first endothermic step at 155 °C and 180 °C respectively involves the dehydrazination to form $M(p\text{-}C_6H_4(OH)COO)_2N_2H_4$. The second-step mass loss (almost 50%) corresponds to two peaks in DTA (one exotherm and the other endotherm) showing the formation of the

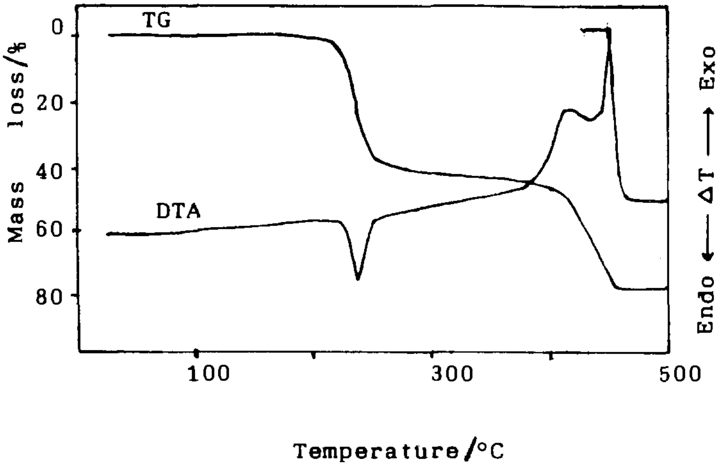

Fig. 2.

intermediate M(p-C_6H_4(O)COO). The intermediates melt as shown by the endotherms at 340 °C and 330 °C respectively. The final exothermic decompositions occur at 385 °C to produce the corresponding metal oxides. The simultaneous TG-DTA of the cobalt complex is given in Fig. 3.

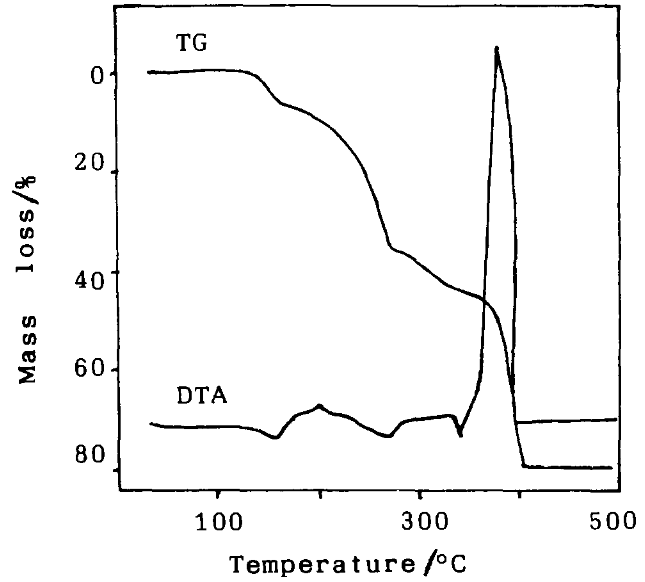

Fig. 3.

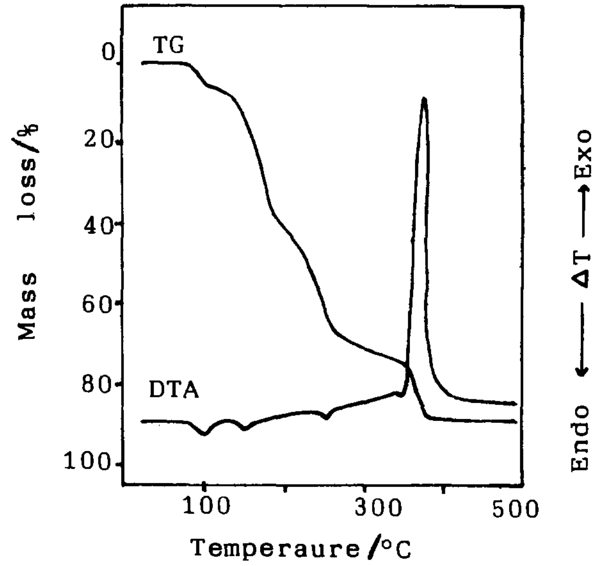

Fig. 4.

Table 4
X-ray powder diffraction data: *d* in Å; (*I*) in %

$Mn(o\text{-}C_6H_4(OH)COO)_2N_2H_4 \cdot 2H_2O$	$ZnL_2N_2H_4$		$M(o\text{-}C_6H_4(OH)COO)_22N_2H_4$		$M(p\text{-}C_6H_4(OH)COO)_22N_2H_2$		$(N_2H_5)_2M(o\text{-}C_6H_4(OH)COO)_4$	
	L = *o*-compd.	L = *p*-compd.	Co	Ni	Co	Ni	Co	Ni
9.94(80)	12.63(100)	12.70(100)	–	6.80(20)	6.80(80)	6.80(80)	8.34(15)	8.30(20)
8.68(10)	6.40(50)	6.45(60)	6.08(40)	6.03(100)	5.92(15)	5.68(15)	7.90(20)	7.91(20)
8.14(20)	5.69(20)	5.70(30)	5.54(100)	5.60(30)	4.98(30)	5.10(20)	7.50(20)	7.48(25)
7.16(85)	4.31(40)	4.35(50)	4.86(15)	4.90(75)	–	–	7.14(30)	–
6.38(40)	3.90(10)	3.92(10)	4.50(50)	4.55(20)	4.60(100)	4.60(100)	6.81(15)	6.80(20)
5.74(100)	3.80(10)	3.78(15)	3.86(90)	3.88(80)	3.82(50)	3.76(55)	6.51(100)	6.48(50)
4.86(90)	3.22(10)	3.25(50)	3.54(80)	3.56(40)	3.44(50)	3.42(60)	5.95(40)	5.92(45)
4.70(15)	3.03(10)	3.00(20)	3.28(40)	3.31(50)	3.26(25)	3.20(20)	5.54(50)	5.50(40)
4.54(10)	2.38(15)	2.40(20)	3.12(70)	3.13(60)	3.02(35)	3.02(30)	5.34(40)	5.32(35)
4.30(10)	2.17(15)	2.20(10)	2.80(40)	2.85(30)	2.80(40)	2.84(30)	5.07(50)	5.00(40)
4.06(10)	1.98(10)	1.95(10)	2.60(40)	2.64(40)	2.62(20)	2.70(20)	4.93(20)	4.90(25)
3.86(10)	1.63(10)	1.60(10)	2.50(10)	2.46(25)	2.52(35)	2.54(50)	4.82(10)	–
3.76(20)	–	1.52(15)	2.44(45)	2.42(10)	–	–	4.72(25)	4.70(30)
3.48(25)			–	2.33(20)	2.22(10)	2.22(15)	4.52(20)	4.46(25)
3.30(30)			2.14(20)	2.25(20)	2.14(20)	2.16(30)	4.33(20)	4.31(30)
3.24(25)			2.06(60)	2.05(40)	2.02(60)	2.02(30)	4.19(10)	4.16(25)
3.06(50)			2.00(10)	2.00(15)	1.96(25)	–	3.98(60)	3.96(100)
2.80(40)			1.92(20)	1.92(10)	–	–	3.77(35)	3.80(15)
2.42(40)			1.86(30)	1.88(10)	1.86(25)	1.86(20)	3.65(10)	3.65(10)
2.16(15)			1.84(30)	1.85(20)	1.82(20)	1.82(25)	3.60(15)	3.57(60)
2.04(20)			1.68(10)	1.70(10)	1.62(15)	1.60(20)	3.28(60)	3.33(40)
1.82(30)			1.54(30)	1.56(10)	1.54(25)	1.54(20)	3.18(15)	3.20(20)
1.78(20)			1.50(10)	1.51(10)	1.48(20)	1.48(25)	3.10(15)	–
1.64(10)			1.42(10)	1.40(10)	–	–	3.04(15)	–
1.52(10)			–	–	1.32(10)	1.32(10)	2.98(20)	2.95(20)
1.20(40)			1.28(20)	1.27(15)	1.28(10)	1.28(10)	2.89(20)	2.87(20)
1.16(35)			1.22(30)	1.21(10)	1.22(15)	1.20(25)	2.82(20)	2.80(15)
1.10(30)			1.10(25)	–	1.10(30)	1.10(30)	2.73(25)	2.71(20)
			1.08(10)	1.08(15)	–	–	2.68(15)	2.67(15)

$(N_2H_5)_2M(o\text{-}C_6H_4(OH)COO)_4$: M is Co(II) and Ni(II)

Although the complexes decompose in three steps through isomeric intermediates, $M(o\text{-}C_6H_4(O)COO)$, there is a subtle difference in their modes of decomposition in the first two steps. The cobalt complex exhibits an initial endothermic decomposition at 100 °C with loss of N_2H_4, whereas the Ni complex (endotherm at 160 °C) loses a molecule each of N_2H_4 and salicylic acid. In the second step, the former compound undergoes endothermic decomposition at 150 and 250 °C, and the latter exothermic decomposition at 300 °C, both producing the isomeric intermediates. These melt respectively at 340 °C and 330 °C before both decomposing exothermically at 375 °C to give the corresponding metal oxides. Fig. 4 gives the simultaneous TG-DTA recording of the cobalt complex.

3.5. X-ray diffraction studies

X-ray diffraction data for the synthesised complexes are given in Table 4. The values of *d*-spacings and intensity are compared to ascertain isomorphism among the complexes. The four bishydrazine Co and Ni complexes of *o*- and *p*-hydroxybenzoates are isomorphs. The bishydrazinium complexes of Co and Ni show isomorphism. The zinc complexes also exhibit isomorphism. Mn and Cu complexes do not show isomorphism with any other complexes as evidenced by their different composition and geometry respectively.

3.6. Coordination geometry

From the results of magnetic, spectral, thermal and XRD studies, it is reasonable to propose six-coordination around Mn(II), Co(II) and Ni(II), four-coordination tetrahedral geometry around Zn(II), and square-planar geometry around Cu(II).

4. Conclusions

Except for the bishydrazine nickel salicylate and Mn complexes, all the complexes undergo thermal decomposition, via $M(C_6H_4(O)COO)$, intermediate formation. A similar difference in decomposition for the Ni complexes has already been observed in the thermal studies of bishydrazine metal formate [8] and acetate [9] complexes. All the complexes form the corresponding metal oxides at low temperatures around 300–500 °C. Ni and Cu salicylate complexes show complete exothermic decomposition, whereas other complexes show both endothermic and exothermic decomposition. It is interesting to note that for Co and Ni complexes, the metal salicylates (divalent) formed as intermediates invariably undergo melting before decomposition. The fact that phenolic oxygen is not normally involved in coordination in salicylate complexes is substantiated by this study.

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