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Benzoate Complexes of Dipositive First Row Transition Metal Ions with Hydrazine

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BENZOATE COMPLEXES OF DIPOSITIVE FIRST ROW TRANSITION METAL IONS WITH HYDRAZINE

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ABSTRACT

Hydrazine metal benzoate complexes of the formula $M(C_6H_5COO)_2N_2H_4$, where M = Mn and Zn and bis(hydrazine) metal benzoate complexes of the formula $M(C_6H_5COO)_2(N_2H_4)_2$, where M = Fe, Co, Ni, Zn and Mg, and bis(hydrazinium) nickel benzoate complex have been prepared in aqueous solution by the reaction of hydrazinium benzoate and the corresponding metal nitrate hydrates. The complexes were characterised by analyses, magnetic, spectral, thermal and XRD chemical studies. The magnetic moments and electronic spectra reveal that $M(C_6H_5COO)_2N_2H_4$ is tetrahedral and the other complexes are octahedral. Infrared spectra show that hydrazine is bidentate bridging, while $N_2 H_5^+$ and carboxylate ions are Simultaneous TG-DTA shows that the unidentate. complexes undergo both exothermic and endothermic decomposition via metal benzoate or oxalate intermediates to form the metal The benzoate intermediates for the Mn, Co and Mg oxide. complexes melt before decomposition, whereas the $(N_{2}H_{5})_{2}Ni(C_{6}H_{5}COO)_{4}$ itself melts complex before

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decomposition. X-rav powder pattern reveals that tetrahedral complexes are isomorphous and except $(N_{2}H_{5})_{2}Ni(C_{6}H_{5}COO)_{4}$, the other octahedral complexes are isomorphous.

INTRODUCTION

The hydrazine derivatives of metal carboxylates are better potential precursors to fine particle metal or mixed metal oxides than their non-carboxylate counterparts¹. This type of complexes containing aliphatic carboxylates such as acetate^{3,4} oxalate⁵⁻⁸ formate². and and hydrazinecarboxylate9-13 have been alreadv reported. Interestingly, some studies have been reported from our laboratory on EDTA¹⁴, malonate¹⁵, succinate¹⁵, glycinate¹⁶ and glycolate¹⁶ complexes. Because of our interest in carboxylate systems in general and aromatic carboxylate systems in particular, we have endeavoured to synthesise and conduct an exhaustive study of the spectral and thermal behaviour of complexes of hydrazine metal benzoates. This report presents the results of these studies.

RESULTS AND DISCUSSION

The bis(hydrazine) metal benzoate complexes have been prepared by the reaction of the corresponding metal nitrate hydrates and hydrazinium benzoate in aqueous solution. The reaction may be represented as follows.

$$M(NO_3)_2 nH_2 O + 2 C_6 H_5 COON_2 H_5 \longrightarrow M(C_6 H_5 COO)_2 (N_2 H_4)_2 + 2 HNO_3 + n H_2 O$$

where M = Fe, Co and Ni. The Mg, Mn, Zn and $(N_2H_5)_2Ni(C_6H_5COO)_4$ compounds have been prepared by mixing the metal nitrate hydrate and hydrazinium benzoate with/without hydrazine hydrate. The analytical data of the complexes are summarized in Table I. These complexes are stable towards air and insoluble in water.

Magnetic Moments

The room temperature magnetic moments of the compounds (Table I) show that they are paramagnetic except the Zn and Mg complexes which are diamagnetic. The values correspond to high spin octahedral coordination for the Fe, Co and Ni complexes and tetrahedral coordination for the Mn complex which is a d^5 system. The structures of the complexes are given in Fig.1.

Electronic Spectra

The electronic spectra of the Fe, Co and Ni complexes are in support of octahedral coordination around the metal ions. For example, the nickel complexes exhibit two bands at 9710 and 28,330 cm⁻¹ which are assigned to ${}^{3}A_{2g}(F) \longrightarrow {}^{3}T_{2g}(F)$ and ${}^{3}A_{2g}(F) \longrightarrow {}^{3}T_{1g}(P)$, respectively. The intense yellow-green colour of Mn complex and the absorption around 22220 cm⁻¹ confirms the high spin tetrahedral coordination around Mn¹⁷.

Compound	Colour	Melting point(°C)	% Hydrazine Found/(Calcd.)	% Metal Found/(Calcd)	Yield %	Magnetic moment (B.M)
Mn(C_H_COO) _N_H,	Yellow green	195 ^a	10.00	16.30	80	5.82
MnC ₁₄ H ₁₄ O ₄ N ₂			(9.73)	(16.69)		
Zn(C ₆ H ₅ COO) ₂ N ₂ H ₄	Colourless	160 ^a	9.20	19.80	80	Dia-
ZnC ₁₄ ^H 14 ^O 4 ^N 2			(9.44)	(19.25)		magnetic
Fe(C ₆ H ₅ COO) ₂ (N ₂ H ₄) ₂	Light green	160 ^a	17.50	15.40	75	5.27
FeC ₁₄ ^H 18 ^O 4 ^N 4			(17.70)	(15.42)		
Co(C_H_COO) 2(N_H,) 2	Pink	180 ⁸	17.70	15.70	95	4.85
CoC ₁₄ H ₁₈ O ₄ N ₄			(17.55)	(16.13)		
Ni(C_H_COO) 2(N_H_) 2	Blue	150 ^a	17.70	15.70	90	3.44
NiC ₁₄ H ₁₈ O ₄ N ₄			(17.56)	(16.08)		
Zn(C_H_COO) 2(N_H_) 2	Colourless	180 ⁸	17.50	17.20	90	Dia-
ZnC ₁₄ H ₁₈ O ₄ N ₄			(17.24)	(17.59)		magnetic
Mg((C_H_COO) 2(N_H_)),	, Colourless	70 ^a	19.60	7.70	75	Dia-
MgC ₁₄ H ₁₈ O ₄ N ₄	<u>-</u>		(19.38)	(7.35)		magnetic
(N ₂ H ₅) ₂ Ni(C ₆ H ₅ COO) ₄	Light blue	121	10.80	10.20	85	3.52
NiC ₂₈ ^H 30 ⁰ 8 ^N 4			(10.52)	(9.64)		

Table I. Analytical and Magnetic Data

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a: decomposition

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 $M(C_6H_5COO)_2N_2H_4$, Where M = Mn and Zn





M (C6H5COO)₂ (N₂H₄)₂ Where M= Fe, Co, Ni, Zn and Mg





Infrared Spectra

The infrared spectra of the complexes are presented in Table II. The hydrazinate complexes show the asymmetric and symmetric stretching frequencies of carboxylate groups in the range 1560-1620 and 1390-1415 cm⁻¹, respectively. The $\Delta \mathcal{V}$ ($\mathcal{V}_{asym} - \mathcal{V}_{sym}$) separation around 200 cm⁻¹ is in

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	м(с ₆ н ₅	5 ^{COO)} 2 ^N 2	^H 4	M(C ₆	н ₅ соо) ₂	^{(N} 2 ^H 4 ⁾ 2		(N2 ^H 5)2 ^{Ni(C6^H5^{CC})}	⁰⁰⁾ 4	Assignments -1	
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	100	260	270	4.00	200	4.00	280	4.00	M_N	Letrotching	
400 300 370 400 330 400 300 400 10 Stretching	400	360	370	400	390	400	220	400	13-14	screcching	

BENZOATE COMPLEXES

support¹⁸ of monodentate coordination of the carboxylate The N-N stretching frequencies in the region 965groups. 980 cm⁻¹ are assigned to bidentate bridging¹⁹ coordination N_2H_4 in hydrazinate complexes. The hydrazinium complex of distinguished from the hydrazinate complex by the N-N is stretching frequency²⁰ of coordinated $N_2H_5^+$ at 1015 cm⁻¹. Moreover, the stretching frequencies of carboxylate and bending frequencies of NH₂ in hydrazinium complex are greater^{4,7} than those of hydrazinate complexes. This is probably due to the more polarised nature of the hydrazinium complex than the hydrazinate complex.

Thermal Studies

 $M(C_6H_5COO)_2N_2H_4$ (where M = Mn and Zn). The thermal decomposition of the complexes reflect their composition (Table III). They undergo two-step decompositions. In the first step, hydrazine is lost exothermically to form the benzoate intermediate. The manganese metal benzoate intermediate melts at 257°C which is observed as an endotherm in the DTA curve, whereas for the zinc benzoate such a phase transition is not observed. The second step involves the decomposition of the intermediate to form the corresponding metal oxide. The DTA curves show an endotherm and exotherm(s) for this decomposition. This may be interpreted that this step represents a continuous decomposition with the formation of other, less stable intermediates before forming the metal oxide. Simultaneous

Compound	DTA Peak Temperature (⁰ C)	Therm Temp.	ogravimetry Weight	y loss (%)	Decomposition product
	()	()	Found	Calcd.	
	210(-) 257(+) 210(-)	195-225	10.00	9.73 -	Mn(C _c H ₅ COO) ₂ melting
⁶ ⁶ ⁵ ⁶	368(+)) m 400(-))	280-430	74.00	73.59	Mn0 ₂
	180(-)	160-235	10.00	9.44	Zn(C ₆ H ₅ C00) ₂
Zn(C ₆ H ₅ COO) ₂ N ₂ H ₄	385(+) 455(-)	300-500	75.50	76.04	2n0
F=(C H COO) (N H)	324(-)	162-425	48.40	48.12	Fe ₂ (C ₂ O ₄) ₃
re(c ₆ ^H 5 ^{COO)} 2 ^{(N} 2 ^H 4 ['] 2	400(-)) 660(+)	600-685	77.00	77.95	Fe ₂ 03
	190(-) 270(+)	180-240 -	18.00	17.55	Co(C ₆ H ₅ COO) melting
co(c ₆ H ₅ co0) ₂ (N ₂ H ₄) ₂	395(+) 450(-)	300-470	77.50	78.03	^{Co} 3 ⁰ 4
N1(C6 ^H 5 ^{COO)} 2 ^{(N} 2 ^H 4)2	305(-) 325(+) 380(-)	150-320 320-420	51.00 79.00	51.02 79.53	N1C2 ⁰ 4. ^N 2 ^H 4 N10 ²
	215(-) 225(+)	1 80- 235	13,50	12,93	Zn(C ₆ H ₅ C00) ₂ 0.5N ₂ H ₄
Zn(C ₆ H ₅ C00) ₂ (N ₂ H ₄) ₂	390(+)	235-425	58,70	58,73	ZnC ₂ 04
	495(-) ^d	425-520	78.00	78.11	ZnO
	100(+)	7 0- 250	19.00	19.38	Mg(C ₆ H ₅ COO) ₂
Mg((C ₆ H ₅ COO) ₂ (N ₂ H ₄)	$\frac{120(+)}{2}$	-	-	-	Melting
	525(-)	400-53 5	88.00	88.44	Mg0
(N2H5)2N1(C6H5C00)4	120(+) 170(-) 255(-) 260(+)	- 130-240 240-325	- 30.00 50.50	- 30.56 50.61	Melting Ni(C ₆ H ₅ COO) ₂ C ₆ H ₅ COO Ni(C ₆ H ₅ COO) ₂
	375(+) 375(+) 405(-)	325-380 380-450	76.00 88.00	75.92 87.74	NIC NIO ²⁰ 4

TG-DTA of the manganese complex is given as a representative example in Fig.2.

 $Fe(C_6H_5COO)_2(N_2H_4)_2$. This complex shows an unusually high decomposition temperature compared to the low decomposition temperature of other complexes in this series. The pattern the TG curve indicates that of this complex undergoes of decomposition to the metal oxide in two steps. In the first step, the exotherms at 324 and 400°C correspond to the formation of ferric oxalate intermediate. The weight loss, as shown in the TG curve, is in good agreement with the proposed intermediate (Found: 48.40%; Calcd.: 48.12%). This intermediate is able to sustain heat upto 600°C without decomposition as it has been observed in the case of a lanthanum oxalate intermediate reported elsewhere²¹. Above 600° C finally it starts decomposing to give Fe₂O₂. The decomposition is endothermic $(660^{\circ}C)$ as shown by DTA.

 $M(C_6H_5COO)_2(N_2H_4)_2$ (Where M = Co and Mg). The simultaneous TG-DTA of the above complexes reveal that both follow the same two-step decomposition with the metal benzoate intermediate undergoing phase transition during melting. The melting temperature of the cobalt benzoate (270°C) is less than that of magnesium benzoate which melts at 340°C. The DTA shows an endotherm corresponding to this change without weight loss in the TGA. The formation of the intermediate is accompanied by a weight loss corresponding to two hydrazine molecules. The loss of hydrazine molecules



Fig. 2 Simultaneous TG-DTA of Mn (C6H5COO)2 N2H4

in the former compound is exothermic at 190° C whereas the same loss in the latter compound is endothermic around 100° C. This may be due to a weaker Mg-N bond which lacks d-orbital contribution. In the second step, the intermediate undergoes endothermic decomposition followed by an exotherm in a single step to produce the respective metal oxide. Fig. 3 shows the TG-DTA thermograms of the cobalt complex.

 $\frac{\text{Ni}(\text{C}_{6}\text{H}_{5}\text{COO})_{2}(\text{N}_{2}\text{H}_{4})_{2}}{\text{is presented in Fig. 4. TG shows a two-step decomposition pattern. The initial weight loss corresponds to the formation of <math>\text{NiC}_{2}\text{O}_{4}$. N_{2}H_{4} by an exothermic decomposition at 305°C . This intermediate decomposes to give NiO as the



Fig.3 Simultaneous TG-DTA of Co(C6H5COO)2(N2H4)2



Fig.4 Simultaneous TG-DTA of Ni (C6H5COO)2 (N2H4)2

final product. This is observed as an endotherm at $325^{\circ}C$ and an exotherm at $380^{\circ}C$ in the DTA. Its acetate⁴ counterpart also undergoes a two-step decomposition giving NiO as the end product.

 $Zn(C_6H_5COO)_2(N_2H_4)_2$. This compound follows a different mode of decomposition compared to its monohydrazinate complex. Simultaneous TG-DTA shows that the thermal decomposition takes place in three steps. The first exotherm at $215^{\circ}C$ corresponds to the loss of $1.5 N_2H_4$ as supported by TG. This species undergoes endothermic decomposition at 325 and $390^{\circ}C$ to produce the zinc oxalate intermediate. Finally, the intermediate decomposes exothermically at 475 and $495^{\circ}C$ (doublet) to form ZnO as the final product.

 $(N_2H_5)_2Ni(C_6H_5COO)_4$. This is the only complex in this series that melts before decomposition. This is observed as an endotherm in the DTA at $120^{\circ}C$. TG shows four steps corresponding to the formation of nickel benzoate benzoic acid, nickel benzoate, nickel oxalate and oxide. The exotherms at 170 and $255^{\circ}C$, respectively, indicate the formation of the first two solid products. The formation of the first product is supported by the fact that benzoic acid is not lost before $250^{\circ}C$ as its boiling point is $250^{\circ}C$. Nickel benzoate decomposes endothermically at 360 and $375^{\circ}C$ (doublet) to form the oxalate. This finally undergoes exothermic decomposition at $405^{\circ}C$ to form the solid product NiO. Simultaneous TG-DTA curves of the complex is given in Fig. 5.



Fig.5 Simultaneous TG-DTA of (N2H5)2Ni(C6H5COO)4

X-Ray Powder Diffraction Studies

Table IV gives the X-ray powder diffraction data of the complexes. The values of d-spacings and percentage of intensity reveal the following findings.

 $Mn(C_6H_5COO)_2N_2H_4$ and $Zn(C_6H_5COO)_2N_2H_4$ complexes have almost the same values of d-spacings and number of peaks. Hence, both are isomorphous and possess tetrahedral structure.

 $M(C_6H_5COO)_2(N_2H_4)_2$, where M = Fe, Co, Ni, Zn and Mg, have more or less the same values of d-spacings indicating isomorphism among them.

In the case of $(N_2H_5)_2Ni(C_6H_5COO)_4$, the values of d-spacings are different from those of $Ni(C_6H_5COO)_2(N_2H_4)_2$ and other hydrazinate complexes confirming that its structure is different from the other complexes reported in this paper. Downloaded by [Moskow State Univ Bibliote] at 21:03 08 July 2013

Table IV. X-Ray Powder Diffraction Data; $d(\mathbf{A})$ and I (%)

и (с ⁶ н ² соо)	$2^N 2^H 4 d(I)$) W	с ₆ 4 ₅ соо) ₂ (1	"Z ^H 4)2 d(()	2 _{N)}	H_5) $_{d(I)}^{Ni}$ (\mathcal{C}_{H_5} $_{c00}$) $_{4}$
иW	Zn	Ъe	Co	Ni	Zn	ВW	
18.80(50)	19.19(40)	7.20(100)	7.25(90)	7.30(85)	7.31(100)	7.31(35)	7.38(95)
14.48(100)	14.72(100)	5.90(75)	6.00(100)	6.00(100)	6.41(50)	6.30(47)	6.86(80)
7.31(49)	7.49(50)	ı	5.61(78)	5.61(40)	5.64(52)	5.68(100)	6.76(75)
6.23(50)	6.32(30)	4.93(65)	4.93(88)	5.07(48)	4.90(97)	4.95(42)	6.28(74)
5.57(72)	5.54(35)	4.82(95)	1	4.80(32)	,	ı	
4.90(54)	4.98(90)	4.53(65)	4.42(65)	ı	4.55(20)	4.50(24)	6.11(67)
3.62(54)	3.74(25)	4.19(72)	4.19(72)	ı	4.19(11)	1	5.61(100)
3.05(60)	2.98(50)	3.92(88)	3.97(66)	3.97(64)	,	1	5.41(85)
2.42(47)	2.43(20)	3.70(89)	3.77(68)	3.80(34)	3.86(10)	3.75(50)	5.10(78)
2.11(46)	2.13(60)	•	3.59(64)	3.58(40)	3.60(10)	ı	4.96(62)
1.97(40)	1.86(50)	I	3.47(62)	3.48(38)	ı	ı	4.93(62)
		3.38(67)	3.38(62)	3.36(34)	3.36(20)	3.21(47)	4.82(57)
		1	ı	ı	,	3.14(46)	4.55(87)
		2.90(65)	2.90(60)	2.90(26)	ı	ı	4.40(53)
		ı	2.81(58)	2.81(27)	2.80(14)	2.87(34)	4.13(55)
		2.38(55)	2.34(55)	2.34(23)	2.38(14)	2.41(26)	4.00(61)
		2.27(55)	2.26(40)	2.25(35)	2.27(07)	1	3.95(58)
		2.08(45)	2.07(30)	2.08(30)	2.09(21)	2.10(22)	3.71(75)
		1.85(45)	1.84(40)	1.83(40)	1.83(09)	1.86(14)	3.43(64)
		1.80(20)	1.76(15)	1.77(15)	•	1.78(13)	3.20(55)
		1.62(15)	1.59(10)	1.59(10)	1.60(10)	1.61(10)	3.16(48)
							3.14(49)
							3.02(42)
							2.95(48)
							2.90(43)

Structure and Metal Coordination

Based on analytical data, general behaviour and physicochemical studies, the following structures may be proposed for the compounds reported.

EXPERIMENTAL

All chemicals used were of analytical grade and the solvents were distilled before use. The ligand hydrazinium benzoate was prepared as reported earlier²². Hydrazine hydrate (99-100%) was used as received in these preparations.

Preparation of Complexes

 $\underline{\operatorname{Mn}(\operatorname{C}_{6}\operatorname{H}_{5}\operatorname{COO})_{2}}\cdot\operatorname{N}_{2}\operatorname{H}_{4}$. Manganese nitrate hexahydrate (2.87 g, 0.01 mol) in 50 mL water and 50 mL of an aqueous solution containing a mixture of hydrazinium benzoate (6.17 g, 0.04 mol) and hydrazine hydrate (2 mL, 0.04 mol) were mixed and stirred well. The crystalline precipitate formed after a few minutes was filtered, washed with alcohol and ether and dried over P₂O₅.

 $\frac{Zn(C_6H_5COO)_2 \cdot N_2H_4}{mol}$. Zinc nitrate hexahydrate (2.97 g, 0.01 mol) was dissolved in 100 mL of distilled water. To this clear solution was added an aqueous solution (50 mL) containing hydrazinium benzoate (6.17 g, 0.04 mol) with constant stirring. After a few minutes the solid product

formed was filtered, washed with alcohol and ether and airdried.

 $\frac{M(C_6H_5COO)_2(N_2H_4)_2}{W}$ (where M = Fe, Co and Ni). The complexes were prepared by mixing an aqueous solution (50 mL) containing the corresponding metal nitrate hydrates (e.g., $Co(NO_3)_2.6H_2O$, 2.91 g, 0.01 mol) and an aqueous solution (50 mL) of hydrazinium benzoate (3.08 g, 0.02 mol) with constant stirring. The complexes which formed slowly were allowed to settle for sometime and separated as mentioned above.

 $\frac{Zn(C_6H_5COO)_2(N_2H_4)_2}{Containing zinc nitrate hexahydrate (2.97 g, 0.01 mol) and a solution containing a mixture of hydrazinium benzoate (6.17 g, 0.04 mol) and hydrazine hydrate (2 mL, 0.04 mol) were mixed and stirred well. The complex formed immediately and was digested over a water bath at <math>70^{\circ}C$ and filtered, washed with alcohol and air-dried.

 $\underline{Mg(C_6H_5COO)_2(N_2H_4)_2}$. Magnesium nitrate hexahydrate (2.56 g, 0.01 mol) was dissolved in 50 mL of water and to this an aqueous solution (100 mL) containing a mixture of hydrazinium benzoate (3.08 g, 0.02 mol) and hydrazine hydrate (7 mL, 0.14 mol) was added slowly with stirring. The clear solution was concentrated on a water bath for a few hours. A white solid separated. It was filtered and processed as described above.

 $(N_2H_5)_2Ni(C_6H_5COO)_4$. This was the only complex formed as hydrazinium containing metal benzoate. It was prepared by mixing an aqueous solution (50 mL) containing nickel nitrate hexahydrate (2.91 g, 0.01 mol) and a solution containing hydrazinium benzoate (6.17 g, 0.04 mol) and stirring well. The complex was formed immediately. It was then filtered and handled as before.

Physico-chemical Techniques

The hydrazine content in the complexes was determined by titrating against 0.025 M KIO₃ solution under Andrews conditions²³. The metal content was determined volumetrically using a standard EDTA solution after decomposing a known amount of the complex with concentrated nitric acid²³.

The magnetic susceptibility of the complexes was measured using a Gouy balance at room temperature using mercurytetrathiocyanatocobaltate [HgCo(CNS)₄] as the calibrant.

Electronic spectra in the solid state were obtained using a Hitachi U-3400 spectrophotometer and dispersing the solid samples in Nujol.

Infrared spectra in the region 4000-200 cm⁻¹ were recorded on pressed pellets of KBr using a Perkin Elmer 597 spectrophotometer.

The simultaneous TG-DTA data of the complexes were recorded employing a STA 1500 thermal analyser. All the

experiments were carried out in air, at a heating rate of 10° C per minute. The amounts of the complexes taken for analyses were 5-10 mg. Platinum cups were used as sample holders and alumina as reference.

The X-ray powder diffraction pattern of the complexes was recorded using a Philips X-ray diffractometer model PW 1050/70 employing CuK_{∞} radiation with a nickel filter.

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