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THERMAL REACTIVITY OF METAL ACETATE HYDRAZINATES

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ABSTRACT

Metal acetate hydrazinates, $M(CH_3COO)_2(N_2H_4)_2$ (M = Mn, Co, Ni, Zn, Cd) have been prepared and characterized by chemical analysis and infrared absorption spectra. Thermal decomposition of the complexes has been studied using simultaneous TG–DTG–DTA technique. Metal acetate hydrazinates decompose exothermically through metal acetate intermediates to the respective metal oxides.

INTRODUCTION

The preparation of metal acetate hydrazinates [1–4] and the crystal structure of $Zn(CH_3COO)_2(N_2H_4)_2$ [1] have been reported previously. However, there seems to be no detailed study on the thermal properties of these complexes. In continuation of our studies on metal hydrazine complexes of carboxylic acids like oxalate [5] and formate [6], we now report the preparation, infrared spectra and thermal analysis of a few metal acetate hydrazinates.

EXPERIMENTAL

Metal acetate hydrazinates, $M(CH_3COO)_2(N_2H_4)_2$ (M = Mn, Co, Ni, Zn, Cd) were prepared by reaction of freshly prepared metal acetate hydrates with excess hydrazine hydrate (99–100%). The reaction was instantaneous and yielded hydrazinate complexes as shown below

$$M(CH_3COO)_2 \cdot xH_2O + 2N_2H_4 \cdot H_2O \rightarrow M(CH_3COO)_2(N_2H_4)_2 + (x+2)H_2O \quad (1)$$

where M = Mn, Co, Ni, Zn or Cd. The products of the reaction were filtered, washed with alcohol and ether and dried over P_2O_5 in a vacuum desiccator. The composition of the complexes was fixed by chemical analysis and characterized by infrared spectra. The metal content was determined by

EDTA titration and hydrazine content by titrating against 0.025 M KIO_3 solution under Andrew's conditions [7]. Infrared spectra of the complexes were recorded as nujol mulls using a Perkin-Elmer 781 spectrophotometer. Simultaneous TG–DTG–DTA of the complexes were recorded in air employing a Ulvac Sinku-Riko TA 1500 instrument. The heating rate employed was 10°C min^{-1}. Platinum cups were used as sample holders. Samples of 5–6 mg were used for each experiment.

X-ray powder diffraction patterns of the decomposition products (metal oxides) were obtained with a Philips PW 1050/70 diffractometer using CuK_α and CoK_α radiation.

RESULTS AND DISCUSSION

Results of the chemical analysis of the complexes are given in Table 1 and conform to the formula $M(CH_3COO)_2(N_2H_4)_2$. The infrared absorption frequencies of the complexes are listed and assigned in Table 2. A typical infrared spectrum of $Ni(CH_3COO)_2(N_2H_4)_2$ is shown in Fig. 1. The assignments are made on the basis of earlier studies on metal hydrazine complexes [5,6] and metal acetates [8–11]. The absorption band in the region 980–965 cm^{-1} has been attributed to ν_{N-N} of bridged hydrazine. Since the metal ion in these complexes is reported [1] to have octahedral coordination, acetate groups may be coordinated to metal through the O atom as monodentate ligands. The observed large separation ($\Delta\nu \simeq 190$ cm^{-1}) between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ of the acetate group in all the complexes (Table 2) also supports coordination of acetate group via a monodentate ligand [1].

Simultaneous TG–DTG–DTA data of the complexes are summarized in Table 3. Typical thermograms of $Mn(CH_3COO)_2(N_2H_4)_2$ and $Ni(CH_3COO)_2(N_2H_4)_2$ are shown in Figs. 2 and 3, respectively. The compositions of the intermediates are those which best fit the observed weight loss in TG. The main features of the thermal analysis are as follows.

TABLE 1

Chemical analysis data of $M(CH_3COO)_2(N_2H_4)_2$

M	Hydrazine (%)		Metal (%)	
	Found	Calcd.	Found	Calcd.
Mn	26.40	27.01	23.00	23.19
Co	25.80	26.56	24.75	24.46
Ni	26.15	26.59	23.80	24.39
Zn	25.40	25.87	26.80	26.43
Cd	21.50	21.74	38.50	38.18

TABLE 2

Infrared absorption frequencies of $M(CH_3COO)_2(N_2H_4)_2$ (cm^{-1})

Mn	Co	Ni	Zn	Cd	Band Assignment
3340	3340	3350	3340	3350	N–H stretching
3300	3300	3300	3300	3300	
3250	3240	3260	3250	3250	
3180	3190	3210	3210	3180	
1620	1625	1625	1625		
1610	1605	1605	1610	1615	COO asym. stretching
1420	1420	1420	1420	1420	COO sym. stretching
(190)	(195)	(195)	(190)	(195)	$\Delta\nu\ [\nu_{asym}(COO^-) - \nu_{sym}(COO^-)]$
1535	1535	1535	1535	1535	C–O stretching
1335	1335	1335	1335	1335	
1295	1305	1305	1305		CH_3 deformation
1165	1190	1210	1185		
1120	1145	1155	1140	1150	NH_2 twisting + wagging
1045	1050	1045			
1015	1015	1015	1010	1015	CH_3 rocking
965	975	980	975	970	N–N stretching
920	925	925	920	920	C–C stretching
645	655	655	650	650	NH_2 rocking
620	620	615		620	COO rocking

(i) All the metal acetate hydrazinates decompose exothermically in three steps to the respective metal oxides.

(ii) Manganese, cobalt, zinc and cadmium complexes decompose through

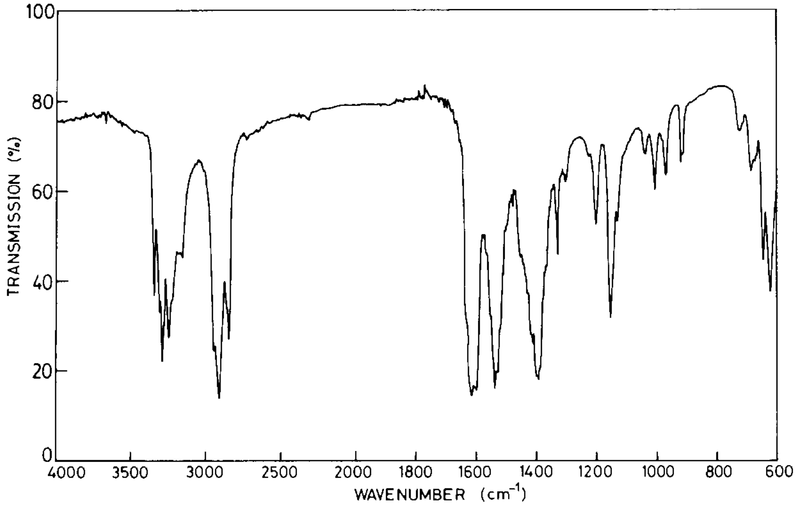

Fig. 1. Infrared spectrum of $Ni(CH_3COO)_2(N_2H_4)_2$.

TABLE 3

Thermal analysis data of $M(CH_3COO)_2(N_2H_4)_2$

M	Step No.	Thermogravimetry temp. range (°C)	Weight loss (%)		DTA peak temp. (°C)	Reaction
			Found	Calcd.		
Mn	1	130–170	21	20.26	150 (exo)	$Mn(CH_3COO)_2(N_2H_4)_2 \rightarrow Mn(CH_3COO)_2 \cdot 0.5N_2H_4$
	2	170–205	27	27.01	190 (exo)	$Mn(CH_3COO)_2(N_2H_4)_2 \rightarrow Mn(CH_3COO)_2$
	3	205–280	64.5	63.31	275 (exo)	$Mn(CH_3COO)_2(N_2H_4)_2 \rightarrow MnO_2$
Co	1	160–190	20	19.92	180 (exo)	$Co(CH_3COO)_2(N_2H_4)_2 \rightarrow Co(CH_3COO)_2 \cdot 0.5N_2H_4$
	2	190–220	27	26.56	222 (exo)	$Co(CH_3COO)_2(N_2H_4)_2 \rightarrow Co(CH_3COO)_2$
	3	220–315	66	66.69	305 (exo)	$Co(CH_3COO)_2(N_2H_4)_2 \rightarrow Co_3O_4$
Ni	1	190–215	49		205 (exo)	–
	2	215–245	52	51.10	230 (exo)	$2Ni(CH_3COO)_2(N_2H_4)_2 \rightarrow Ni + Ni(CH_3COO)_2$
	3	245–335	69	68.97	330 (exo)	$Ni(CH_3COO)_2(N_2H_4)_2 \rightarrow NiO$
Zn	1	150–195	26	25.87	130 (exo)	$Zn(CH_3COO)_2(N_2H_4)_2 \rightarrow Zn(CH_3COO)_2$
	2	195–310	46	46.49	280 (exo)	$2Zn(CH_3COO)_2(N_2H_4)_2 \rightarrow ZnO + Zn(CH_3COO)_2$
	3	310–450	69	67.10	410 (exo)	$Zn(CH_3COO)_2(N_2H_4)_2 \rightarrow ZnO$
Cd	1	115–170	14	16.30	165 (exo)	$Cd(CH_3COO)_2(N_2H_4)_2 \rightarrow Cd(CH_3COO)_2 \cdot 0.5N_2H_4$
	2	170–215	21	21.74	200 (exo)	$Cd(CH_3COO)_2(N_2H_4)_2 \rightarrow Cd(CH_3COO)_2$
	3	215–395	57	56.38	385 (exo)	$Cd(CH_3COO)_2(N_2H_4)_2 \rightarrow CdO$

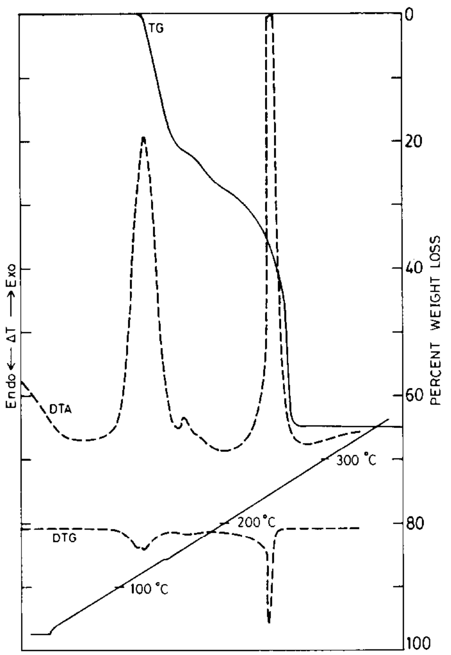

Fig. 2. TG–DTA–DTG curves of $Mn(CH_3COO)_2(N_2H_4)_2$.

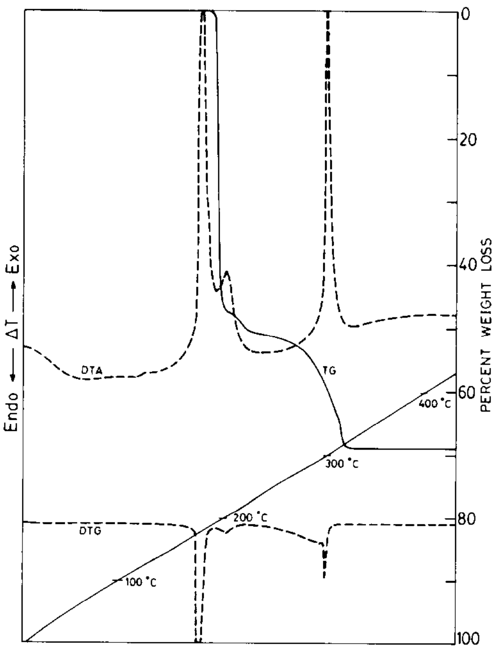

Fig. 3. TG–DTA–DTG curves of $Ni(CH_3COO)_2(N_2H_4)_2$.

the corresponding metal acetates, and the nickel complex decomposes through a mixture of nickel metal and nickel acetate.

(iii) Whereas the zinc complex loses both hydrazine molecules in a single step, Mn, Co and Cd complexes lose hydrazine in two steps. In the case of the nickel complex, loss of hydrazine is accompanied by partial decomposition of nickel acetate to nickel metal.

(iv) The metal oxide formation temperatures from the decomposition of metal acetate hydrazine complexes (275–400°C) are lower than those reported [11,12] for metal acetate hydrates (350–400°C).

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