Studies on Bis-hydrazine Complexes of Metal Propionates and Mixed Metal Propionates

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Metal propionate hydrazinates, $M(CH_3CH_2COO)_2(N_2H_4)_2$ where M = Mn, Co, Ni, Zn or Cd, and mixed metal propionate hydrazinates with cobalt, $M_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$ where M = Mg, Mn, Ni, Zn or Cd, have been prepared and characterized by analytical, magnetic, spectral, thermal and X-ray diffraction studies. The thermal decomposition of the former complexes yields the metal oxides while the latter mixed metal complexes give the corresponding metal cobaltites as the final residue. Formation of metal cobaltites has been confirmed by TG weight loss, IR spectra and X-ray diffraction.

Introduction

The interest in hydrazine metal complexes are due to their low temperature decomposition to the metal oxides. Though extensive work has been carried out in hydrazine metal complexes with variety of anions [1], the corresponding aliphatic carboxylate complexes are studied only to a limited extent which includes formate, acetate and oxalate complexes [2–8]. In the monocarboxylic acid series, the metal formate hydrazinates and the metal acetate hydrazinates have been studied [2–6] and are known to decompose in multiple steps giving metal oxide or metal powder as the final residue. However, no attempt has been made to establish the structure of these complexes. Similar to formic and acetic acids, propionic acid is also expected to form hydrazine metal complexes, and indeed these complexes have been prepared in the present work and these metal propionate hydrazinates, $M(CH_2CH_2COO)_2(N_2H_4)_2$ where M = Mn, Co, Ni, Zn or Cd, are found to be isomorphous. So these are expected to form solid solution precursors having the composition $M_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$, where M = Mg, Mn, Ni, Zn or Cd. Since the ionic radii of Mg^{2+} ion is comparable with Co^{2+}, it also forms the solid solution. The advantage in the propionate complexes over formate and acetate complexes are due to the single step decomposition of the former to the corresponding metal oxide. Also these complexes decompose at very much lower temperatures than the corresponding formate and acetate complexes [3, 6]. The method involved in the preparation of formate and acetate complexes was the addition of hydrazine hydrate to corresponding metal carboxylates. However, a new methodology is adopted for the preparation of metal propionate hydrazinates and successfully extended to the mixed metal complexes. Since the complexes are precipitated from the clear solutions this method achieves excellent stoichiometry and low impurity content. Unlike the hydrazine complexes of mixed metal hydrazidocarboxylates these mixed metal propionate hydrazinates are stable in air. The mixed metal propionate hydrazinates are exploited in the present work for the preparation of cobaltites, MCo_2O_4, where M = Mg, Mn, Ni, Zn or Cd, at low temperatures.

The increasing interest in the fine-particle cobaltites are due to their use as catalysts and oxide electrode materials [9]. The conventional procedure for the preparation of spinel oxides is the ceramic method [10, 11] which requires higher temperatures (~1400 °C). However, certain cobaltites, *e.g.*, $NiCo_2O_4$ and $ZnCo_2O_4$ could not be prepared by this method, because of their instability at such higher temperatures [12]. Also, the cobaltites obtained by the ceramic method have low surface area, consequently, they are unsuitable as catalysts. A number of attempts have been made to bring down the cobaltite formation temperature by using either the "wet method" [13, 14] or the precursor method [15–20]. The precursor tech-

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nique is advantageous, since it is highly stoichiometric and provides a route to higher surface area complex oxides. In this paper, we report the preparation and characterization of the metal propionate hydrazinate and mixed metal propionate hydrazinate complexes and their thermal decomposition.

Results and Discussion

The metal propionate hydrazinates, $M(CH_3CH_2COO)_2(N_2H_4)_2$ where M = Mn, Co, Ni, Zn or Cd, have been prepared and are found to be isomorphous from their X-ray powder diffraction studies (Table I). The X-ray powder diffraction patterns of the solid solution precursors, $M_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$, are also identical to the metal propionate hydrazinates indicating the formation of solid solutions (Table I). The chemical analysis data (Table II and III) of the complexes conform to the desired composition [21, 22].

The magnetic moments of the metal propionate hydrazinates (Table II) are in accordance with the high spin octahedral nature of the complexes [23]. However, the corresponding zinc and cadmium complexes are diamagnetic as expected.

The electronic spectra of cobalt propionate hydrazinate shows a band at 20,790 cm^{-1} which is attributed to the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition. The corresponding nickel complex shows two bands at 17,400 and 27,300 cm^{-1} and are assigned to $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions, respectively. These transitions of cobalt and nickel complexes are characteristic of octahedral geometry around the metal ion [24].

The infrared spectra of all the complexes show the characteristic N–N stretching frequency of N_2H_4 groups in the region 960–970 cm^{-1} indicating the bidentate bridging nature of these hydrazine molecules [25]. The two bands observed at 1600 and 1380 cm^{-1} for these complexes are assigned to the ν_{sym} and ν_{asy} stretchings of the carboxylate ions. The observed large separation ($\Delta\nu$ = 220 cm^{-1}) between $\nu_{asy}(COO^-)$ and $\nu_{sym}(COO^-)$ of the propionate groups in all the complexes indicates the monodentate coordination of the propionate ions [26].

The TG and DTA studies show that all the complexes decompose exothermically in a single step, to give respective metal oxide as the end product in the case of metal propionate hydrazinates, while the mixed metal precursors yield the respective metal cobaltites. The TG-DTA data of all the complexes are summarized in Table IV.

The formation of cobaltites from the mixed metal precursors was confirmed by the analytical determination of metal ions, infrared spectra and X-ray powder diffraction. The analytical, infrared and X-ray diffraction data of these cobaltites are given in Table V. The chemical analysis data of the cobaltites show that cobalt and metal are in 2:1 ratio. The infrared spectra of the cobaltites show

Table I. X-ray powder diffraction data ("d"-spacings) in Å.

$M(CH_3CH_2COO)_2(N_2H_4)_2$					$M_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$				
Mn	Co	Ni	Zn	Cd	Mg	Mn	Ni	Zn	Cd
11.33	10.92	11.05	11.19	10.85	11.05	10.92	11.19	10.92	11.33
7.37	7.14	7.20	7.25	7.26	7.20	7.20	7.14	7.31	7.25
6.42	6.33	6.37	6.33	6.46	6.33	6.37	6.42	6.33	6.42
5.41	5.50	5.47	5.44	5.50	5.41	5.47	5.50	5.50	5.44
4.82	4.87	4.90	4.93	4.90	4.85	4.90	4.87	4.87	4.82
4.10	4.13	4.11	4.17	4.23	3.92	3.90	3.95	3.95	3.93
3.90	3.92	3.93	3.95	3.95	3.60	3.61	3.63	3.60	3.64
3.61	3.63	3.60	3.59	3.63	3.40	3.41	3.41	3.39	3.38
3.41	3.38	3.40	3.39	3.40	3.33	3.34	3.31	3.34	3.34
3.31	3.34	3.33	3.31	3.38	3.18	3.21	3.18	3.22	3.21
3.22	3.18	3.21	3.18	–	2.78	2.78	2.79	2.78	2.80
2.80	2.78	2.79	2.77	2.91	2.59	2.58	2.59	2.59	2.58
2.59	2.58	2.58	2.59	2.59	2.53	2.53	2.51	2.51	2.52
2.52	2.53	2.51	2.52	2.46	2.26	2.26	2.25	2.26	2.26
2.25	2.26	2.25	2.26	2.31	2.18	2.18	2.17	2.17	2,18
2.17	2.18	2.18	2.17	2.18	1.98	1.98	1.97	1.98	1.97
1.98	1.98	1.98	1.98	1.98	1.96	1.95	1.95	1.96	1.95
1.96	1.95	1.96	1.96	1.96					

Table II. Analytical data of $M(CH_3CH_2COO)_2(N_2H_4)_2$.

M	Empirical formula	Colour	Yield [%]	Decomp. temp. [°C]	Metal [%] calcd	Metal [%] found	Hydrazine [%] calcd	Hydrazine [%] found	Magnetic moment (μ_{eff}) in BM
Mn	$(C_6H_{18}O_4N_4)Mn$	colourless	80	170	24.17	24.00	20.72	20.00	5.8
Co	$(C_6H_{18}O_4N_4)Co$	pink	90	160	23.82	23.60	21.89	21.50	4.7
Ni	$(C_6H_{18}O_4N_4)Ni$	violet	90	175	23.84	23.50	21.83	21.30	3.4
Zn	$(C_6H_{18}O_4N_4)Zn$	colourless	90	210	23.26	23.40	23.72	23.10	diamagnetic
Cd	$(C_6H_{18}O_4N_4)Cd$	colourless	85	250	19.87	20.00	34.84	34.00	diamagnetic

Table III. Analytical data of $M_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$.

M	Empirical formula	Colour	Yield [%]	Decomp. temp. [°C]	Hydrazine [%] calcd	Hydrazine [%] found	Mole ratio Co^{2+}/M^{2+}
Mg	$(C_{18}H_{54}O_{12}N_{12})MgCo_2$	light-red	80	180	24.88	24.60	1.96
Mn	$(C_{18}H_{54}O_{12}N_{12})MnCo_2$	dark-red	80	195	23.93	24.00	1.98
Ni	$(C_{18}H_{54}O_{12}N_{12})NiCo_2$	bluish violet	85	190	23.82	24.10	2.01
Zn	$(C_{18}H_{54}O_{12}N_{12})ZnCo_2$	light-red	90	195	23.63	23.30	2.05
Cd	$(C_{18}H_{54}O_{12}N_{12})CdCo_2$	light-red	85	185	22.34	22.80	1.99

Table IV. Thermal data.

Compound	DTA peak temp. [°C]	Thermogravimetry temp. range	weight loss [%] calcd	weight loss [%] found	Final product
$Mn(CH_3CH_2COO)_2(N_2H_4)_2$	210 (exo)	170–240	73.25	74.00	MnO
$Co(CH_3CH_2COO)_2(N_2H_4)_2$	171 (exo) 260 (exo)[d]	160–280	70.18	70.00	Co_3O_4
$Ni(CH_3CH_2COO)_2(N_2H_4)_2$	181 (exo)	175–200	72.22	72.60	NiO
$Zn(CH_3CH_2COO)_2(N_2H_4)_2$	225 (exo) 270 (exo)[d]	210–300	70.48	70.90	ZnO
$Cd(CH_3CH_2COO)_2(N_2H_4)_2$	270 (exo)	250–280	60.20	59.80	CdO
$Mg_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$	210 (exo)	180–220	73.33	73.90	$MgCo_2O_4$
$Mn_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$	205 (exo)	195–230	70.53	71.00	$MnCo_2O_4$
$Ni_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$	200 (exo)	190–220	70.20	71.00	$NiCo_2O_4$
$Zn_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$	205 (exo)	195–230	69.63	70.20	$ZnCo_2O_4$
$Cd_{1/3}Co_{2/3}(CH_3CH_2COO)_2(N_2H_4)_2$	200 (exo)	185–220	65.82	66.50	$CdCo_2O_4$

[d] Doublet.

Table V. Properties of ultrafine cobaltites.

Compound	XRD a(Å)	IR [cm^{-1}] ν_1	IR [cm^{-1}] ν_2	Mole ratio Co^{3+}/M^{2+}
$MgCo_2O_4$	8.120	660	550	1.98
$MnCo_2O_4$	8.221	650	560	2.02
$NiCo_2O_4$	8.118	650	555	2.03
$ZnCo_2O_4$	8.117	660	550	2.03
$CdCo_2O_4$	8.123	650	560	1.97

absorption bands at 650 (ν_1) and 550 cm^{-1} (ν_2) due to the metal-oxygen stretching in tetrahedral and octahedral sites, respectively [15]. The X-ray powder diffraction patterns of the cobaltites correspond to those reported in the literature [27]. The line broadening observed is due to the small crystallite size. Further, this solid solution technique can be exploited for the preparation of fine-particle oxides through mixed metal formate hydrazinate and mixed metal acetate hydrazinate precursors using the present experimental conditions.

Experimental

All the chemicals used were of analytically pure grade, hydrazine hydrate (99–100%) and propionic acid (99%) were used as received. All the solvents were distilled before use.

Preparation of metal propionate hydrazinates

These complexes were prepared by adding an aqueous solution containing a mixture of propionic acid (1.5 g, 0.02 mol) and hydrazine hydrate (2 g, 0,04 mol) to an aqueous solution of the respective metal nitrate hydrate, *e.g.*, $Ni(NO_3)_2 \cdot 6H_2O$ (2.91 g, 0,01 mol). The resulting solution was allowed to stand at room temperature, and the precipitate obtained after 30–40 min was filtered, washed with alcohol and dried in vacuum desiccator over P_2O_5.

Preparation of mixed metal propionate hydrazinates

These mixed metal precursors were prepared by adding an aqueous solution containing a mixture of propionic acid (4.5 g, 0.06 mol) and hydrazine hydrate (6 g, 0.12 mol) to an aqueous solution containing a mixture of cobalt nitrate hexahydrate (5.82 g, 0.02 mol) and the corresponding metal nitrate hydrate, *e.g.*, $Ni(NO_3)_2 \cdot 6H_2O$ (2.91 g, 0.01 mol). The clear solution was allowed to stand at room temperature. The precipitate formed after 30–40 min was filtered, washed with alcohol and dried in vacuum desiccator containing P_2O_5.

The hydrazine content in all the complexes was determined volumetrically by titration with 0.025 M potassium iodate solution under Andrews' condition [21]. The cobalt content in the mixed metal precursors and the cobaltites was determined by separating cobalt as the $Co(C_{10}H_6ONO)_3$ complex using α-nitroso β-naphthol [22]. The filtrate of these separations containing divalent metal ions was treated with chloroform to remove excess α-nitroso β-naphthol, and the metal ions were estimated by titration with standard EDTA solution. The metal content in the metal propionate hydrazinates was determined by EDTA complexometric titrations [21] after decomposing a known amount of the complex with concentrated nitric acid. The magnetic moments at room temperature were determined by Gouy's method using $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra were recorded on a Shimadzu UV-visible 240 A spectrophotometer. Infrared spectra of the complexes and the cobaltites were recorded on a Perkin-Elmer 597 spectrophotometer, using KBr discs in the range 4000–200 cm^{-1}. A DuPont DTA-750 instrument was used to carry out differential thermal analyses and a Perkin-Elmer TGS-2 thermogravimetric system was used for thermogravimetry. All experiments were performed in air under ambient atmosphere with a heating rate of 10 °C/min. Platinum cups were used to hold 10–12 mg samples for the analyses. X-ray powder diffraction patterns of the samples were obtained using a Philips X-ray diffractometer model PW 1050/70 using CuK_α and CoK_α radiations. The XRD patterns for the cobaltites were recorded after heating the mixed metal precursors at 250 °C in a silica crucible for at least 15 min.

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[1] E. W. Schmidt, Hydrazine and its Derivatives, Wiley, New York (1985).
[2] F. J. Arnaiz Garcia, An. Quim. **73,** 1121 (1977).
[3] P. Ravindranathan, K. C. Patil, Thermochim. Acta **71,** 53 (1983).
[4] A. Ferrari, A. Braibanti, G. Bigliardi, A. M. Lanfredi, Acta Crystallogr. **19,** 548 (1965).
[5] A. K. Srivastava, A. L. Varshney, P. C. Jain, J. Inorg. Nucl. Chem. **42,** 47 (1980).
[6] G. V. Mahesh, K. C. Patil, Thermochim. Acta **99,** 188 (1986).
[7] K. C. Patil, D. Gajapathy, K. Kishore, Thermochim. Acta **52,** 113 (1982).
[8] D. Gajapathy, S. Govindarajan, K. C. Patil, H. Manohar, Polyhedron **2,** 865 (1983).
[9] M. R. Tarasevich, B. N. Efremev, in S. Trasatti (ed.): Electrodes of Conductive Metallic Oxides, p. 221, Elsevier, New York (1980).
[10] S. Holgersson, A. Karlson, Z. Anorg. Chem. **183,** 384 (1929).
[11] A. Wold, J. Chem. Educ. **57,** 531 (1980).
[12] J. Robin, C.R. Acad. Sci. **235,** 1301 (1952).
[13] A. C. C. Tseung, J. R. Goldstein, J. Mat. Sci. **7,** 1383 (1972).
[14] N. Yamamoto, S. Higashi, S. Kawano, N. Achiwa, J. Mater. Sci. Lett. **2,** 525 (1983).
[15] K. C. Patil, D. Gajapathy, V. R. Pai Verneker, J. Mater. Sci. Lett. **2,** 272 (1983).
[16] D. Gajapathy, K. C. Patil, Mat. Chem. Phys. **9,** 423 (1983).
[17] P. Ravindranathan, G. V. Mahesh, K. C. Patil, J. Solid State Chem. **66,** 20 (1987).
[18] P. Ravindranathan, K. C. Patil, Am. Ceram. Soc. Bull. **66,** 688 (1987).
[19] B. N. Sivasankar, S. Govindarajan, Indian J. Chem. **33 A,** 329 (1994).
[20] J. S. Budkuley, K. C. Patil, Synth. React. Inorg. Met.-Org. Chem. **19,** 909 (1989).
[21] A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, p. 380 and 433, Longmans Green, London (1975).
[22] L. Erdey, in I. Buzas (ed.): Gravimetric Analysis, Part II, Pergamon, London (1965).
[23] B. N. Figgis, J. Lewis, J. Prog. Inorg. Chem. **6,** 197 (1964).

[24] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam (1984).
[25] A. Braibanti, F. Dallavalle, M. A. Pellinghelli, E. Leporati, Inorg. Chem. **7,** 1430 (1968).
[26] G. Wilkinson, R. D. Gillard, J. A. McCleverty (eds): Comprehensive Coordination Chemistry, Vol. II, Pergamon Press, London (1987).
[27] Powder Diffraction File, Inorganic Vol. PDSI-5iRB. Joint Committee on Diffraction Standards, Swarthmore, Pennsylvania (1967).