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Spectral, thermal, and X-ray studies on some new bis and tris-hydrazine and hydrazinium metal pyruvates

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Abstract Some bis-hydrazine metal pyruvates of transition metal ions of the formula $M[CH_3COCOO]_2\ [N_2H_4]_2$, where M = Co, Ni, Zn or Cd, tris-hydrazine metal pyruvates of the formula $M[CH_3COCOO]_2\ [N_2H_4]_3$, where M = Co, Ni, Zn or Cd, and hydrazinium metal pyruvates $[N_2H_5]_2M[CH_3COCOO]_4$, where M = Co or Ni have been prepared and the compositions of the complexes have been determined by chemical analysis. The magnetic moments and electronic spectra of the complexes suggest a high-spin octahedral geometry for them. Infrared spectral data of bis-hydrazine complexes indicate the bidentate bridging mode shown by hydrazine molecules and mono dentate coordination by pyruvate ions. However, in tris-hydrazine complexes the pyruvate ions are ionic in nature. In hydrazinium complexes two hydrazinium ions and four pyruvate ions show unidentate coordination mode resulting in six coordination around metal ions. Thermo gravimetry and differential thermal analysis in air reveal that most of the complexes decompose in one step to give the respective metal carbonate as the final residue. However, the hydrazinium complexes yield Co_2O_3 or NiO as the residue. The final residues were identified by their X-ray powder data. The X-ray powder diffraction patterns of each series of complexes reveal isomorphism among the series.

Keywords Bis-hydrazine metal pyruvates · Tris-hydrazine metal pyruvates · Hydrazinium cation · Metal carbonates · TG–DTA · X-ray powder diffraction

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Introduction

The coordination behaviour of aliphatic carboxylic acids with aldehyde or keto groups are interesting due to the presence of multi-coordination sites. The anions of these acids can act as monodentate, bridging bidentate or chelating ligands showing ambidentate character. Among the substituted aliphatic carboxylic acids especially containing carbonyl moieties, the formic acid shows dual character as aldehyde and carboxylic acid and the glycolic acid has both aldehydic and carboxylic acid groups. The hydrazine complexes of the above two acids have been isolated from the aqueous basic solutions and their spectral and thermal properties have been investigated [1–4]. However, the hydrazine complexes of a keto carboxylic acid, the pyruvic acid which is capable of coordination through both keto and carboxylate moieties have not been studied so far. Further more, the tris-hydrazine complexes of transition metal carboxylates are scarce in the literature [5]. Several bis-hydrazine and hydrazinium metal carboxylates have been recently reported and their structures have been established [6–9]. However, tris-hydrazine metal carboxylates are reported only with glycinate ($H_2NCH_2COO^-$) and glycolate ($HOCH_2COO^-$) ions both have one neutral donor atom along with a carboxylate ion. The pyruvate ion, CH_3COCOO^- with similar donor atoms is also expected to form tris-hydrazine complexes. Hence, attempt has been made to prepare and characterize the hydrazine derivatives of metal pyruvates and the results of our investigations are presented in this paper.

Experimental

The chemicals used were of analar grade and 99–100% hydrazine hydrate was used in all the reactions. The solvents were distilled before use.

Preparation of bis-hydrazine cobalt pyruvate and tris-hydrazine nickel, zinc and cadmium pyruvates

To an aqueous solution (20 mL) of the respective metal nitrate hydrates (0.01 mol), aqueous solution (20 mL) of pyruvic acid (1.4 mL, 0.02 mol) was added and the resulting solution was filtered and concentrated to about 20 mL in a boiling water bath. To this hot concentrated solution, hydrazine hydrate (2 ml, 0.04 mol) was added drop by drop with vigorous stirring. The complexes thus formed immediately were allowed to settle and then filtered. The complexes were washed several times with water, then with alcohol and dried in air.

Preparation of bis-hydrazine nickel pyruvate and tris-hydrazine cobalt pyruvate

An aqueous solution (30 mL) containing a mixture of pyruvic acid (1.4 mL, 0.02 mol) and hydrazine hydrate (2 mL, 0.04 mol) was added with stirring to an aqueous solution (20 mL) of nickel or cobalt nitrate hexa hydrate (2.91 g, 0.01 mol). The resulting solution was immediately filtered and the clear solution was kept at room temperature. The crystalline complex formed was filtered, washed with water, then with alcohol and dried in air. The cobalt complex is hygroscopic and hence stored in vacuum desiccator.

Preparation of bis-hydrazine zinc and cadmium pyruvate

$$\mathrm{M(CH_3COCOO)_2(N_2H_4)_2} \quad \text{where } \mathrm{M = Zn\ or\ Cd}$$

To an aqueous solution containing 0.01 mol of zinc nitrate hexa hydrate or cadmium nitrate tetra hydrate, an aqueous mixture of pyruvic acid (1.4 mL, 0.02 mol) and hydrazine hydrate (2 mL, 0.04 mol) was added with constant stirring. Then to the turbid solution pyruvic acid was added drop by drop while warming the solution in a water bath. The precipitate formed was slowly dissolved by the addition of pyruvic acid. The addition of pyruvic acid was stopped when the solution become clear. Then the resulting solution was concentrated to 20 mL and kept at room temperature. The white crystalline substance that formed after 3 days was removed, washed with alcohol and dried in air.

Preparation of hydrazinium cobalt and nickel pyruvates

$$\mathrm{(N_2H_5)_2M(CH_3COCOO)_4} \quad \text{where } \mathrm{M = Co\ or\ Ni}$$

To an aqueous solution (20 mL) of cobalt nitrate hexa hydrate (2.91 g, 0.01 mol), aqueous solution (20 mL) containing a mixture of pyruvic acid (2.8 mL, 0.04 mol) and hydrazine hydrate (2 mL, 0.04 mol) was added and the resulting solution was filtered and heated on a water bath for 8 h. The resulting solution was concentrated to about 20 mL in a boiling water bath. The concentrated solution was allowed to crystallize inside a vacuum desiccator. The dark red crystals formed in the case of cobalt and blue crystals formed by nickel after a week were removed, washed with absolute alcohol and dried in the vacuum desiccator. These complexes are water soluble and hygroscopic.

Physico-chemical studies

The physico-chemical techniques involved in the present study are similar to those that were reported earlier [3].

Results and discussions

Bis-hydrazine and tris-hydrazine metal pyruvates were prepared by the aqueous reaction between metal salts and pyruvic acid in the presence of excess hydrazine hydrate. The method of preparation and ratio differs for different metal complexes. The hydrazinium complexes of metal pyruvates were prepared by the aqueous reaction between the respective metal ions with aqueous solution containing a mixture of pyruvic acid and hydrazine hydrate in 1:4 ratio. However, we were able to isolate only cobalt and nickel complexes. Our attempt to prepare other metal complexes was not successful and resulted in the formation of respective metal pyruvates.

The composition of the complexes were assigned on the basis hydrazine analysis by titrating with standard KIO_3 solution and metal analysis by EDTA complexometric titrations. The observed percentage of hydrazine and metal are very well in agreement with the calculated values for the assigned composition. The chemical analysis data of all the complexes are summarized in Table 1.

Magnetic moment data

The room temperature magnetic moment of all the cobalt complexes are in the range of 4.6–4.8 BM and for the nickel complexes, the magnetic moments are in the range 2.9–3.1 BM respectively. These data indicate the high spin nature of these complexes [10]. The higher magnetic moment value observed for cobalt complexes are attributed to the spin orbit coupling. Thus, the cobalt (II) and nickel (II) ions in these complexes contain three and two unpaired electrons respectively. Due to the completely filled 'd' orbitals both zinc and cadmium complexes are diamagnetic.

Table 1 Analytical data

Complex (molecular mass)	Colour	Yield/%	Hydrazine/%		Metal/%	
			Found	Calc.	Found	Calc.
$Co(CH_3COCOO)_2\ (N_2H_4)_2$ (297.054)	Pink	90	22.00	21.57	19.00	19.83
$Ni(CH_3COCOO)_2\ (N_2H_4)_2$ (296.876)	Green	95	21.00	21.56	20.00	19.77
$Zn(CH_3COCOO)_2(N_2H_4)_2$ (303.522)	Colourless	90	21.00	21.11	20.80	21.54
$Cd(CH_3COCOO)_2\ (N_2H_4)_2$ (350.464)	Colourless	85	18.00	18.28	30.00	32.06
$Co(CH_3COCOO)_2(N_2H_4)_3$ (329.186)	Rosy red	75	28.50	29.21	17.00	17.90
$Ni(CH_3COCOO)_2\ (N_2H_4)_3$ (328.876)	Light blue	80	29.00	29.23	17.10	17.85
$Zn(CH_3COCOO)_2(N_2H_4)_3$ (335.434)	Colourless	85	28.00	28.65	18.50	19.48
$Cd(CH_3COCOO)_2(N_2H_4)_3$ (382.464)	Colourless	80	24.50	25.13	28.70	29.37
$(N_2H_5)_2\ Co(CH_3COCOO)_4$ (473.108)	Pink	80	14.00	13.55	14.00	12.47
$(N_2H_5)_2\ Ni(CH_3COCOO)_4$ (472.798)	Blue	85	14.00	13.53	13.00	12.41

Electronic spectra

The electronic spectra of bis and tris-hydrazine cobalt pyruvate shows a band at 21,400–21,700 cm^{-1} which is assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. The respective nickel complexes shows two bands at 27,200–27,300 cm^{-1} and 16,670–16,800 cm^{-1} which are attributed to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively [11].

Infrared spectra

Infrared spectra of both bis and tris-hydrazine metal pyruvates show the ν_{asy} and ν_{sym} stretching of carboxylate ions at 1,620–1,630 and 1,355–1,370 cm^{-1} respectively. The N–N stretching in all the complexes are seen at 970–980 cm^{-1}. This shows the bridged bidentate nature of hydrazine moieties [12]. Though it is below 990 cm^{-1} a higher frequency (5–10 cm^{-1}) than the bands observed normally for various bis-hydrazine complexes may be due to the strong interaction between metal ion and nitrogen. All the complexes show two sharp and strong bands in the regions 3,320–3,330 and 3,240–3,250 cm^{-1} which are due to N–H stretching of hydrazine molecules. A sharp band at 1,760–1,770 cm^{-1} in all the cases is attributed to the carbonyl stretching of ketonic group [13]. This indicates the carbonyl oxygen has not been involved in coordination. Infact C=O stretching of keto group of pyruvate anion in the complex absorbs at the same frequency as sodium pyruvate which is an evidence for the non-coordination of carbonyl oxygen. The ν_{sym} and ν_{asy} stretching of carboxylate groups in tris-hydrazine complexes are also comparable with that of sodium pyruvate which suggests the ionic nature of pyruvate ions in the complexes.

Thermal decomposition

Bis-hydrazine pyruvates

The bis-hydrazine cobalt and nickel complexes undergo decomposition in single stage in the temperature range 200–320 °C to give the respective carbonates as the final residue. The DTA of nickel complex shows multiplets at 220, 240 and 265 °C and the degradation is exothermic in nature.

The zinc and cadmium complexes decompose exothermically at 250 and 260 °C respectively and these processes are found to be explosive. Hence, the exact TG mass loss could not be determined. However, the degradations were manually carried out with a closed preheated silica crucible and the product of decomposition were found to be the respective metal carbonates.

Tris-hydrazine metal pyruvates

The tris-hydrazine cobalt pyruvate complex undergoes single step decomposition in air and gives $Co_2(CO_3)_3$ as the end product in the temperature range 340–390 °C as shown by the TG curve. The DTA of this complex shows only one sharp exotherm at 350 °C.

The thermal degradation of tris-hydrazine nickel pyruvate complex takes place in two stages both exothermic to give nickel carbonate as the final residue and nickel pyruvate as the intermediate. The TG temperature range is 220–260 °C for the first stage and 250–330 °C for the second stage. The DTA of this complex shows sharp exotherm at 250 °C and another broad exotherm at 310 °C.

The zinc complexes after endothermic dehydrazination at 240 °C undergoes exothermic decomposition to give $ZnCO_3$ in the temperature range 200–270 °C. The first stage

Table 2 Thermal degradation data

Complex	Stage	DTA peak/°C	TG-temperature range/ °C	TG mass loss/%		Residue
				Foun.	Calc.	
$Co(CH_3COCOO)_2 (N_2H_4)_2$	I	240(endo)	200–320	52.68	49.86	$Co_2(CO_3)_3$
$Ni(CH_3COCOO)_2 (N_2H_4)_2$	I	220(exo) 240(exo) 265(exo)	200–320	60.32	60.01	$NiCO_3$
$Cd(CH_3COCOO)_2 (N_2H_4)_2$	–	260(exo)	260–280	51	50.8	$CdCO_3$
$Co(CH_3COCOO)_2 (N_2H_4)_3$	I	350(exo)	340–390	52.68	54.73	$Co_2(CO_3)_3$
$Ni(CH_3COCOO)_2 (N_2H_4)_3$	I	250(exo)	220–260			
	II	310(exo,b)	250–330	63.7	63.9	$NiCO_3$
$Zn(CH_3COCOO)_2 (N_2H_4)_3$	I	240(exo)	200–270	63.62	62.62	$ZnCO_3$
$Cd(CH_3COCOO)_2 (N_2H_4)_3$	I	260(exo)	240–270	73	70.07	$CdCO_3$
$(N_2H_5)_2 Co(CH_3COCOO)_4$	I	130(endo)	120–180	11.91	13.52	$Co(Py)_2 (PyH)_2$
	II	240(exo)	215–245	63.38	67.87	$Co(Py)_2 (PyH)$
	III	300, 335(exo,d)	245–350	74.12	71.04	Co_2O_3
$(N_2H_5)_2 Ni(CH_3COCOO)_4$	I	210(endo)	200–220	12	13.54	$Ni(Py)_2 (PyH)_2$
	II	225(exo)	220–330	50.73	50.36	$Ni(Py)_2$
	III	340(exo)	330–360	68.24	66.58	NiO

Exo exotherm, *endo* endotherm, *d* doublet, *b* broad, *Py* pyruvate ($C_3H_3O_3$), *PyH* pyruvic acid

corresponds to the dehydrazination to give bis-hydrazine pyruvate as an intermediate which further decomposes sharply in one step to give the final residue. The tris-hydrazine cadmium pyruvate also decompose sharply and exothermically at 260 °C. The decomposition is similar to the bis-hydrazine complex and highly explosive.

Hydrazinium metal pyruvates

The hydrazinium cobalt and nickel pyruvates show multi-step decomposition. The DTA of nickel and cobalt complex shows an endotherms at 130 °C and two exotherms at 240 and 300 °C to give Co_2O_3 or NiO as the final residue. The DTA of nickel complex shows the above endotherms at 210 °C and the exotherms at 225 and 340 °C. In the first stage two hydrazine moieties are eliminated followed by the pyrolysis of acid parts to give the oxide as the final product.

The simultaneous TG–DTA data of the complexes are summarized in Table 2. The simultaneous TG–DTA curves of the bis-hydrazine, tris-hydrazine nickel pyruvates and hydrazinium cobalt pyruvate are shown in Figs. 1, 2 and 3 respectively as representative examples.

X-ray diffraction

Though the infrared spectra of the complexes of individual series of complexes are almost similar, the X-ray powder diffraction patterns of the complexes were recorded to support the similarity in the structure. The X-ray powder

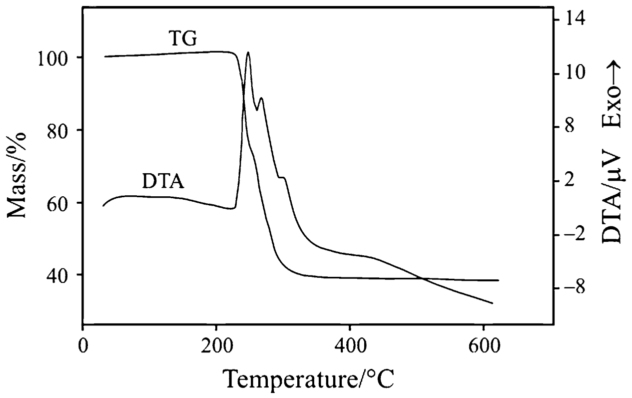

Fig. 1 Simultaneous TG–DTA of bis-hydrazine nickel pyruvate

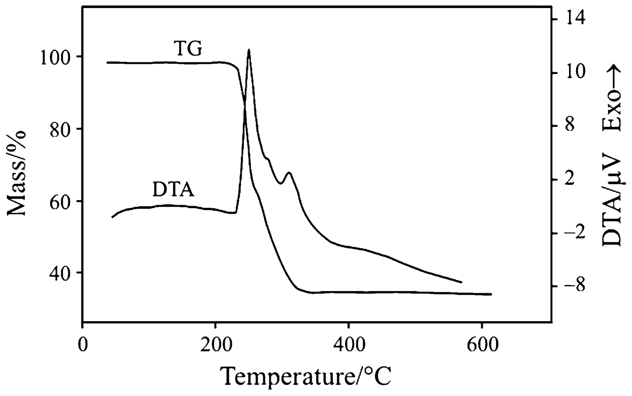

Fig. 2 Simultaneous TG–DTA of tris-hydrazine nickel pyruvate

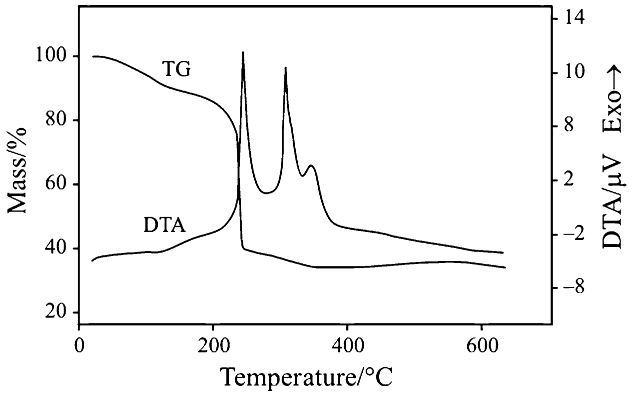

Fig. 3 Simultaneous TG–DTA of hydrazinium cobalt pyruvate

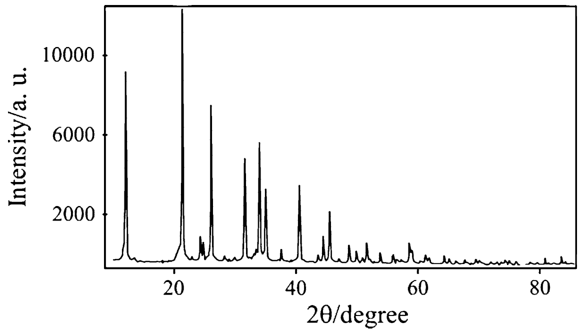

Fig. 4 X-ray powder pattern of bis-hydrazine nickel pyruvate

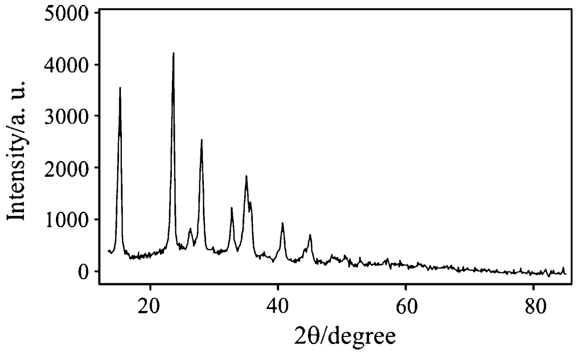

Fig. 5 X-ray powder pattern of bis-hydrazine zinc pyruvate

diffraction patterns of bis-hydrazine metal pyruvates are almost superimposable indicating the isomorphism among the series of the compounds. The X-ray powder pattern of bis-hydrazine nickel and zinc pyruvates are shown in Figs. 4 and 5 respectively.

The X-ray powder diffraction patterns of tris-hydrazine pyruvate complexes of nickel and cadmium are shown in Figs. 6 and 7 respectively as representative models. The patterns of all the tris-hydrazine complexes are also similar indicating the isomorphism. Due to the hygroscopic nature, we were not able to record the X-ray powder data of hydrazinium complexes.

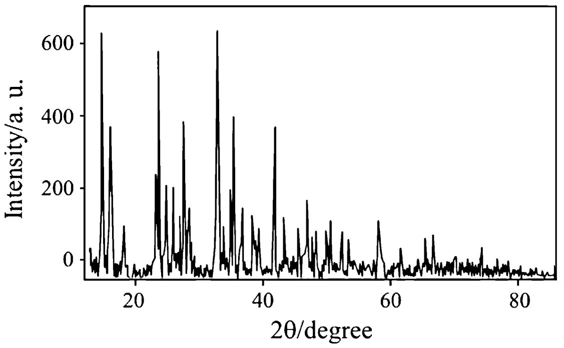

Fig. 6 X-ray powder pattern of tris-hydrazine nickel pyruvate

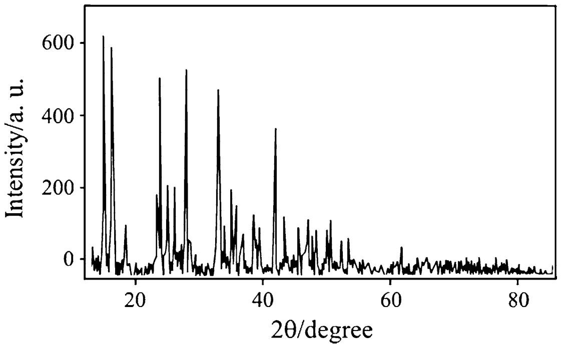

Fig. 7 X-ray powder pattern of tris-hydrazine cadmium pyruvate

Conclusions

Bis and tris-hydrazine metal pyruvates were prepared by the aqueous reactions of respective transition metal ions such as Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}, pyruvic acid and excess hydrazine hydrate. The hydrazinium metal pyruvates were prepared by the reaction between aqueous mixture of pyruvic acid and hydrazine hydrate and the respective metal nitrate hydrate in 4:1 ratio.

The magnetic moments and electronic spectra of Co, Ni, Zn and Cd complexes are in accordance with the high-spin octahedral nature of these complexes. Infrared spectra indicates the monodentate nature of the carboxylate ions and bidentate nature of the hydrazine. The zinc and cadmium complexes are diamagnetic as expected. During thermal degradation, bis and tris-hydrazine metal pyruvate complexes undergo decomposition in single step or two steps to give the respective metal carbonate as the final residue. However, the hydrazinium complexes give metal oxides as the final product. The final degradation products are identified by X-ray powder patterns. The X-ray powder patterns of the individual series of complexes are superimposable indicating the isomorphism among the series.

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