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SOME NEW BIS- AND TRIS-HYDRAZINE TRANSITION METAL AROMATIC CARBOXYLATES : PREPARATION AND CHARACTERIZATION

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ABSTRACT

Bis- and tris- hydrazine complexes of metal phenoxyacetates have been prepared by aqueous reactions. These complexes have been characterized by analytical, spectral and thermal studies. The compositions of the complexes have been determined by analytical studies. The electronic spectra suggest high-spin octahedral geometry for the metal complexes. Infrared spectral data indicate that the bidentate bridging by hydrazine molecules and monodentate coordination by carboxylate ions to the cental metal ion. Thermogravimetry (TG) and differential thermal analyses (DTA) in air have been used to study the thermal behaviour of the complexes. The simultaneous TG-DTA curves of all the complexes in air resulted in the formation of respective metal or metal oxide as final residue. These complexes decompose exothermically either in single step or decompose through respective metal carboxylate intermediates. X-ray powder diffraction patterns of the complexes are almost superimposable with in each of the series indicating isomorphism.

Key words: Metal phenoxyacetate, Electronic spectra, IR, TG-DTA, XRD.

INTRODUCTION

Hydrazine carboxylates of the transition metal ions with variety of acids have been reported. These include simple aliphatic mono carboxylic acid[1–4], aliphatic dicarboxylic acids[5-11], aromatic mono and dicarboxylic acids[12,13] and heterocyclic acids[14,15]. The review of the literature reveals that the complexes of transition metal ions with hydrazine phenoxyacetates has not yet been carried out. Hence an attempt has been made to prepare the complexes of phenoxyacetic acidd with hydrazine and transition metal ions. These acids have phenyl-oxy linkage which is responsible for its insecticidal and herbicidal properties[16,17]. Therefore in these studies we report the synthesis, analytical, spectral, thermal studies of transition metal bis- and tris- hydrazine complexes of phenoxyacetic acid.

EXPERIMENTAL

Preparation

$M (PhOAc)_2 (N_2H_4)_3$ where M = Co or Ni

The phenoxyacetic acid (1.0142 g, 0.007 mol) is added to 50 mL of distilled water containing 99-100%

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pure hydrazine hydrate (0.6 mL, 0.012 mol). The mixture is stirred well and heated over water bath to get clear solution. It is filtered and added slowly to an aqueous solution of the corresponding metal nitrate hexahydrates (0.9701 g, 0.003 mol) with constant stirring. The clear solution is kept aside for crystallization. Within three hours solid products are settled down, filtered off, washed with distilled water, alcohol followed by diethylether and then air dried.

$Cd (PhOAc)_2 (N_2H_4)_2.H_2O$

The above procedure is followed with aqueous solution of phenoxyacetic acid (1.0136 g, 0.007 mol), hydrazine hydrate (0.6 mL 0.012 mol) and cadmium nitrate tetrahydrate (1.0282 g, 0.003 mol).

$Mn (PhOAc)_2 (N_2H_4)_2$

The phenoxyacetic acid (1.2172 g, 0.008 mol) is added to 50 mL of distilled water containing 99-100% pure hydrazine hydrate (0.8 mL, 0.016 mol). The solution is heated over water bath to get clear solution. Then to this clear solution, manganese acetate tetrahydrate (0.9803 g, 0.004 mol) is added with constant stirring. The resulting clear solution is concentrated over water bath at 80°C. When it is evaporated to 15 mL the complex formation starts, it is kept aside for completion of the precipitation. It is filtered, washed with distilled water, alcohol followed by diethylether and then air dried.

RESULTS AND DISCUSSION

Cobalt, nickel and cadmium complexes have been prepared by the reaction of the aqueous solution of the corresponding metal nitrate hydrate, aqueous solution of hydrazine hydrate and phenoxyacetic acid.

$$M (NO_3)_2 + 2\ C_6H_5OCH_2COOH + 3\ N_2H_4 \rightarrow M (C_6H_5OCH_2COO)_2 (N_2H_4)_3 + 2\ HNO_3$$

where M = Co or Ni

$$Cd (NO_3)_2 + 2\ C_6H_5OCH_2COOH + 2\ N_2H_4 + H_2O \rightarrow Cd (C_6H_5OCH_2COO)_2 (N_2H_4)_2.H_2O + 2\ HNO_3$$

Bis-hydrazine manganese complexes are prepared by the reaction of aqueous solution of manganese acetate tetrahydrate and aqueous solution of the mixture of hydrazine hydrate and phenoxyacetic acid.

$$Mn (CH_3COO)_2 + 2\ C_6H_5OCH_2COOH + 2\ N_2H_4 \rightarrow Mn (C_6H_5OCH_2COO)_2 (N_2H_4)_2 + 2CH_3COOH$$

All the metal hydrazine carboxylates prepared are insoluble in water, alcohol and other organic solvents. The compositions of these complexes are assigned on the basis of hydrazine and metal contents. The analytical data of the complexes are in good agreement with the proposed compositions.

Electronic spectrum

The electronic spectrum of the above mentioned cobalt and nickel complexes are in support of octahedral coordination around the metal ions. For example cobalt complexes display a band at 28, 330 cm^{-1} which is assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. This band and pink colour of the compounds are in indicative of the octahedrally coordinated Co (II) ion[18]. Nickel complexes exhibit a band at 28, 980 cm^{-1}, which is also attributed to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition, characteristic of octahedral geometry.

Infrared spectra

The hydrated complexe shows bands in the region 3546-3419 cm^{-1} due to O-H stretching of water molecules[19]. All bis-hydrazine metal carboxylates show the asymmetric and symmetric stretching frequencies of the carboxylate groups in the range 1596 cm^{-1} and 1420-1339 cm^{-1}, respectively. The $\Delta\nu$ ($\nu_{asymm} - \nu_{sym}$) separation in the range 176-257 cm^{-1} is in support of monodentate coordination of the carboxylate groups. Tris-hydrazine metal carboxylates show small separation between asymmetric and symmetric stretching frequency i.e., nearly 130 cm^{-1} and higher value of asymmetric and symmetric stretching. These values are similar to that of metal carboxylate salts. It indicates the presence of carboxyl group as non-coordinated one. All prepared complexes show N-N stretching frequency in the region 948-980 cm^{-1} are assigned to bidentate bridging coordination of N_2H_4[20].

Thermal analysis

The thermal properties of metal hydrazine complexes change dramatically with different anions. Such data not only corroborate the stiochiometric formulae, number of hydrazine and water molecules, but also reveal different intermediates formed including the end products.

Co $(PhOAc)_2 (N_2H_3)_3$

This complex follows four step decomposition. In the first step a mass loss of 24% results in the formation of Co (PhOAc) (HCOO) $(N_2H_3)_3$. In the second step, this intermediate undergoes exothermic decomposition by loss of three molecules of hydrazine. On further heating it decomposes to the mixture of cobalt oxide and cobalt carbonate.

Ni $(PhOAc)_2 (N_2H_4)_3$

This complex decomposes in two steps to give Ni as the final product. DTA shows two exotherms at 227 and 432°C corresponding to the two steps.

Cd $(PhOAc)_2 (N_2H_4)_2.H_2O$

This complex undergoes three step decomposition. In the first step the decomposition sequence corresponds to the dehydration of the complex. The endotherm at 132°C, suggest the presence of H_2O as water of crystallization. In the second step the anhydrous intermediate decomposes in the exothermic mode at 165°C to form metal carboxylate. This undergoes exothermic decomposition at 463°C gives CdO as the final product.

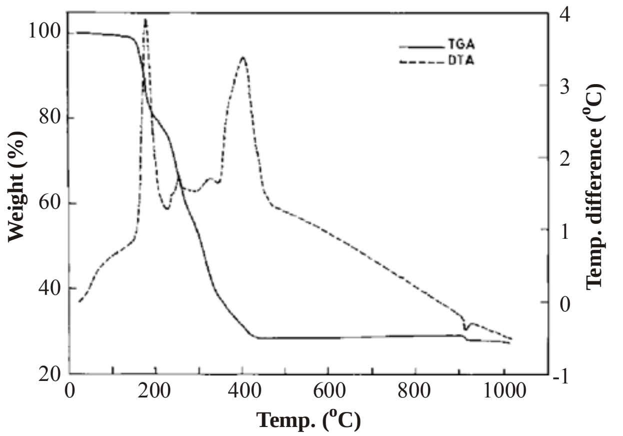
Mn $(PhOAc)_2 (N_2H_4)_2$

This complex undergoes two step decomposition. The first step mass loss corresponds to the removal of hydrazine. Second step is the decomposition of metal carboxylate to metal carbonate. This corresponds to DTA peak at 366°C.

The loss of water molecule in the hydrated complexes at above 100°C may be due to strong association of the H_2O molecule to lattice is due to intramolecular hydrogen bonding with N-H or C=O group of the ligands.

The thermal decomposition of cobalt, cadmium and manganese complexes containing phenoxyacetate as the ligand decompose to give mixture of respective metal carbonate and metal oxide, metal carbonate or metal oxide as the final product. The nickel complex containing phenoxyacetate alone gives nickel as the final product. Most of the nickel complexes prepared by using various ligands invariably decompose thermally to give metal as the final product[21,22]. This may be due to catalytic activity of nickel.

TG – DTA curves of the complexes are given (Fig. 1 – 4) as representative examples.



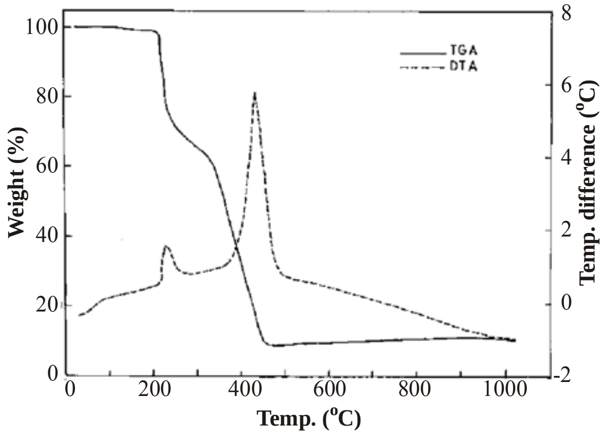
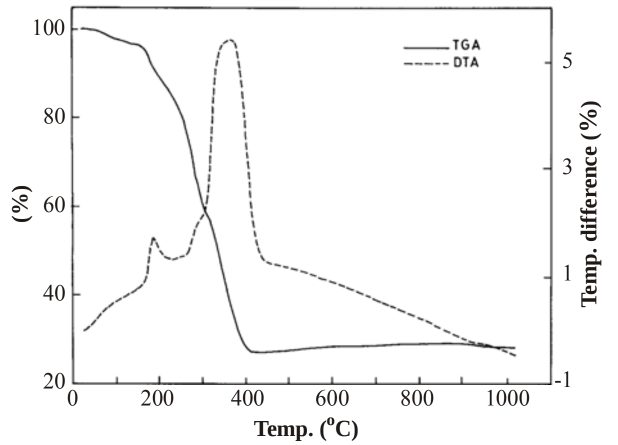


Fig. 1: TG – DTA pattern of Co $(PhOAc)_2(N_2H_4)_3$

Fig. 2: TG – DTA pattern of Ni $(PhOAc)_2(N_2H_4)_3$



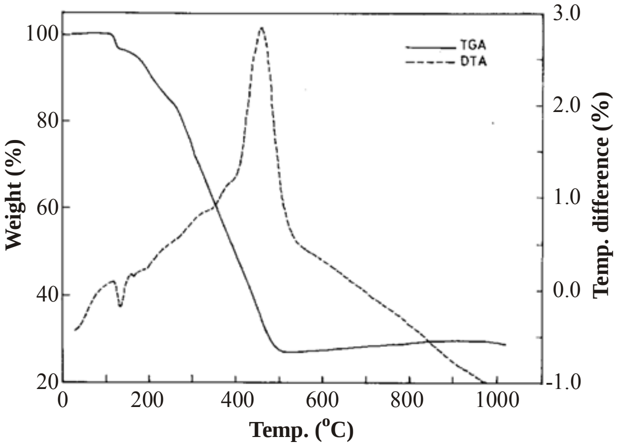


Fig. 3: TG – DTA pattern of Mn $(PhOAc)_2 (N_2H_4)_2.H_2O$

Fig. 4: TG – DTA pattern of Cd $(PhOAc)_2 (N_2H_4)_2.H_2O$

X - ray diffraction studies

In order to compare and also to confirm the structural similarity among the cobalt and nickel complexes, the 'd spacing' of these complexes have been compared. Both complexes have almost same values of d-spacing and number of peaks. Hence, both are isomorphous in nature.

Coordination geometry

The fact that the compounds are obtained as amorphous powder and not as single crystals means that no complete structure determination could be carried out. However, spectroscopic and thermal data enable us to suggest the environment of the metal in each of the complexes. Therefore six coordination has been tentatively proposed for all complexes with octahedral stereochemistry. The insoluble nature of these complexes confirms the polymeric structure.

CONCLUSION

Transition metal ions such as Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+} react with phenoxyacetic acid in the presence of excess hydrazine hydrate to yield bis- and tris – hydrazine metal carboxylates.

The electronic spectra suggest the high-spin octahedral nature of the complexes. Infrared spectra indicate the monodendate nature of carboxylate ions and bidendate bridged nature of hydrazine moieties.

In fact the compounds are obtained as amorphous powder and not as single crystals means that no complete structure determination could be carried out. However, analytical, spectroscopic and thermal data unable us to suggest the environment of the metal ion. Therefore six coordination has been tentatively proposed for all prepared complexes with octahedral stereochemistry. Out of this six coordination, two are satisfied by carboxylate ions and four are from hydrazine ligands. In Tris- hydrazine complexes one of the carboxylate group present outside the coordination sphere. In the hydrated complexe the water molecule is lost just above 100^{o}C, indicate that the water molecules are involved in strong intramolecular hydrogen bonding with –NH group of hydrazine. The insoluble natures of these complexes confirm the polymeric structure.

The X-ray powder patterns of cobalt and nickel complexes were superimposable and the ‘d’ value suggested isomorphism among the complexes.

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