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RESEARCH ARTICLE

Coordination Aspects of Newly Synthesised Complexes of Some Divalent Transition Metals with 2,4-Dichlorophenoxy Acetate and Hydrazine

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Abstract: A new series of hydrazine complexes of 3d transition metal 2,4 dichlorophenoxy acetates of the formula $M(2,4\ di\text{-}Cl\ PhOAc)_2(N_2H_4)_2$, where M = Mn, Co, Ni or Cd have been prepared and studied. The compositions of the complexes have been determined by chemical analyses. Infrared spectral data indicate the bidentate bridging by hydrazine molecules and unidentate coordination by carboxylate ions. Thermogravimetry and differential thermal analyses in air have been used to study the thermal behaviour of the complexes. The simultaneous TG-DTA traces of all the complexes show multi-step degradation and the final products are found to be the respective metals.

Keywords: Hydrazine, 2,4 Dichlorophenoxy acetate, TG-DTA, Divalent transition metals

Introduction

Today the study of coordination compound has emerged as the major center of attraction for inorganic chemists due to their interesting molecular assemblies held together by forces such as hydrogen bonding, p-p stacking interactions, and metal–ligand coordination[1,2]. These assemblies are anticipated to find utilities as new materials with novel catalytic, magnetic, electronic, and optical properties[3,4].

Hydrazine, the simplest diamine even after getting protonated as $N_2H_5^+$, evinces its coordinating ability and forms several salts with mineral as well as carboxylic acids. The chemistry of hydrazine is of interest because it forms various complexes with transition metals whose stability changes dramatically, depending upon the anions as well as the cations[5-7]. Numerous studies have been reported on complexes containing coordinated and uncoordinated hydrazinium moieties, such as hydrazinium metal oxalates, malonates and phthalates in the recent years. Thermal reactivity of metal carboxylates with hydrazine is of increasing interest, since they serve as precursors to fine-particle oxide materials and metal carbonates[8-10]. Neutral hydrazine coordinates to the metal ions in various fashions as either monodentate or bidentate bridging ligand. In the presence of mono and dicarboxylic acids, hydrazine may exist as hydrazinium cation, which is also capable of coordination with metal ions. The concentration of hydrazine, pH of the reaction mixture and property of the metal ion decide the nature of complex formed. Though mono-protonated hydrazine (hydrazinium) complexes are structurally interesting, thermally they are less effective than neutral hydrazine complexes.

All the above facts prompted us to synthesise new complexes of some divalent transition metals (Co, Ni, Cd & Mn) with 2,4 dichlorophenoxy acetate and hydrazine.

Experimental

Stoichiometric quantity of 2,4-dichlorophenoxyacetic acid (1.5244 g, 0.007 mol) was added to 50 mL of distilled water containing 99-100% pure hydrazine hydrate (0.3 mL, 0.006 mol). The mixture was heated over water bath to get clear solution. It was then added slowly to an aqueous solution of the corresponding metal nitrate hexahydrate (1.0034 g, 0.003 mol) under hot condition with constant stirring. The clear solution was kept aside for crystallization. The complex formed after 15 minutes was filtered off, washed with distilled water, alcohol followed by diethylether and then air dried.

Preparation of $Cd(2,4\ di\text{-}Cl\ PhOAc)_2(N_2H_4)_2.H_2O$

The above procedure was repeated with stoichiometric quantities of 2,4-dichlorophenoxyacetic acid (0.7368 g, 0.003 mol), hydrazine hydrate (0.3 mL, 0.006 mol) and cadmium nitrate tetrahydrate (0.5141 g, 0.002 mol). The precipitated complex was filtered off, washed with distilled water, alcohol followed by diethylether and then air dried.

Preparation of $Mn(2,4\ di\text{-}Cl\ PhOAc)_2(N_2H_4)_2.H_2O$

This complex was prepared by mixing equal volumes of clear aqueous solutions (50 mL) of 0.004 mol of 2,4dichlorophenoxyacetic acid containing 0.008 mol of hydrazine hydrate (0.4 mL) with an aqueous solution of 0.002 mol of manganese acetate tetrahydrate (0.5001 g). The clear solution obtained was kept aside for crystallization. The complex formed after 3 h, was filtered off, washed with distilled water, alcohol followed by diethylether and then air dried.

Results and Discussion

Cobalt, nickel, cadmium and manganese complexes have been prepared by the reaction of the aqueous solution of the corresponding metal salt hydrates, aqueous solution of hydrazine hydrate and 2,4-dichlorophenoxyacetic acid.

$$M(NO_3)_2 + 2C_6H_3Cl_2OCH_2COOH + 2N_2H_4 + nH_2O \rightarrow M(C_6H_3Cl_2OCH_2COO)_2(N_2H_4)_2.nH_2O + 2HNO_3$$

[M = Co or Cd where n=1 or M = Ni where n = 0]

$$Mn(CH_3COO)_2 + 2C_6H_3Cl_2OCH_2COOH + 2N_2H_4 \rightarrow Mn(C_6H_3Cl_2OCH_2COO)_2(N_2H_4)_2.H_2O + 2CH_3COOH$$

All the metal hydrazine carboxylates prepared were insoluble in water, alcohol and other organic solvents.

Chemical analysis

The composition of the complexes were assigned based on the observed percentage of hydrazine and metal. The analytical data of the complexes are in good agreement with the proposed compositions.

Electronic spectra

In the electronic spectra of the cobalt and nickel complexes, bands appear at 28,330 cm^{-1} and 28,980 cm^{-1} respectively, which is assigned to $^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transition, characteristic of octahedral geometry of the metal ions. Also, the pink colour of the compound is indicative of the octahedrally coordinated Co(II) ion[11].

Infrared spectra

The infrared spectra of the hydrated complexes show bands in the region 3546-3419 cm^{-1} due to O – H stretching of water molecules[12]. All bis-hydrazine metal carboxylates show the asymmetric and symmetric stretching frequencies of the carboxylate groups in the range 1613-1560 cm^{-1} and 1429-1339 cm^{-1} respectively. The $\Delta\nu$ ($\nu_{asymm} - \nu_{sym}$) separation in the range 176-257 cm^{-1} indicates the monodentate linkage of the carboxylate groups. The N-N stretching frequency in at 948-980 cm^{-1} unambiguously proves the bidentate nature of N_2H_4[13].

Thermal analysis

The TG-DTA curves of Co(2,4 di-Cl PhOAc)$_2$(N_2H_4)$_2$.H_2O and Mn(2,4 di-Cl PhOAc)$_2$ (N_2H_4)$_2$.H_2O are displayed in Figure 1 & 2. 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.

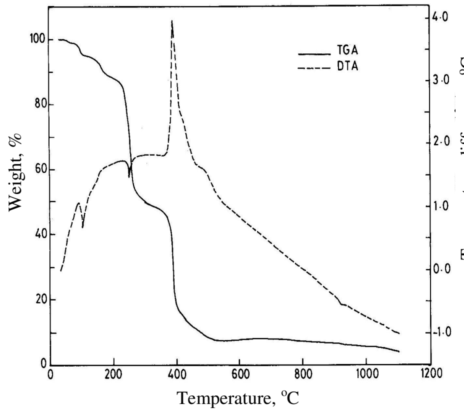

Figure 1. TG - DTA pattern of Co(2,4 di-Cl PhOAc)$_2$(N_2H_4)$_2$.H_2O

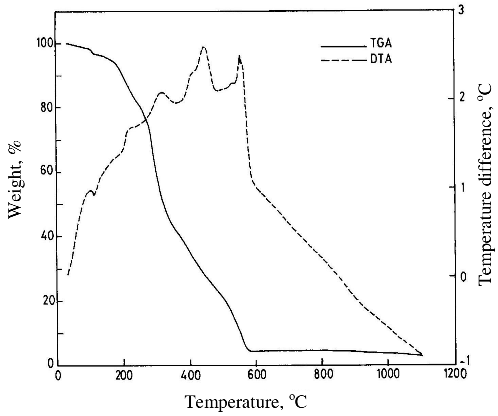

Figure 2. TG - DTA pattern of Mn(2,4di-Cl PhOAc)$_2$(N_2H_4)$_2$.H_2O

Co(2,4 di-Cl PhOAc)$_2$(N_2H_4)$_2$.H_2O

The TG curve of this compound shows four mass loss steps with two major ones. The first step, which occurs in the range 25-107 °C is attributed to the loss of H_2O molecule. The corresponding DTA peak is endothermic. Such a low temperature of dehydration supports the presence of one lattice H_2O. The second step mass loss is in accordance with the loss of two molecules of hydrazine. It occurs in the temperature range 107-188 °C. At 395 °C, it undergoes decomposition to give another intermediate as the third step. Cobalt as metal was obtained in the final step.

Ni(2,4 di-Cl PhOAc)$_2$*(N*$_2$*H*$_4$*)*$_2$

This compound undergoes three-step decomposition. First step is the formation Ni (2,4 di-Cl PhOAc)$_2$ (HCOO) intermediate with DTA exothermic peak at 242 °C. The second step mass loss corresponds to the formation of nickel formate. Finally it is decomposes to nickel metal with DTA exothermic peak at 557 °C.

Cd(2,4 di-Cl PhOAc)$_2$*(N*$_2$*H*$_4$*)*$_2$*.H*$_2$*O*

Five steps of weight loss occur in the TG-DTA curve of this complex. The first step in the range 25-145 °C and the second in the range 145-242 °C are attributed to the loss of water molecule and loss of two molecules of hydrazine respectively. In the third step, decomposition takes place at 388 °C to give an intermediate. Fourth step of mass loss takes place at 477 °C to give cadmium oxide. The final step occurs in the range 650-850 °C, where cadmium metal is obtained. The melting point and boiling point of cadmium are 320 °C and 767 °C respectively. From the prolonged TG - DTA curves, we infer that the cadmium thus obtained is melted and evaporated, as the temperature is above its boiling point. Carbon particles settle down as the residue. This form of thermal decomposition is peculiar one and has not been reported so far.

Mn(2,4 di-Cl PhOAc)$_2$*(N*$_2$*H*$_4$*)*$_2$*.H*$_2$*O*

This compound also follows five step of thermal decomposition with the loss of water molecule (20-124 °C) and loss of two molecules of hydrazine (218 °C) in the first and second steps respectively. On further heating, further decomposition takes place at 318 °C with DTA exothermic peak. The metal carboxylate intermediate undergoes decomposition at 448 °C to give a mixture of compounds *i.e*., manganese carbonate and manganese formate. Final step which occurs in the range 490-600 °C, gives metal as the final residue.

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.

All the prepared metal 2,4-dichlorophenoxyacetates decompose to give the respective metal as the final product. This is due to the presence of two chlorine substituents in the ring which causes steric effect (ortho effect). Therefore, they are more easily decomposed. This may also be due to the catalytic activity of the metal[14,15].

Coordination geometry

The fact that the compounds were 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

A new series of complexes of the transition metal ions such as Co^{2+}, Ni^{2+}, Cd^{2+} and Mn^{2+} with 2,4-dichlorophenoxyacetic acid and hydrazine hydrate have been successfully synthesized and characterized by electronic and IR spectra and TG-DTA.

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.

Six coordination has been tentatively proposed for all prepared complexes with octahedral stereochemistry as they possess no long-range order of the positions of atoms. Out of the six coordination, two are satisfied by carboxylate ions and four are from hydrazine ligands. In all hydrated complexes the water molecule is lost just above 100 °C which indicates that the water molecules are involved in strong intramolecular hydrogen bonding with –NH group of hydrazine. The insoluble nature of these complexes confirms the polymeric structure.

Thermogravimetry data reveal that the final decomposition product of all the prepared complexes is the respective metal. Hence, this may be an effective route to synthesise metal nanoparticles, which are of much importance.

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