Synthesis, characterisation and thermal analysis of copper(II) and chromium(II, III) hydrazine carboxylates

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Abstract. Copper(II) hydrazine carboxylate monohydrate, $Cu(N_2H_3COO)_2 \cdot H_2O$ and chromium (II, III) hydrazine carboxylate hydrates, $Cr(N_2H_3COO)_2 \cdot H_2O$ and $Cr(N_2H_3COO)_3 \cdot 3H_2O$ have been prepared and characterised by chemical analysis, IR, visible spectra and magnetic measurements. Thermal analysis of the copper complex yields a mixture of copper metal and copper oxide. Chromium complexes on thermal decomposition yield Cr_2O_3 as residue. Decomposition of chromium(III) complex under hydrothermal conditions yield CrOOH, a precursor to CrO_2.

Keywords. Copper and chromium hydrazine carboxylates; IR and Vis spectra; thermal analysis.

1. Introduction

Metal hydrazine carboxylates are of interest as precursors to fine particle oxides (Ravindranathan and Patil 1985, 1986), ferrites (Ravindranathan and Patil 1987; Sundar Manoharan and Patil 1989) and cobaltites (Ravindranathan *et al* 1987). The preparation, IR spectra and thermal analysis of transition metal hydrazine carboxylates (Patil *et al* 1979, 1983), rare earth and uranyl hydrazine carboxylates (Mahesh *et al* 1986) have been reported. Presently, we report the preparation, spectra and thermal properties of copper(II), chromium(II) and chromium(III) hydrazine carboxylate hydrates.

2. Experimental

Hydrazine carboxylic acid, N_2H_3COOH, was prepared by saturating $N_2H_4 \cdot H_2O$ (99%) with $CO_2(g)$. AnalaR $CrCl_3 \cdot 9H_2O$ and $CuCl_2 \cdot 2H_2O$ were used for the preparation of Cr(III) and Cu(II) complexes respectively. Chromous chloride was prepared by passing an aqueous solution of chromium(III) chloride hexahydrate through a zinc amalgam column in an atmosphere of nitrogen. The change in colour of the solution from green to blue in the column indicates the formation of chromous chloride. This freshly prepared solution was used for the preparation of Cr(II) complex.

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2.1   *Preparation of copper hydrazine carboxylate monohydrate,* $Cu(N_2H_3COO)_2 \cdot H_2O$

Copper(II) complex was prepared by treating a saturated solution of cupric chloride with N_2H_3COOH. The blue precipitate formed was filtered, washed with alcohol and stored over P_2O_5 in vacuum. The composition of the complex was fixed by chemical analysis as $Cu(N_2H_3COO)_2 \cdot H_2O$.

2.2   *Preparation of chromium(II) hydrazine carboxylate monohydrate,* $Cr(N_2H_3COO)_2 \cdot H_2O$

The air-stable Cr(II) complex was prepared by the addition of solid N_2H_3COOH to a freshly prepared chromous chloride solution. A lilac-coloured precipitate was obtained which was filtered, washed and stored over P_2O_5 in vacuum. The composition of the precipitate corresponds to $Cr(N_2H_3COO)_2 \cdot H_2O$ based on chemical analysis.

2.3   *Preparation of chromium(III) hydrazine carboxylate trihydrate,* $Cr(N_2H_3COO)_3 \cdot 3H_2O$

The chromium(III) complex was prepared by saturating with $CO_2(g)$ the reddish pink solution obtained by treating an aqueous chromium(III) chloride with a solution of N_2H_3COOH in $N_2H_4 \cdot H_2O$ ($N_2H_3COON_2H_5$). The crystalline red precipitate obtained was filtered, washed and stored over P_2O_5. The composition of the precipitate was fixed as $Cr(N_2H_3COO)_3 \cdot 3H_2O$ by chemical analysis.

2.4   *Analysis*

The amount of chromium present in Cr(II) and Cr(III) complexes were determined volumetrically (Vogel 1961) by titrating an excess of standard ferrous ammonium sulphate with standard $K_2Cr_2O_7$ solution. Cu(II) (Vogel 1961) was estimated iodimetrically using standard sodium thiosulphate $Na_2S_2O_3$. Hydrazine content was determined volumetrically using 0·025 M KIO_3 under Andrew's conditions (Vogel 1961). Infrared spectra were recorded with a Perkin-Elmer-597 IR spectrophotometer. Powder X-ray diffraction patterns were taken using a Philips PW 1050/70 diffracto-meter. Thermogravimetric and differential thermal analysis were carried out using Ulvac Sinku Riko 2100 M thermal analyser. Magnetic susceptibility was measured by the standard Gouy method at room temperature (298 K) using powdered samples of the complexes. The electronic spectra of the solids were recorded with a Hitachi U-3400 spectrophotometer.

3.   Results and discussion

Copper(II) and chromium(II, III) ions react with $N_2H_3COO^-$ forming the corresponding metal hydrazine carboxylate hydrates. Formation of $Cu(N_2H_3COO)_2 \cdot H_2O$ appears to need an optimum concentration of $N_2H_3COO^-$. Addition of solid N_2H_3COOH to a saturated solution containing Cu^{2+} ions facilitates the precipitation of $Cu(N_2H_3COO)_2 \cdot H_2O$ without the reduction of Cu^{2+} ions. Even trace amounts

Table 1. Thermoanalytical data.

Complex	Hydrazine(%) Obs.	Hydrazine(%) Calc.	Metal(%) Obs.	Metal(%) Calc.	DTA peak* temp. (°C)	Temp. range (°C)	% wt. loss Obs.	% wt. loss Calc.	Product[†]
$Cu(N_2H_3COO)_2 \cdot H_2O$	26·1	26·7	28·1	27·4	70(en)	60–90	7·0	7·8	$Cu(hc)_2$
					115(ex)	90–130	70·5	70·2	Cu & CuO
$Cr(N_2H_3COO)_2 \cdot H_2O$	28·3	28·1	23·1	23·6	90(en)	80–110	9·0	8·2	$Cr(hc)_2$
					180(ex)	110–250	65·0	65·4	Cr_2O_3
$Cr(N_2H_3COO)_3 \cdot 3H_2O$	28·1	28·5	15·6	15·1	90(en)	80–100	8·0	8·0	$Cr(hc)_3 \cdot 1 \cdot 5H_2O$
					120(en)	100–130	15·0	16·0	$Cr(hc)_3$
					190(ex)	130–240	76·0	77·0	Cr_2O_3

*en = endotherm, ex = exotherm; [†] hc = $N_2H_3COO^-$

of N_2H_4 in solution seem to reduce Cu^{2+} ions to metallic copper. Formation of Cr(II, III) hydrazine carboxylates is also instantaneous with the addition of N_2H_3COOH to saturated solutions of Cr(II, III) salts. This procedure is simpler as compared to the reported synthesis of chromium(II) hydrazine carboxylate by the reaction of chromous acetate and $N_2H_4 \cdot H_2O$ saturated with CO_2 (Bellerby *et al* 1986). The results of the chemical analysis of copper and chromium hydrazine carboxylates are summarized in table 1 and are in good agreement with the proposed formula.

3.1 Infrared spectra

Infrared spectra of Cu(II) and Cr(II, III) hydrazine carboxylates are similar to those reported earlier for metal hydrazine carboxylate hydrates (Patil *et al* 1983). In all the complexes the $N_2H_3COO^-$ group acts as a bidentate ligand and coordinates to the metal through both the N and O atoms forming a five-membered ring. The absorption frequencies at $3500 \, cm^{-1}$ (ν_{OH}), 2980 (ν_{N-H}), $1655 \, cm^{-1}$ ($\nu_{asy} \, COO^-$), $1495 \, cm^{-1}$ ($\nu_{sym} \, COO^-$), $1010 \, cm^{-1}$ (ν_{N-N}), 805 and $755 \, cm^{-1}$ (ν_{O-C-O}) are characteristic of the $N_2H_3COO^-$ group.

3.2 Electronic spectra and magnetic moments

The electronic spectra of $Cu(N_2H_3COO)_2 \cdot H_2O$ show an absorption at 625 nm which may be assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition of Cu^{2+} in an octahedral field (Cotton and Wilkinson 1972). Apart from the two molecules of the hydrazine carboxylate ligand and water there appears to be an interaction between either the Cu–Cu or the copper and carbonyl oxygen of the ligand as observed in $Cd(N_2H_3COO)_2 \cdot H_2O$ (Braibanti *et al* 1968). This is further evident from the low magnetic moment value of 1·52 BM at 298 K, which is less than the expected spin only magnetic moment for Cu^{2+} of 1·73 BM. The observed magnetic moment is comparable with the values reported for a number of cupric dicarboxylates (Figgis and Martin 1966; Dubicki *et al* 1966). In all these complexes the reduction in the magnetic moment has been

attributed to the magnetic exchange of an antiferromagnetic nature consequent upon either the formation of a weak bond between two or more copper atoms or a super exchange process via intervening oxygen or other atoms.

The electronic spectrum of Cr(II) hydrazine carboxylate monohydrate shows an absorption band at 550 nm which is assigned to $^5E_g \rightarrow {}^5T_{2g}$ transition of Cr(II) (d^4 icn) in an octahedral field. The magnetic moment was found to be 2·79 BM at 298 K. This value is considerably lower than the expected magnetic moment of 4·95 BM for the
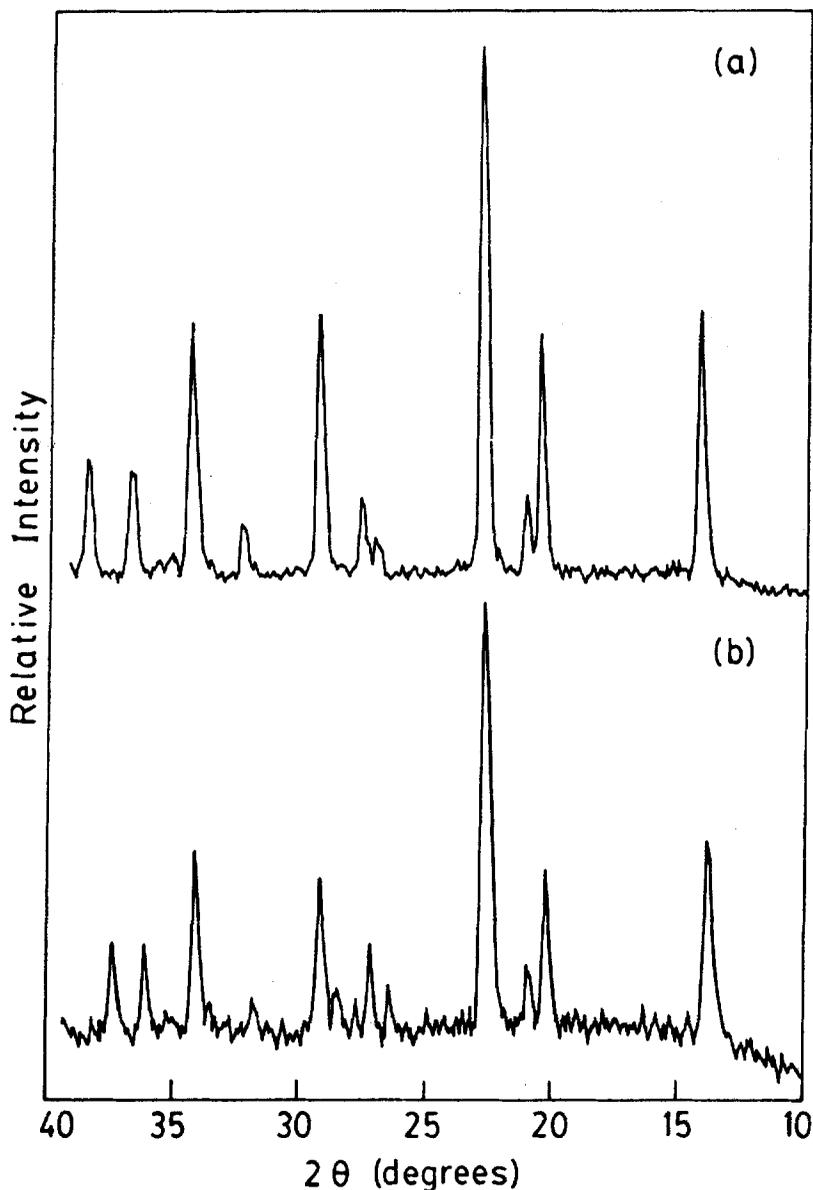

Figure 1. Powder X-ray diffraction pattern of (a) $Cu(N_2H_3COO)_2 \cdot H_2O$, (b) $Cr(N_2H_3COO)_2 \cdot H_2O$.

high spin Cr(II) ion in an octahedral field as reported by Bellerby *et al* (1986). This may be attributed either to the formation of a weak bond between chromium atoms or to a strong magnetic exchange as observed for the Cu(II) complex since both Cu(II) and Cr(II) hydrazine carboxylate monohydrate have similar X-ray diffraction patterns (figure 1). The electronic spectra of the chromium(III) hydrazine carboxylate complex shows three absorption bands at 700, 515, and 397 nm corresponding to $^4A_{2g} \rightarrow {}^2E_g$, $^4T_{2g} \rightarrow {}^4T_{1g}$ transitions, respectively, of the Cr(III) ion in an octahedral field. The three bidentate hydrazine carboxylate ligands seem to provide an octahedral symmetry while the three water molecules remain uncoordinated.

3.3 Thermal analysis

The results of the TG-DTA studies of Cu(II), Cr(II) and Cr(III) hydrazine carboxylate have been summarised in table 1. Both Cu(II) and Cr(II) hydrazine carboxylate initially undergo dehydration losing the water molecule. The anhydrous copper hydrazine carboxylate decomposes exothermically at 115°C which is in agreement with earlier observations (Patil *et al* 1979). However, the Cu(II) complex yields a mixture of CuO and metallic copper while the Cr(II) complex gave Cr_2O_3. The TG-DTA curve of $Cr(N_2H_3COO)_3 \cdot 3H_2O$ shows two endothermic peaks at 90° and 120°C corresponding to the loss of three water molecules in two steps. This is followed by an exothermic decomposition of the anhydrous $Cr(N_2H_3COO)_3$ complex to yield Cr_2O_3 as the final product. It is interesting to note that the hydrothermal decomposition of $Cr(N_2H_3COO)_3 \cdot 3H_2O$ gave CrOOH, which was identified by its characteristic X-ray powder diffraction pattern. The importance of this intermediate is due to its use as precursor to CrO_2 a well-known recording material.

Acknowledgement

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