

Bis-hydrazine metal maleates and fumarates: Preparation, spectral and thermal studies

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MS received 29 May 1995; revised 1 September 1995

Abstract. Hydrazinium hydrogenmaleate (HHM) and hydrogenfumarate (HHF) have been prepared and characterized by analytical, spectral and thermal studies. Bis-hydrazine metal maleates and fumarates of the general formula $\text{MX}(\text{N}_2\text{H}_4)_2$, where M = Co, Ni or Zn and X = maleate or fumarate have been prepared by the reaction of corresponding metal nitrate hydrates with a mixture of maleic or fumaric acid (1 part) and hydrazine hydrate (4 parts). Electronic spectra and magnetic susceptibility measurements indicate that all are high-spin octahedral complexes. The IR data show that the bonding of the hydrazine and maleate/fumarate dianion to the metal ion is bidentate. Thermal decomposition studies show that the simple hydrazinium salts undergo melting followed by endothermic decomposition into gaseous products, whereas the metal complexes undergo violent exothermic decomposition to give either metal or metal oxide as the final product.

Keywords. Bis-hydrazine metal maleates; bis-hydrazine metal fumarates; thermal analysis.

1. Introduction

Aliphatic monocarboxylic acids which have been by far the most studied as ligands are low molecular weight carboxylic acids, namely formic, acetic and propionic acids etc. Dicarboxylic acids and their derivatives have also received much attention and the coordination compounds of these with a wide variety of metal ions have also been studied (Birdes *et al* 1979). However, complexes of unsaturated dicarboxylic acids, viz. maleic and fumaric acids, have not been so extensively studied. Both the acids have two potential coordinating sites. They form stable 1:1 and 1:2 (metal:ligand) complexes with metals depending on the chemical environment. A few complexes of maleic and fumaric acids with various metal ions (Gupta and Saha 1977; Gupta and Mahanta 1978; Gupta *et al* 1983; Lis 1983) are known. However, there appears to be no report on metal hydrazine maleates and fumarates, though the metal hydrazine formates (Ravindranathan and Patil 1983), acetates (Mahesh and Patil 1986), propionates (Sivasankar and Govindarajan 1994), oxalates (Gajapathy *et al* 1982) and malonates and succinates (Sivasankar and Govindarajan 1994) have been studied. Even simple salts of maleic and fumaric acids with hydrazine are not known. Hence, an attempt has been made to prepare simple salts of these acids and also their metal complexes with hydrazine. It was gratifying that we were not only able to prepare hydrazinium maleate and fumarate but

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could also obtain metal hydrazine complexes of cobalt, nickel and zinc with the above mentioned acids. In this paper, we report the preparation, spectral and thermal properties of hydrazinium hydrogenmaleate and hydrogenfumarate and also some new bis-hydrazine metal maleates and fumarates.

2. Experimental

All the chemicals used were of AnalaR grade and the solvents were freshly distilled before use. Hydrazine hydrate (99–100%) was used in all the reactions.

2.1 Preparation of hydrazinium hydrogenmaleate

Hydrazinium hydrogenmaleate, $N_2H_5HC_4H_2O_4$, was prepared by mixing an aqueous solution (50 ml) of maleic acid (5.8 g, 0.05 m) with an aqueous solution (50 ml) of hydrazine hydrate (2.5 g, 0.05 m) in equimolar ratio. The resulting solution ($pH \sim 4$) was kept on a water bath for a few minutes and then left for crystallization at room temperature. Crystals began to appear after a few days. These were collected, washed with ether and dried in air. The salt is soluble in water and melts at $149^\circ C$.

2.2 Preparation of hydrazinium hydrogenfumarate

This salt, $N_2H_5HC_4H_2O_4$, was prepared by a method similar to that above by substituting fumaric acid (5.8 g, 0.05 m) for maleic acid. The hydrazinium hydrogenfumarate has lower solubility in water when compared to the corresponding maleate salt. It melts at $158^\circ C$.

2.3 Preparation of bis-hydrazine metal maleates

Aqueous solution (25 ml) mixture containing maleic acid (1.16 g, 0.01 m) and hydrazine hydrate (2 ml, 0.04 m) in 1:4 molar ratio was added to an aqueous solution of the respective metal nitrate hydrate (0.01 m) slowly with constant stirring. The precipitate obtained immediately after mixing was filtered, washed with alcohol and dried over a vacuum pump and stored in airtight bottles.

2.4 Preparation of bis-hydrazine metal fumarates

These complexes were prepared as described by using fumaric acid (1.16 g, 0.01 m) instead of maleic acid as mentioned above.

2.5 Analyses

The metal content in all the complexes was determined by EDTA complexometric titration, after decomposing a known weight of the sample with concentrated nitric acid. The hydrazine content was determined volumetrically using 0.025 M KIO_3 solution under Andrews' conditions (Vogel 1961).

2.6 Physicochemical studies

The magnetic moments of the complexes at room temperature were measured by Gouy's method using mercury tetrathiocyanato cobalt(II) as a calibrant. Diamagnetic corrections were estimated from Pascal's constants. The electronic spectra of the solid complexes were recorded on a Shimadzu UV-visible 240 A spectrophotometer by using barium sulphate as the reference material. The infrared spectra of the samples were recorded as KBr discs on a Perkin-Elmer Model 597 spectrophotometer in the range

4000–400 cm^{-1} . Simultaneous DTG-TG experiments were carried out using the Mettler TA 3000 system, and DSC using Perkin–Elmer Model DSC 7 in static air. The heating rate was 10°C per minute and 2–3 mg of the samples were used for each experiment.

3. Results and discussion

3.1 Hydrazinium hydrogenmaleate and hydrogenfumarate

These salts were prepared by mixing aqueous solutions of maleic or fumaric acids respectively, with hydrazine hydrate in equimolar ratio. The chemical analyses (table 1) of these salts conform to the desired composition.

Our attempt to prepare dihydrazinium maleate and fumarate, $(\text{N}_2\text{H}_5)_2\text{C}_4\text{H}_2\text{O}_4$, by the reaction of the respective acid and hydrazine hydrate in 1:2 ratio was unsuccessful. This may be due to the considerable difference between pK_a values, ($pK_{a1} = 1.92$ and $pK_{a2} = 6.23$ for maleic acid and $pK_{a1} = 3.02$ and $pK_{a2} = 4.38$ for fumaric acid). Also in the case of hydrogenmaleate anion, the O–H bond may be stabilised by the formation of a symmetrical intramolecular hydrogen bonding. Hence, a proton cannot be abstracted by a weak base like hydrazine which prevents the formation of dihydrazinium salt.

The characteristic infrared absorption of the carboxylate ion, $\nu_{\text{asy}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ are seen at 1620 and 1390 cm^{-1} , in both cases. The $\nu_{\text{asy}}(\text{COO}^-)$ of the free acid group is observed at 1710 cm^{-1} , as reported for maleic and fumaric acids. The relatively strong absorption at 985 cm^{-1} has been assigned to $\nu_{\text{N-N}}$ of N_2H_5^+ ion. The $\nu_{\text{N-N}}$ of N_2H_5^+ ion is known (Braibanti *et al* 1968) to occur in the region 960–990 cm^{-1} . Absorptions at 3300, 3170 and 3070 cm^{-1} have been attributed to $\nu_{\text{N-H}}$ of N_2H_5^+ ion.

The DSC of both the salts shows an almost identical decomposition pattern except for a slight difference in the decomposition temperature. The DSC shows two distinct endotherms. The first endotherm (149°C for maleate salt and 158°C for fumarate salt) is due to melting. The second broad endotherm is assigned to the decomposition of the melt into gaseous products such as CO, CO₂, NH₃, N₂, H₂O etc.

Table 1. Analytical data.

Compound	Colour	Yield (%)	Metal (%)		Hydrazine (%)		Magnetic moment μ_{eff} (BM)
			Found	Calc.	Found	Calc.	
HHM	Colourless	80	—	—	21.8	21.77	—
HHF	Colourless	75	—	—	21.6	21.77	—
Co(Mal)(N ₂ H ₄) ₂	Peach	90	24.4	24.87	26.9	27.01	4.54
Ni(Mal)(N ₂ H ₄) ₂	Lavender	95	24.1	24.80	26.6	27.03	2.82
Zn(Mal)(N ₂ H ₄) ₂	Colourless	80	26.0	26.86	26.8	26.30	Diamagnetic
Co(Fum)(N ₂ H ₄) ₂	Peach	85	24.5	24.87	27.3	27.01	4.45
Ni(Fum)(N ₂ H ₄) ₂	Lavender	90	24.3	24.81	27.5	27.03	2.90
Zn(Fum)(N ₂ H ₄) ₂	Colourless	80	27.0	26.86	25.3	26.30	Diamagnetic

Abbreviations: HHM – hydrazinium hydrogenmaleate; HHF – hydrazinium hydrogenfumarate; Mal – maleate; Fum – fumarate.

Table 2. Thermal data.

Compound	DTA peak temp. (°C)	Thermogravimetry				Final product
		Temp. range (°C)	Weight loss (%)			
			Found	Calc.		
HHM	149(+)	—	—	—	Melting	
	205(+)	150–600	98.00	100.00	Complete decomp.	
HHF	158(+)	—	—	—	Melting	
	200(+)	150–600	98.00	100.00	Complete decomp.	
Co(Mal)(N ₂ H ₄) ₂	77(–)	45–185	7.10	6.75	Co(Mal)(N ₂ H ₄) _{1.5}	
	335(–)	185–390	67.10	66.12	Co ₃ O ₄	
Ni(Mal)(N ₂ H ₄) ₂	227(–)	195–260	97.18	75.20	Ni	
Zn(Mal)(N ₂ H ₄) ₂	227(–)	155–245	14.00	13.14	Zn(Mal)(N ₂ H ₄) _{1.5}	
	280(–)	245–325	93.01	66.56	ZnO	
Co(Fum)(N ₂ H ₄) ₂	262(–)	225–330	95.50	75.13	Co	
Ni(Fum)(N ₂ H ₄) ₂	245(–)	205–280	95.60	75.20	Ni	
Zn(Fum)(N ₂ H ₄) ₂	257(–)	155–295	20.22	19.72	Zn(Fum)(N ₂ H ₄) _{1.5}	
	335(–)	295–385	42.58	43.55	ZnC ₂ O ₄	
	430(–)	385–470	65.52	66.56	ZnO	

Abbreviations as in table 1; decomp—decomposition; (+): Endotherm; (–): Exotherm; Fum—fumarate; Mal—maleate; The large difference in weight loss between the observed and theoretical values has been explained in the text.

The TG also shows a distinct single step decomposition (150–600°C) with almost 100% weight loss (table 2) for both the salts.

3.2 Bis-hydrazine metal maleates and fumarates

Reactions of aqueous solutions of hydrazinium hydrogenmaleate or hydrogenfumarate with metal ions, in appropriate ratios, did not yield the desired products. Hence, an aqueous mixture of 1:4 maleic/fumaric acid and hydrazine hydrate was used as such for the preparation of metal complexes.

The reaction of metal nitrate hexahydrates (one part) with maleic/fumaric acid (one part) and hydrazine hydrate (four parts) yielded the bis-hydrazine metal maleates/fumarates of the formula MX(N₂H₄)₂, where X = maleate or fumarate and M = Co, Ni or Zn (table 1).

3.3 Magnetic moments and electronic spectra

The magnetic moments of the complexes calculated from corrected magnetic susceptibility are given in table 1. The effective magnetic moments of cobalt and nickel maleate complexes are found to be 4.54 and 2.82 BM respectively, which suggest spin-free octahedral geometry. The magnetic moment values obtained for the corresponding fumarate compounds are 4.45 and 2.90 BM. The zinc compounds are diamagnetic as expected (Cotton and Wilkinson 1980).

The electronic reflectance spectrum of bis-hydrazine cobalt maleate shows a strong band at 23 810 cm⁻¹ which may be assigned to the transition ⁴T_{1g}(F) → ⁴T_{1g}(P) in the

octahedral environment of Co(II). The similar transition for the bis-hydrazine cobalt fumarate is shown by the band at $23\,530\text{ cm}^{-1}$. The bis-hydrazine nickel maleate shows two bands at $14\,390$ and $22\,730\text{ cm}^{-1}$. These bands are attributed to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively, characteristic of octahedral geometry (Lever 1984). Corresponding fumarate complexes show these bands at $14\,705$ and $23\,810\text{ cm}^{-1}$, respectively.

3.4 Infrared spectra

The infrared spectra of the complexes are similar and all of them show four bands in the region $3450\text{--}3150\text{ cm}^{-1}$ characteristic of N–H stretching frequency. The maleate and fumarate dianions in these complexes coordinate to the metal as a bidentate ligand via both the carboxylate groups. The asymmetric and symmetric stretching frequencies of carboxylate ions are seen around 1610 and 1380 cm^{-1} respectively with $\Delta\nu(\text{v}_{\text{asy}} - \text{v}_{\text{sym}})$ separation of $\sim 230\text{ cm}^{-1}$ indicating the monodentate linkage of both carboxylate groups in the dianions.

The observed N–N stretching frequencies in the range $960\text{--}970\text{ cm}^{-1}$ for all these complexes reveal clearly that the hydrazine moieties are present as bridging bidentate ligands (Braibanti *et al* 1968).

3.5 Thermal analyses

The thermal data of all the complexes are summarized in table 2. The salient features of the thermal analysis results are as follows.

All the complexes undergo violent exothermic decomposition except the bis-hydrazine cobalt maleate and zinc fumarate. Among the maleates, the nickel compound undergoes single-step decomposition to give nickel metal as the final product, whereas the cobalt and zinc compounds show two-step decomposition to give Co(maleate) $(\text{N}_2\text{H}_4)_{1.5}$ and Zn(maleate) (N_2H_4) intermediates, which further decompose to give respective metal oxides as the end product. While fumarate complexes of cobalt and nickel show single-step violent decomposition with the corresponding metal powders as the final residue, the zinc fumarate complex undergoes three-step decomposition, with Zn(fumarate) $(\text{N}_2\text{H}_4)_{1.5}$ and zinc oxalate as intermediates, to give zinc oxide as the final product. Among all the compounds, the bis-hydrazine nickel maleate is thermally more reactive and bis-hydrazine zinc fumarate, the least.

In most cases the observed weight losses for the formation of metal/metal oxides are found to be higher than that of the theoretical values. These discrepancies may be attributed to the violent exothermic decomposition of the complexes during which the substances are thrown out from the crucible. However, the final products were confirmed by collecting the residues after gradually heating the complexes in portions in a closed container and analysing the residues by analytical, infrared, spectral and X-ray powder diffraction studies. As compared to the bis-hydrazine metal formate, acetate and oxalate complexes, the present complexes are thermally more reducing giving mostly metal powder as the end product, whereas the former complexes give metal oxide as the decomposition residue.

3.6 Structure and metal coordination

The analytical data and physico-chemical studies suggest that the hydrazine molecules and maleate or fumarate ions are coordinated to the metal in all the complexes.

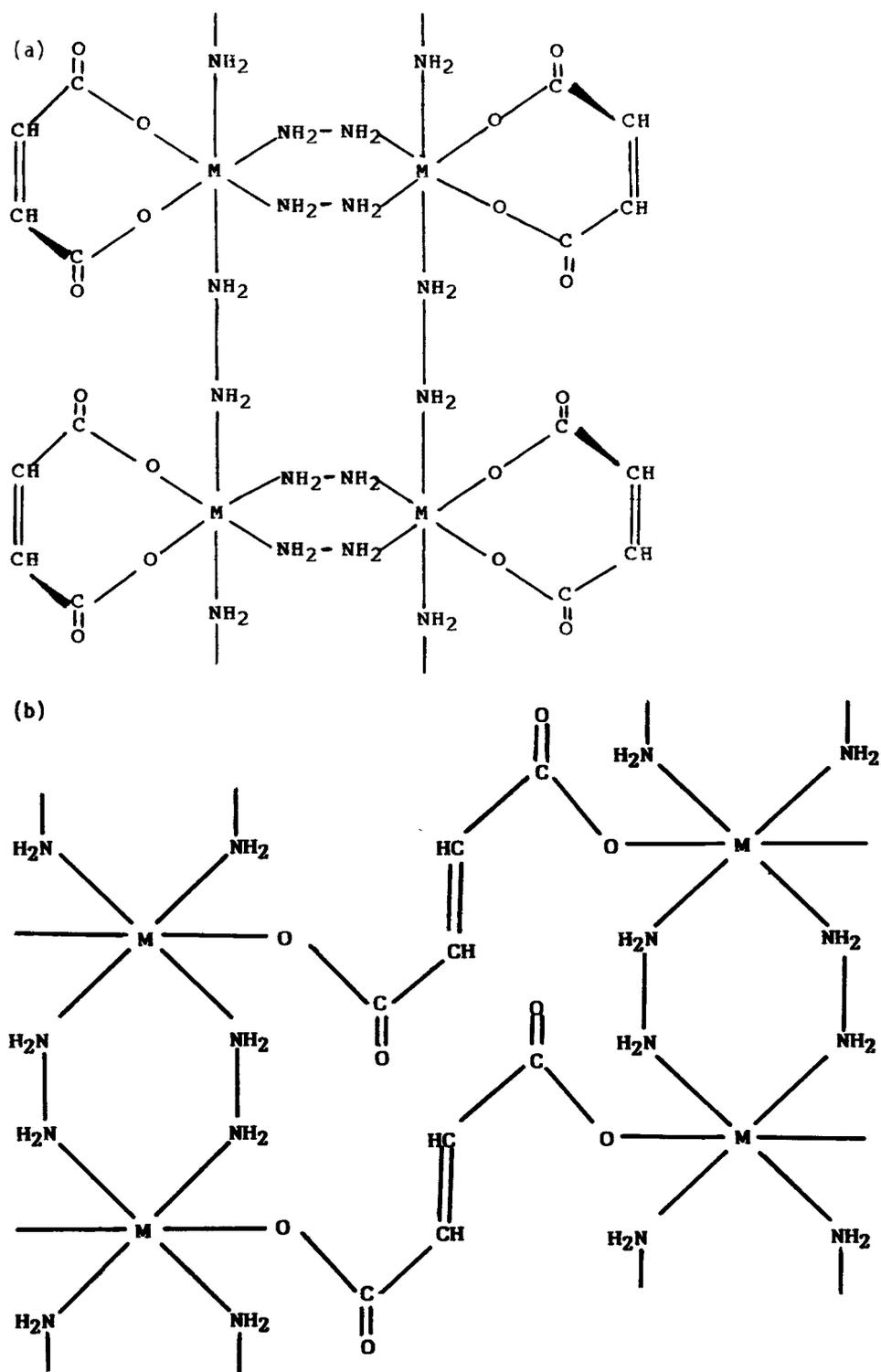


Figure 1. Structure of $\text{MX}(\text{N}_2\text{H}_4)_2$ where $\text{M} = \text{Co}, \text{Ni}$ or Zn and $\text{X} = \text{maleate (a)}$ or fumarate (b) .

Hydrazine molecules are found to be present as bridging bidentate ligands and maleate/fumarate dianions as bidentate bridging or chelating ligands as evidenced from the infrared spectra. Further, in most of the metal complexes it has been shown that both the carboxyl groups in the maleate/fumarate are twisted out of the plane containing the carbon atoms (Gupta and Mahanta 1978; Gupta *et al* 1983), thereby favouring chelation or bridging. Hence, in these complexes the metal can have coordination number six, considering four nitrogen atoms of two hydrazine molecules and two oxygens of maleate/fumarate ion as (bidentate-chelate/bridging) coordinating sites. The above evidences indicate that the compounds reported herein may consist of polymeric structures (figures 1a and b) with octahedral geometry around the metal. Further, the insoluble nature of these compounds conforms to the polymeric structure.

Acknowledgement

BNS thanks the Council of Scientific and Industrial Research, New Delhi for a fellowship.

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