

THERMOCHEMICAL ANALYSES OF SOLID ISONICOTINIC HYDRAZIDE TRANSITION METAL COMPLEXES

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(Received 9 March 1984)

ABSTRACT

New solid metal complexes of isonicotinic hydrazides with considerable biological activities were synthesized in neutral media for metal/ligand ratios of 1:1 and 1:2. The materials thus prepared were subjected to careful courses of elemental analysis, quantitative thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Results obtained were promising and in conformity amongst each other which may lead to a better understanding of the exact molecular formulae of the intended solid complexes and their thermal stability in correlation with mode of preparation and various substitutions in the organic ligand molecules. Nickel-acetate solid complexes prepared in neutral medium ($M/1 = 1:2$) seemed to have lower thermal stabilities. Generally, solid metal acetate complexes were found to have a unique decomposition exotherm shape which could be used as a rapid and sensitive tool for the detection of acetate-containing complexes.

INTRODUCTION

Hydrazides are known to form stable complexes with some heavy metal ions either in aqueous or alcoholic solutions. Studies on metal chelates with organic hydrazides drew the attention of some investigators [1–3] to solve the problem concerning their exact molecular structures. Thus, Bell and Rose [4] studied the thermal stability of pyridine 2-aldehyde-2-pyridylhydrazone complexes with platinum metals. Chang et al. [5] studied the thermal behavior of rare earth metal ion chelates of 8-hydroxyquinoline and 8-hydroxyquinoline and their derivatives. They found that the order of heat stability of chelates decreased with decreasing basicity of the ligand and the presence of water- or proton-containing compounds in the chelates seemed to lower their heat stabilities. Abou Sekkina et al. [6] investigated the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of cadmium formate dihydrate single crystal and a mechanism was suggested

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for water loss in hydrous cadmium formate single crystals for the first time.

As far as the authors are aware, no work has been found in the literature concerning the thermographic studies even on similar metal complexes which are the major goal of the present investigation.

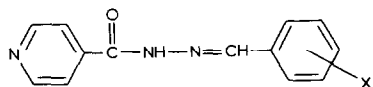
EXPERIMENTAL

Preparation of metal chelates in the solid state

This includes preparations of the organic ligand molecules and their corresponding solid metal chelates.

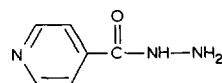
Preparation of the organic ligands

Isonicotinic hydrazides were prepared by a method similar to that described by Sturve [7]. The ester of isonicotinic acid was refluxed with the required quantity of hydrazine hydrate in ethanol. On allowing the reaction mixture to cool, the solid hydrazide separated out was then filtered off and recrystallized several times from ethanol. The arylidene derivatives were prepared by condensation of the hydrazide with some aromatic aldehydes in ethanol solvent. The condensation product is separated on cooling, filtered off, washed several times with alcohol and then kept in vacuum desiccator. The arylidene hydrazide derivatives have the general structural formula



where X = *p*-NO₂ (**Ib**), *m*-NO₂ (**Ic**), *o*-NO₂ (**Id**), *p*-Cl (**Ie**), *m*-Cl (**If**), *o*-Cl (**Ig**), *p*-Br (**Ih**), H (**Ii**), *m*-CH₃ (**Ij**), *p*-CH₃ (**Ik**), *o*-OCH₃ (**Il**), *p*-OCH₃ (**Im**), *o*-OH (**In**), *m*-OH (**Io**), *p*-OH (**Ip**).

The chemical formula of isonicotinic hydrazide is



Preparation of the solid complexes

Solid metal complexes were prepared by mixing of an ethanolic solution of the organic ligands (1 or 2 mol) with solution of the metal salt in the same solvent. The mixture was refluxed for 30 min. The solid complexes which separated immediately after mixing or cooling were then filtered off and dried. The materials thus obtained were analysed for their metal content by EDTA titrations [8].

TABLE 1

Chemical analysis of isonicotinic hydrazide metal complexes prepared in neutral medium

Metal ion	Ib		Ie		Suggested formula
	Calc.	Found	Calc.	Found	
Mn ²⁺	20.890	21.200	14.250	13.980	MnCl ₂ , L
Co ²⁺	21.910	20.980	15.130	16.170	CoCl ₂ , L
Ni ²⁺	21.840	21.350	15.080	14.880	NiCl ₂ , L
Cu ²⁺	23.400	22.980	16.120	16.100	CuCl ₂ , L
Zn ²⁺	23.920	24.500	16.510	16.210	ZnCl ₂ , L
Cd ²⁺	35.100	36.000	25.380	25.610	CdCl ₂ , L

Differential thermal analysis (DTA) measurements

For DTA measurements, a Shimadzu (Japan) series 30 thermoanalysis instrument was used from room temperature (20 °C) up to 800 °C in air.

RESULTS AND DISCUSSION

Elemental analysis of the prepared solid complexes

In this respect, the concentration of ammonium hydroxide in the dilute solution of copper must not exceed 0.01 M. Ammonium hydroxide is added

TABLE 2

Chemical analysis of Cu-salt complexes with arylidene derivatives of isonicotinic hydrazide prepared in neutral medium

Complex	Chloride		Acetate	
	Calc.	Found	Calc.	Found
Ib	15.700	15.530	14.070	14.150
Ic	15.700	15.830	14.070	13.980
Id	15.700	15.500	14.070	13.830
Ie	16.120	16.100	14.400	14.310
If	16.120	16.120	14.400	14.580
Ig	16.120	15.900	15.400	14.480
Ih	14.500	14.340	13.090	12.950
Ii	17.70	16.860	15.620	15.820
Ij	17.00	16.750	15.100	15.630
Ik	17.00	16.950	15.100	14.850
Il	16.310	16.150	14.550	14.680
Im	16.310	16.300	14.550	14.810
In	16.910	17.200	15.030	15.310
Io	16.910	17.040	15.030	15.550
Ip	16.910	16.600	15.030	15.950
Formula	CuCl ₂ , L		CuAc ₂ , L	

TABLE 3

Chemical analysis of metal acetate complexes of isonicotinic hydrazides prepared in alkaline and neutral media

Metal ion	Ib		Ih		Suggested formula
	Calc.	Found	Calc.	Found	
<i>Complexes prepared in alkaline medium (1:1)</i>					
Cu ²⁺	20.260	20.250	13.230	13.400	CuAcL, 3 H ₂ O
Co ²⁺	19.070	18.580	12.390	12.160	CoAcL, 3 H ₂ O
Ni ²⁺	19.000	18.200	12.340	12.010	NiAcL, 3 H ₂ O
<i>Complexes prepared in neutral medium (1:2)</i>					
Cu ²⁺	13.940	13.680	8.100	8.450	CuAc ₂ , 2L
Co ²⁺	13.060	13.370	7.510	7.250	CoAc ₂ , 2L
Ni ²⁺	13.020	13.400	7.480	7.050	NiAc ₂ , 2L

to the nickel solution until the nickel ion is converted to the tetramine complex and the end point is indicated by a color change from orange through yellow to purple. Results of the elemental analysis are given in Tables 1–3 based on which the probable constitutional formulae for the various metal chelates are suggested. From the results obtained it was deduced that the ligand under investigation reacts with the intended metal ion in the keto form.

Differential thermal analysis of the solid complexes

By the use of the DTA method the variation in the composition of the investigated compounds from the required stoichiometry can be found. These variations are highly dependent upon bond strength and essential because they affect the physical properties of the investigated materials. To understand the mechanism of complex formation and the stability of the complex thus formed, it is of significance to observe the intermediate products formed by the oxidative action of heat on the investigated solid metal chelates in air. Thermogravimetric analysis (TGA) together with DTA curves give information with more assurance for the various unexpected phenomena observed during heat treatment.

The DTA of metal chloride complexes (1:1) with isonicotinic hydrazides prepared in neutral medium

Figure 1 includes the DTA behavior of the CuCl₂ complex with *p*-hydroxy benzylidene isonicotinic hydrazide prepared in neutral medium. The appearance of a strong broad exothermic peak at 280°C may be correlated with an overlap between two adjacent processes, namely melting and decomposition along the chelate bond by loss of the organic ligand. The latter process

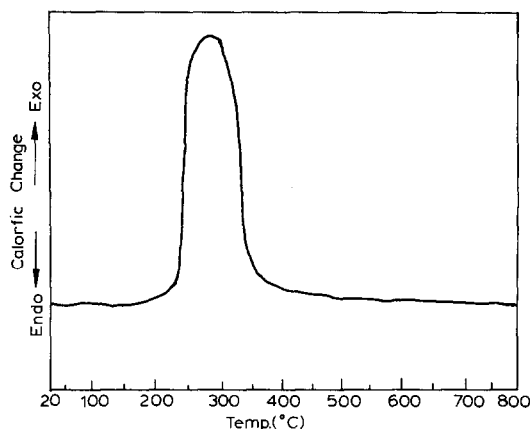


Fig. 1. The DTA behavior of the solid Cu-chloride complex with *p*-hydroxy benzylidene isonicotinic hydrazide prepared in neutral medium for M/L = 1:1.

may lead to the formation of a stable oxidation product. The disappearance of any thermographic change above 280°C is consistent with the formation of only one metal oxide which is most probably cupric oxide, as it shows a good stability on further heating up to 800°C in air which is in conformity with results given in Table 4.

From Table 4, it can be seen that the formation of mixed oxides is favored at M/L = 1:2 particularly for Co and Cu complexes.

The DTA behavior of metal acetate complexes (1:2) with isonicotinic hydrazides prepared in neutral medium

For the Cu-acetate complex (Fig. 2, a) the endothermic peak at 122°C is correlated with the loss of water from the surface of the crystals (moisture

TABLE 4

Quantitative thermogravimetric analysis of isonicotinic hydrazide metal chelates at 19°C and their air-fired final product at 800°C

Metal salt	Organic ligand	Medium	M/L	Weight (g)		%Metal		Final product
				at 20°C	at 800°C	Calc.	Found	
Cu-chloride	Ip	Neutral	1:1	0.0213	0.0029	15.000	14.980	CuO
Co-acetate	Ib	Neutral	1:2	0.0262	0.0070	13.060	13.100	CoO/ Co ₂ O ₃ (minor)
Ni-acetate	Ib	Neutral	1:2	0.0280	0.0080	13.020	23.020	NiO
Cu-acetate	Ib	Neutral	1:2	0.0329	0.0082	13.940	14.240	CuO/ Cu ₂ O (minor)
Cu-acetate	Ih	Neutral	1:2	0.0204	0.0100	8.100	8.050	CuO

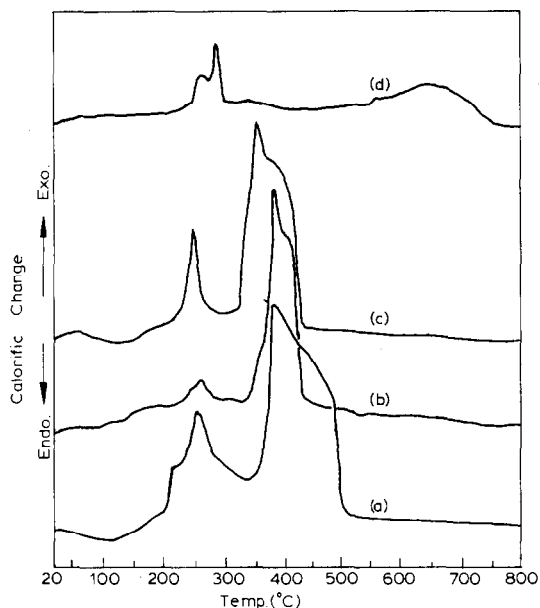


Fig. 2. A diagrammatical representation of the behavior of the DTA curves of solid metal acetate complexes with isonicotinic hydrazides prepared in neutral medium ($M/L = 1:2$): (a) Cu^{2+} -**Ib** complex; (b) Co^{2+} -**Ib** complex; (c) Ni^{2+} -**Ib** complex; (d) Cu^{2+} -**Ih** complex.

content) [4]. An exothermic peak at 215°C is probably assigned to the phase change of the anhydrous complex. The sharp medium exothermic peak at 250°C corresponds to the melting of the anhydrous complex. A strong broad exothermic peak ($380\text{--}500^\circ\text{C}$) combined with a broad shoulder, as a crowded group, includes various changes of: (a) decomposition [5] and loss of the organic portion; (b) the subsequent oxidation of Cu_2O to the final CuO product. The forward convex shape of the curve seems to be correlated with the loss of acetate (organic) portions beside the organic ligand molecules. This observation is further supported by its frequent repetition in thermal decomposition amongst all of the acetate-salt formed complexes (see Fig. 2a-c).

For the Co-acetate complex (Fig. 2b), all peaks are exothermic including the following phenomena: (a) partial decomposition occurs at 115°C ; (b) internal lattice rearrangement [9] of the material occurs at 175°C . The exothermic peak lying at 240°C corresponds with melting of the complex. The strong broad exotherm at $350\text{--}480^\circ\text{C}$ includes various changes in addition to the decomposition to the final product. In this respect the final product comprises mixed valence oxides ($\text{CoO}/\text{Co}_2\text{O}_3$) as shown quantitatively (see Table 4).

For the Ni-acetate complex (Fig. 2c), the following can be evaluated: (a) the broad endotherm at 130°C is assigned to the drying of the material through loss of humidity water from the surface of the crystals; (b) the sharp

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