Thermochimica Acta, 77 (1984) 211–218
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMO-CHEMICAL BEHAVIOR OF SOLID NICOTINIC HYDRAZIDE METAL COMPLEXES IN CORRELATION WITH THEIR STOICHIOMETRY

M.M. ABOU SEKKINA * and (in part) M.G. ABOU EL-AZM

Chemistry Department, Faculty of Science, Tanta University, Tanta (Egypt)

(Received 17 January 1984)

ABSTRACT

New solid metal complexes of nicotinic hydrazides with strong biological activity have been prepared in neutral and alkaline media having 1:1 and 1:2 metal/ligand ratios. The materials obtained were subjected to careful programs of elemental analysis, quantitative thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Interesting results were obtained in agreement with each other leading to a better understanding of the exact molecular formulae of the solid complexes and their thermal stability in relation to the mode of preparation, medium of precipitation and various substitutions in the organic ligand molecules. Finally, metal chelates with an M/L ratio of 1:2 seemed to have lower thermal stabilities.

INTRODUCTION

Differential thermal analysis opens up new possibilities for the investigation, synthesis and thermal stability of solid metal chelates. Therefore, Asker and Abou Sekkina [1] investigated the thermogravimetric and differential thermal analyses of some chalcogenides deducing the high stability of mechanical mixes. Their results were discussed on the basis of electronegativity difference and oxygen affinity towards the non-metallic component. The materials they included have great application as transistors, radards and rectifiers. In previous investigations on trivalent lanthanide oxinates, some authors [2,3] indicated that the 1:3 stoichiometric chelates $L(C_9H_6NO)_3$ are quite difficult to prepare due to their weak stability. Unlike certain divalent metal ion chelates and other trivalent metal ion chelates, sublimation in the pyrolysis of chelates is not serious [4].

Very little work was found in the literature data concerning thermogravimetric studies, even on related metal chelates. Thus, the present investigation

---

* Author to whom all correspondence should be addressed.

0040-6031/84/$03.00

is aimed at evaluating the thermographical behavior of some selected and representative nicotinic hydrazide metal chelates in relation to stoichiometry and substitution in the organic ligand molecules and the nature of the metal ions due to their strong biological activity.

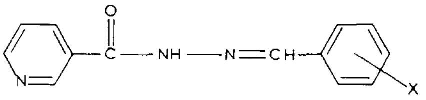
EXPERIMENTAL

Material synthesis

This comprises synthesis of the organic ligands molecules and their corresponding transition metal complexes in the solid state.

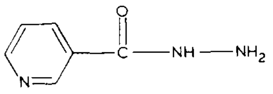
Solid nicotinic hydrazides were prepared by a method similar to that previously described by Struve [5]. For this purpose, the ester of the acid was refluxed with a definite quantity of hydrazine hydrate in ethanol. On cooling, the solid hydrazide separated out, was filtered off, and recrystallized several times in ethanol. The arylidene derivatives were prepared by condensation of the hydrazide with some aromatic aldehydes in ethanol solvent. On cooling the condensation product which separated out, was filtered off, washed several times with alcohol, and kept in a vacuum desiccator over dried silica gel. The arylidene hydrazide derivatives have the general structural formula

L =



where X = *p*-NO_2 (**Ib**), *m*-NO_2 (**Ic**), *o*-NO_2 (**Id**), *p*-Cl (**Ie**), *m*-Cl (**If**), *o*-Cl (**Ig**), *p*-Br (**Ih**), H(**Ii**), *m*-CH_3 (**Ij**), *p*-CH_3 (**Ik**), *o*-OCH_3 (**Il**), *p*-OCH_3 (**Im**), *o*-OH (**In**), *m*-OH(**Io**), *p*-OH (**Ip**)

The formula of hydrazide is



(I)

The corresponding metal complexes were prepared by mixing an ethanolic solution of the synthesized organic ligand (1 or 2 mol) with a solution of the transition metal salts (1 mol) in the same solvent. The mixture was refluxed for ~ 30 min. The solid complexes separated immediately after mixing or cooling were filtered off and dried. The alcoholic medium is used for complex preparation in neutral medium, while for complexes prepared in alkaline medium either NH_4OH or NaOH is added. The materials obtained were then analysed for their metal content by EDTA titration [6].

Differential thermal analysis (DTA)

The solid materials were subjected to a Shimatzu thermoanalysis instrument (series 30) in which the temperature is automatically recorded as a function of time. The system possessed a sensitivity of ±0.5% at the investigated temperature range (20–800°C).

RESULTS AND DISCUSSION

Elemental analysis of the prepared solid complexes

It was found that the direct method for the titration of cobalt using murexide indicator is not suitable under the experimental conditions. This is due to the interference of HNO_3 in the reaction, decreasing the sharpness of the end point. Accordingly, the back titration method was preferred. The solution to be titrated is first neutralized with sodium hydroxide. Buffer solution (5 ml, pH 10) is added, followed by a known excess of standard 0.01 M EDTA solution. The solution is titrated immediately with standard 0.01 M $ZnCl_2$ solution using Eriochrome Black T as indicator. The end point is indicated by a sharp color change from blue to red. The determination of Zn^{2+} and Cd^{2+} by direct titration was utilized using Eriochrome Black T as indicator. Manganese could be determined by the EDTA titration using pyrocatechol violet as indicator. Ascorbic acid is added in a small amount to prevent oxidation of the Mn(II) ion to Mn(III). Results obtained are given in Tables 1–3. Based on these results, probable constitutional formulae for the different metal chelates are suggested. Generally, it was emphasized that the results obtained revealed that the ligand under investigation reacts with the metal ion in the keto form.

TABLE 1

Chemical analysis of nicotinic hydrazide metal complexes prepared in neutral medium

Metal ion	**Ib**		**Ic**		Suggested formula
	Calc.	Found	Calc.	Found	
Mn^{2+}	20.89	22.80	—	—	$MnCl_2$, L
Co^{2+}	—	—	14.70	13.88	$CoCl_2$, L
Ni^{2+}	—	—	14.68	13.85	$NiCl_2$, L
Cu^{2+}	23.38	23.18	15.71	15.57	$CuCl_2$, L
Zn^{2+}	23.92	24.14	16.08	15.84	$ZnCl_2$, L
Cd^{2+}	35.10	35.71	24.78	25.12	$CdCl_2$, L

TABLE 2

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

Complex	Chloride		Acetate	
	Calc.	Found	Calc.	Found
Ib	15.700	15.070	14.070	14.040
Ic	15.700	15.570	14.070	13.940
Id	15.700	15.250	14.070	13.940
Ie	16.120	16.040	14.400	14.270
If	16.120	16.080	14.400	14.930
Ig	16.120	16.080	14.400	14.240
Ih	14.500	14.370	13.090	13.380
Ii	17.700	17.780	15.620	15.300
Ij	17.000	16.840	15.100	15.200
Ik	17.000	17.300	15.100	14.960
Il	16.310	16.040	14.550	14.650
Im	15.310	16.140	14.550	14.170
In	16.910	16.540	15.030	14.830
Io	16.910	16.540	15.030	15.250
Ip	16.910	16.640	15.030	15.030
Formula	$CuCl_2$-L		$CuAc_2$-L	

Differential thermal analysis of the solid complexes

The use of differential thermal analysis (DTA) makes it possible to characterize thermographically the process of phase transformation in the system examined. It permits the study of, for example, the following features: (1) kinetics of phase equilibration; (2) variations of stoichiometric

TABLE 3

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

Metal ion	**Ib**		**Ih**		Suggested formula
	Calc.	Found	Calc.	Found	
Complexes prepared in alkaline medium (1 : 1)					
Cu^{2+}	20.260	20.900	13.230	13.020	CuAcL, 3 H_2O
Co^{2+}	19.070	20.210	12.390	11.870	CoAcL, 3 H_2O
Ni^{2+}	19.00	19.030	12.340	11.280	NiAcL, 3 H_2O
Complexes prepared in neutral medium (1 : 2)					
Cu^{2+}	13.940	12.840	8.100	8.770	$CuAc_2$, 2 L
Co^{2+}	13.060	12.930	7.610	7.690	$CoAc_2$, 2 L
Ni^{2+}	13.020	13.310	7.480	7.870	$NiAc_2$, 2 L

relationships from the required composition of the synthesized preparations; (3) phase inhomogeneity of different preparations; and (4) direct synthesis of specific materials from their constituents.

In the present investigation, some representative solid metal chelates of nicotinic hydrazides were subjected to thermographic analysis (DTA) as well as thermogravimetric analysis (TGA).

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

Figure 1, curve (a) represents the DTA of the $MnCl_2$ complex with nicotinic hydrazide, prepared in neutral ethanolic medium, in the temperature range 20–800°C. From this figure the following could be evaluated:

(1) the endothermic peak at 355°C corresponds to the dechlorination (loss of chlorine content) of the chloride ions which are coordinated into the complex sphere. This was in conformity with, and supports, the suggested chemical formula as deduced from elemental analysis (see Table 1);

(2) the exothermic peak at 400°C corresponds to a lattice rearrangement while that at 430°C is consistent with the melting of the complex;

(3) the sharp exothermic peak at 520°C corresponds to the decomposition [7] of the complex along the chelate bond and loss of the organic portion;

(4) the final two weak exothermic peaks appearing at 610 and 660°C

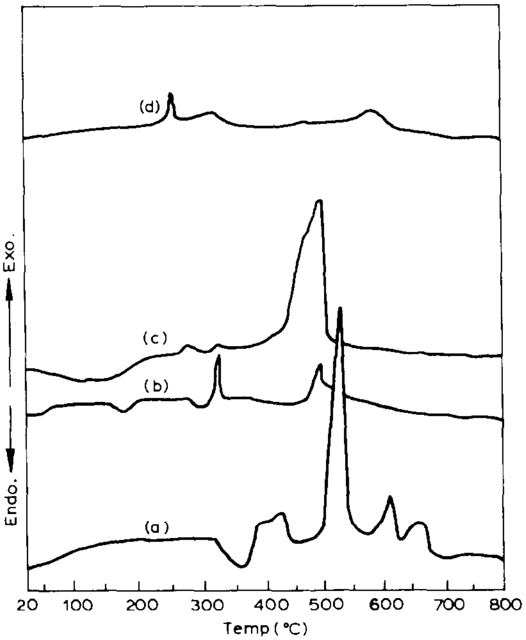


Fig. 1. The behavior of the DTA curves of solid metal chloride complexes with nicotinic hydrazides (M/L = 1 : 1) prepared in neutral (N) and alkaline (A) media: (a) Mn^{2+} -**Ib** complex(N); (b) Mn^{2+} -**Ic** complex(N); (c) Ni^{2+} -**Ic** complex(N); (d) Cu^{2+} -**Ih** complex(A).

correspond to the formation of thermally induced lattice imperfections as well as a lattice rearrangement during the formation of higher Mn oxides and/or a phase change of the high temperature formed Mn oxide, which is most probable as mathematically confirmed (see Table 4). From Table 4 it is clear that the formation of lower metal oxide is favored for manganese complexes at higher molecular weight of organic ligand and it is doubled for copper complexes (using 1 : 2 M/L ratio).

For the *m*-nitrobenzylidene nicotinic hydrazide complex (**Ic**) with Mn (Fig. 1, curve b), the phenomena occurring are: (a) loss of half the chlorine content and/or humidity water from the surface of the crystals at 170°C corresponding to the first weak endothermic peak; (b) loss of the remaining half of the chlorine content at 300°C (see Table 1, second weak endothermic peak), through decomposition [8]; (c) the sharp exothermic peak at 325°C corresponds to melting of the solid complex [9]; and (d) the broad exothermic peak at 475°C may be regarded as a result of decomposition along the chelate bond leading to the final stable product which is the metal oxide, above which no more change takes place.

For the Ni complex with *m*-nitrobenzylidene nicotinic hydrazide prepared in neutral medium, the DTA curve (Fig. 1, curve c) comprises a wide broad endothermic peak at 125°C corresponding to partial decomposition while the two small exothermic peaks at 275°C and 330°C indicate lattice rearrangements. The strong exothermic shoulder beginning at 430°C may be correlated with the melting of the material. The strong broad exotherm at 490°C is largely due to full decomposition of the complex through loss of the organic portion and formation of a stable metal oxide as a final product. Thermogravimetric evaluation (Table 4) proved that the final product is NiO.

The DTA of the metal acetate complex (1 : 1) with nicotinic hydrazides prepared in alkaline medium

For the *p*-bromobenzylidene nicotinic hydrazide complex with Cu acetate (Fig. 1, curve d) prepared in alkaline medium, the sharp exothermic peak at

TABLE 4

Quantitative thermogravimetric analysis of nicotinic hydrazide metal chelates at 20°C and their air fired products at 800°C

Metal salt	Ligand	Medium	M/L	Wt.% metal (g)				Final product
				20°C	800°C	Calc.	Found	
Mn chloride	**Ib**	Neutral	1 : 1	0.0263	0.0091	20.89	21.87	MnO_2
Mn chloride	**Ic**	neutral	1 : 1	0.0166	0.0063	13.87	13.87	Mn_2O_3
Ni chloride	**Ic**	Neutral	1 : 1	0.0248	0.0045	14.68	14.27	NiO
Cu acetate	**Ih**	Alkaline	1 : 1	0.0049	0.0009	13.23	14.67	CuO
Cu acetate	**Ih**	Neutral	1 : 2	0.3050	0.0016	8.100	7.341	Cu_2O (partly)/ CuO

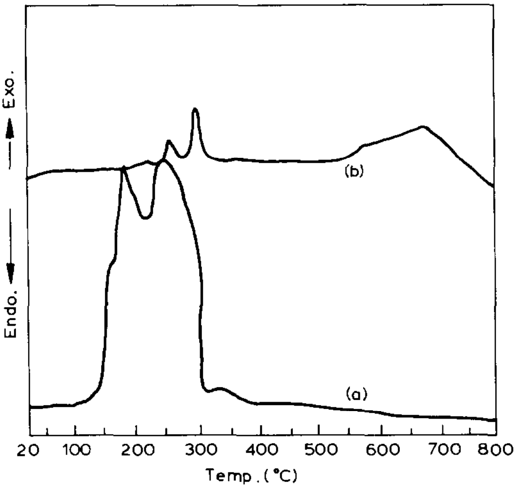


Fig. 2. The behavior of the DTA curves for solid metal acetate complexes with nicotinic hydrazides (M/L = 1 : 2) prepared in neutral media: (a) Cu^{2+}-**Ib** complex; (b) Cu^{2+}-**Ih** complex.

270°C corresponds to decomposition of the complex through rupture of the chelate bond and loss of the organic portion. The two weak exothermic peaks at 330 and 570°C are consistent with lattice rearrangement of the initial formed Cu_2O and its subsequent oxidation to CuO as a final product. This explanation was supported by quantitative thermogravimetric calculations as clearly deduced from Table 4, indicating the existence of cupric oxide as a final product. Thus, from Fig. 1, curve (d), it was concluded that chelates prepared in alkaline medium are less thermally stable than those prepared in neutral medium for the same M/L ratio (1 : 1).

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

The DTA of Cu acetate complex with nicotinic hydrazide (Fig. 2, curve a) shows a detectable internal lattice rearrangement at 115 and 160°C while the sharp strong exothermic peak at 180°C corresponds to the melting of the complex. The strong exothermic peak at 270°C can be ascribed to the decomposition of the complex through loss of the organic portion leaving behind Cu_2O which in turn is further oxidized to Cu_2O at 340°C indicating the existence of mixed valence oxides for copper, namely CuO and Cu_2O (partly). This is further supported by their quantitative thermogravimetric analysis results as given in Table 4.

For copper acetate chelate with *para*-bromobenzylidene nicotinic hydrazide, the DTA thermograph (Fig. 2, curve b) exhibits weak and strong exothermic peaks at 260 and 290°C corresponding to melting and decomposition of the complex, respectively, leaving behind Cu_2O which in turn is further oxidized to CuO (mostly, see Table 4) explaining the appearance of a broad exothermic peak at 660°C. The existence of these two oxides together may cause some internal changes in the crystalline lattice [10].

CONCLUSIONS

Generally, for all complexes under investigation, the final oxidation products after firing at 800°C have been mathematically related to each formula weight of the starting solid metal complexes. Data obtained were found to relate closely with the suggested formula (compositions given in Table 4). Accordingly, it is interesting to attain a general conclusion that the melting points and thermal stabilities of 1 : 2 (M/L) complexes prepared in neutral medium are lower than for those of 1 : 1 complexes and increase with substitution in the nicotinic hydrazide organic ligand. This is explained on the basis of the steric hindrance effect as caused by the location of the two organic ligand molecules attached within the same complex molecule, thus, making it unstable.

In metal acetate complexes the final decomposition exothermic peaks have a forward convex shape which can be used as a rapid and sensitive tool to test for the acetate complexes.

REFERENCES

1 M.H. Asker and M.M. Abou Sekkina, Bull. N.R.C. Egypt, 2 (1977) 22.
2 P. Feng and Q. Fernando, Anal. Chim. Acta, 24 (1961) 548.
3 T.G. Cardwell and R.J. Majee, Anal. Chim. Acta, 43 (1968) 321.
4 W.W. Wendlandt. Anal. Chem., 30 (1958) 58.
5 G. Struve, J. Prakt. Chem., 50 (1958) 295.
6 F.J. Welcker, in The Analytical Uses of Ethylene Diamine Tetraacetic Acid, Prentice Hall, New Jersey, Toronto, London, New York, 1961.
7 S.K. Magumdar and F.K. Paria, J. Indian Chem. Soc., 54 (1978) 998.
8 N. Lukkari, J. Sakari, S. Polonen and T. Maire, Farm. Aikak., 77 (1968) 264.
9 C.F. Bell and R. Rose, Inorg. Chem., 7 (1968) 325.
10 S.V.C. Rao, J. Indian Chem. Soc., 53 (1976) 49.