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THERMOCHEMICAL STUDY OF SOME TRANSITION METAL COMPLEXES OF ISONICOTINIC HYDRAZIDE DERIVATIVES

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ABSTRACT

The thermal decomposition of metal complexes of biacetylmonoxime isonicotinoylhydrazone (H_2BMINH) and 3-isonicotinamido-rhodanine (HINRd) with bivalent nickel, cobalt, copper, cadmium and zinc under an atmosphere of air has been investigated by thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA). Stoichiometric calculations from the obtained thermograms strongly confirm that the complexes $\mathrm{Co(HBMINH)Ac \cdot 4H_2O}$, $\mathrm{Co(INRd)OH \cdot H_2O}$, $\mathrm{Cd(INRd)OH \cdot 2H_2O}$ and $\mathrm{Ni(INRd)OH \cdot 2H_2O}$ decompose through two steps. On the other hand, $\mathrm{Ni(BMINH)C_2H_5OH \cdot 2H_2O}$, $\mathrm{Cu(H_2BMINH)Cl_2 \cdot C_2H_5OH}$ and $\mathrm{Zn(HINRd)(OH)_2 \cdot H_2O}$ complexes are fully decomposed in one step. These are indicative of the nature of the metal–ligand bonds in the above mentioned complexes. Finally, a stepwise thermal character is developed for the compounds under investigation.

INTRODUCTION

The majority of compounds, including complexes, suffer physical and chemical changes such as changes in weight and calorific values, when subjected to heat energy. In differential thermal analysis (DTA) and differential thermogravimetry (DTG), overlapping processes can be distinguished more easily than in the thermogravimetric (TG) method [1].

Very few thermogravimetric studies were found in the literature, even on related metal complexes [2]. Thus, the present study is aimed at evaluating the thermographical behaviour of some selected and representative metal complexes of both biacetylmonoxime isonicotinoylhydrazone (H_2BMINH) and 3-isonicotinamido-rhodanine (HINRd) with bivalent nickel, cobalt copper, cadmium and zinc, and, possibly, at understanding the mechanism of thermal decomposition of these complexes in the solid state.

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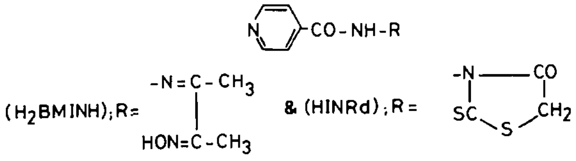
EXPERIMENTAL

The ligands (H_2BMINH), and (HINRd), and their metal complexes were prepared as reported in our previous work [3,4]. The ligands have the general structural formula (I)



(I)

APPARATUS

In order to monitor the thermal behaviour of the complexes, a Thermoanalyser GDTD 16 (Setaram, Lyon, France) capable of the graphical recording of the *T*, TG, DTG and DTA curves was used from room temperature (20 ° C) up to 1000 ° C in air.

RESULTS AND DISCUSSION

Elemental analysis, magnetic measurements, and IR and visible spectral measurements have been used to characterize the isolated solid complexes [3,4].

Thermal behaviour of H_2BMINH complex with copper chloride

During the heating of $Cu(H_2BMINH)Cl_2 \cdot C_2H_5OH$, the DTA curve undergoes a series of thermal changes associated with a weight loss in the TG and DTG curves. These curves show that the complex has great stability up to 250 ° C, at which point a weight loss starts to occur. The TG curve (Fig. 1) displays 11.31% weight loss at 250–270 ° C, which could be correlated with the elimination of an ethanol molecule. As the temperature is raised, the DTA curve shows two weak endothermic peaks at 330 and 350 ° C accompanied by 18.09% weight loss which corresponds to the loss of the chlorine atoms which are covalently bonded into the complex inner sphere [5]. Afterwards, the DTA curve exhibits a series of exothermic effects at 515, 600 and 650 ° C. These effects correlate with full decomposition of the complex: the rupture of the chelate bond and loss of the organic portion, leaving behind Cu_2O which is further oxidized to CuO at 790 ° C; this indicates the presence of mixed valence copper oxides, namely CuO and

TABLE 1

Thermal behaviour of H_2BMINH complexes with Cu(II), Co(II) and Ni(II)

Temp. (° C)	Sample weight (mg)		Chemical formula (established)	Mol. wt. (calculated)	Assignment
	Found	Calculated to fit the chemical formula			
20– 250	26.400	–	Cu(H_2BMINH)$Cl_2 \cdot C_2H_5OH$	400.740	Stable
250– 270	23.415	23.365	Cu(H_2BMINH)Cl_2	354.670	Loss of ethanol
270– 380	18.639	18.694	Cu(H_2BMINH)	283.764	Loss of chlorine
380–1000	5.103	5.240	CuO/Cu_2O (minor)	–	Decomposition to mixed valence oxides as end product
20– 140	39.040	–	Co(HBMINH)Ac$\cdot 4H_2O$	409.254	Stable
140– 230	32.229	32.165	Co(HBMINH)Ac	337.190	Loss of water of crystallization
230– 345	26.695	26.533	Co(HBMINH)	278.146	Loss of acetate
345– 500	17.117	17.079	Remaining portion (II)	179.036	Loss of 2-imino-1-biacetyl-monoxime fragment
500–1000	7.200	7.148	CoO/Co_2O_3 (minor)	–	Decomposition to mixed valence oxides as a final product
20– 140	30.380	–	Ni(BMINH)$C_2H_5OH \cdot 2H_2O$	359.000	Stable
140– 320	27.365	27.331	Ni(BMINH)C_2H_5OH	322.968	Loss of chemically combined water
360– 380	23.489	23.433	Ni(BMINH)	276.898	Loss of ethanol
380–1000	6.261	6.322	NiO	74.690	Decomposition to metal oxide as end product

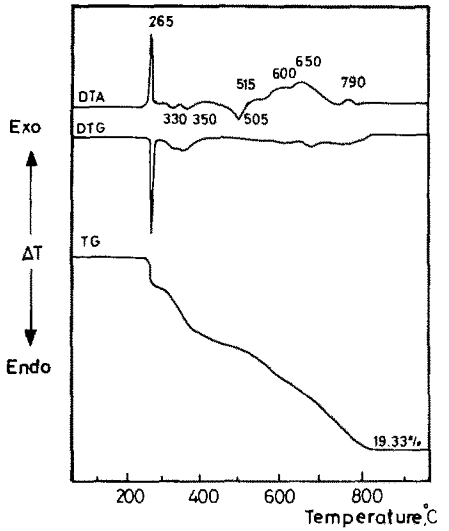


Fig. 1. The thermal curves of H_2BMINH complex with Cu(II).

Cu_2O (minor). This is further supported by the results of quantitative thermogravimetric analysis, given in Table 1. The existence of these two oxides together may cause some internal changes in the crystalline lattice [6]. Above 800 °C, the remaining residue, comprising 19.33% of the initial mass of the complex, is found to be stable up to 1000 °C. The experimental value of copper : ethanol : chlorine : reagent ratio, 0.99 : 1.0 : 2.03 : 1.02, is compatible with the theoretical value 1 : 1 : 2 : 1. The quantitative calculations from the obtained thermograms (Fig. 1) strongly support the following decomposition scheme

$$\mathrm{Cu(H_2BMINH)Cl_2 \cdot C_2H_5OH \xrightarrow{250\text{–}270\,^\circ C} Cu(H_2BMINH)Cl_2 \xrightarrow{270\text{–}380\,^\circ C}}$$

$$\mathrm{Cu(H_2BMINH) \xrightarrow{380\text{–}800\,^\circ C} CuO/Cu_2O(minor) + (CO/CO_2;\ N_2/NO;\ NO_2)}$$

Thermal behaviour of H_2BMINH complex with cobaltous acetate

For Co(HBMINH)Ac · $4H_2O$, the thermal curves show that the complex is thermally stable up to 140 °C, above which point thermal decomposition begins. In the temperature range 140–230 °C, the TG curve (Fig. 2) displays 17.45% weight loss which could be correlated with the elimination of four water molecules in one step. This may suggest that these are identical water of crystallization molecules [3]. The strong exotherm at 320 °C and its connecting shoulder at 345 °C in the forward convex shape of the DTA curve seems to be correlated with loss of the acetate portion (14.18% weight loss) [2]. Next, over the temperature range 345–500 °C, a series of thermal effects caused by partial degradation and pyrolysis of the complex occurs. The sudden weight loss (24.53%) in the TG curve produced by these effects

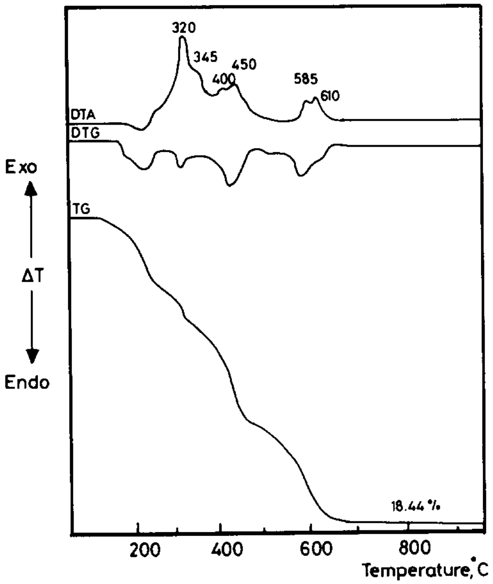
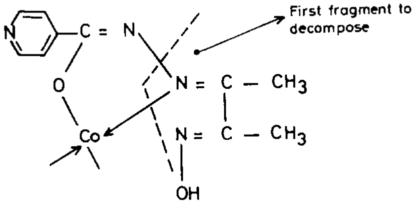


Fig. 2. The thermal curves of H_2BMINH complex with Co(II).

is most probably correlated with the elimination of the 2-imino-1-biacetylmonoxime fragment. Above 500 °C, a double exothermic effect at 585 and 610 °C, attributed to the decomposition of the remaining portion of H_2BMINH, is observed. In this respect, the final product comprises mixed valence oxides CoO/Co_2O_3 (minor) as shown quantitatively in Table 1. In our opinion, the two steps of thermal decomposition of Co(HBMINH)Ac · $4H_2O$ (II) including the relatively low temperature one at which the 2-imino-1-biacetylmonoxime fragment begins to decompose, are attributed to the destruction of the weak coordinating bond of the CN group with respect to the relatively strong covalent bond of the enolized carbonyl oxygen [3].

The experimental cobalt : water : acetate : reagent ratio 1 : 3.98 : 0.99 : 1.01, suggests the theoretical ratio 1 : 4 : 1 : 1.



(II)

Thermal behaviour of H_2BMINH complex with nickel acetate

For Ni(BMINH)C_2H_5OH · $2H_2O$, the TG results (Fig. 3) clearly indicate that the complex has great thermal stability up to 140 °C, above which point

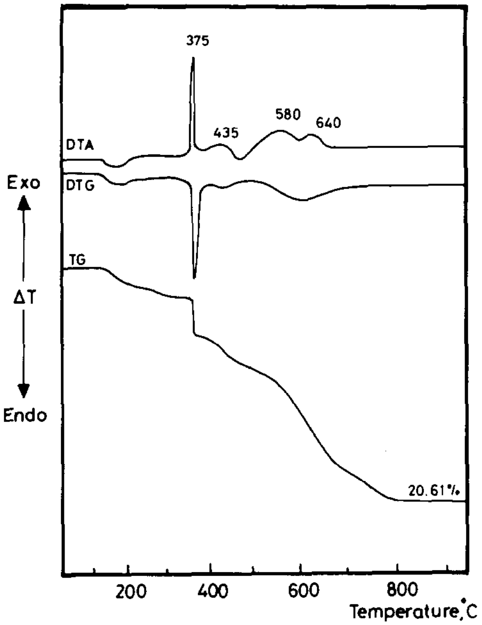


Fig. 3. The thermal curves of H_2BMINH complex with Ni(II).

elimination of water begins.The first decomposition step (9.92% weight loss) is correlated with the elimination of two molecules of water, ending at 320 ° C. This relatively high temperature may confirm that these water molecules are coordinated to the central nickel ion and are not water of crystallization. In the temperature range 360–380 ° C, the sudden 12.76% weight loss is most probably correlated with elimination of the coordinating ethanol molecule. With the increase of the temperature, the DTA curve displays a series of exothermic effects located at 435, 580 and 640 ° C. This step is largely due to the complete decomposition of the complex through loss of the organic portion and formation of a stable NiO as a final fired product, as shown in the thermogravimetric evaluation (Table 1).

The experimental value of nickel : water : ethanol : reagent ratio, 1 : 1.99 : 1 : 1.01, is compatible with the theoretical value 1 : 2 : 1 : 1.

Thermal behaviour of HINRd complexes with cadmium(II), nickel(II), cobalt(II) and zinc(II)

The probable constitutional formulae for the various metal complexes with HINRd are given in Table 2. From these results, it was deduced that HINRd reacts with the metal ions in enol form, with the exception of Zn(II). The thermal curves (Figs. 4–7) show that these complexes are thermally stable up to 140 ° C, above which point weight loss begins.

TABLE 2

Thermal behaviour of HINRd complexes with Cd(II), Ni(II), Co(II) and Zn(II)

Temp. (° C)	Sample weight (mg)		Chemical formula (established)	Mol. wt. (calculated)	Assignment
	Found	Calculated to fit the chemical formula			
20–140	20.9	–	Cd(INRd)OH·$2H_2O$	417.729	Stable
140–235	19.036	19.097	Cd(INRd)OH	381.697	Loss of mainly chemically combined water
235–360	13.029	13.038	Remaining portion (III)	260.583	Loss of the isonicotinylamide fragment
360–800	6.400	6.427	CdO	128.41	Decomposition to metal oxide as end product
20–140	20.8	–	Ni(INRd)OH·$2H_2O$	364.009	Stable
140–220	18.710	18.741	Ni(INRd)OH	327.977	Loss of mainly chemically combined water
220–390	11.975	11.820	Remaining portion (III)	206.863	Dissociation of the isonicotinylamide fragment
390–800	4.311	4.268	NiO	74.69	Decomposition to metal oxide as end product
20–140	21.2	–	Co(INRd)OH·H_2O	346.233	Stable
140–205	20.078	20.087	Co(INRd)OH	328.217	Loss of water hydrogen bonded to pyridine nucleus
205–375	12.676	12.675	Remaining portion (III)	207.103	Dissociation of the isonicotinylamide fragment
375–800	4.600	4.586	CoO/Co_2O_3 (minor)		Decomposition to mixed valence oxides as end product
20–140	24.6	–	Zn(HINRd)$(OH)_2$·H_2O	370.691	Stable
140–205	23.369	23.404	Zn(HINRd)$(OH)_2$	352.675	Loss of water hydrogen-bonded to pyridine nucleus
205–800	5.4	5.401	ZnO	81.38	Full decomposition of the complex leaving metal oxide as end product

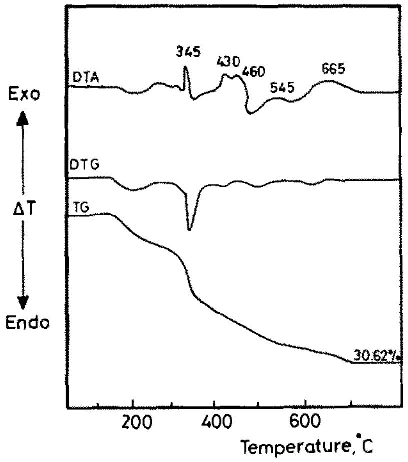
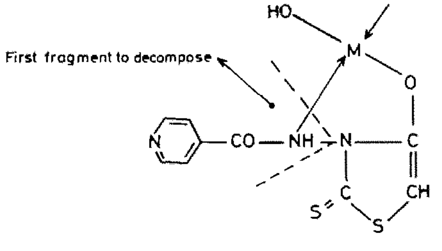


Fig. 4. The thermal curves of HINRd complex with Cd(II).

For the HINRd complex with cadmium acetate (Fig. 4), the phenomena occurring are: the elimination of two coordinating water molecules [4] (8.92% weight loss) in the temperature range 140–235 ° C; the second weight loss (28.74%) at 345 ° C, an exothermic effect, most probably correlated with the partial decomposition of the complex and elimination of isonicotinylamide fragment (**III**); and next, over the temperature range 370–700 ° C, a series of exothermic effects at 430, 460, 545 and 665 ° C, largely due to the complete decomposition of the remaining organic portion leaving CdO as the final product, comprising 30.62% (Table 2).

The experimental cadmium : water : isonicotinylamide : rhodanine nucleus ratio, 1 : 2.06 : 1 : 1, is compatible with the theoretical value 1 : 2 : 1 : 1.

For the HINRd complex with nickel acetate, the DTA curve (Fig. 5) comprises a broad endothermic peak at 170 ° C corresponding to elimination of two coordinating water molecules (10.05% weight loss). The sharp exothermic peak at 355 ° C correlates with the elimination of an iso-



M = Cd(II), Ni(II) and Co(II)

(III)

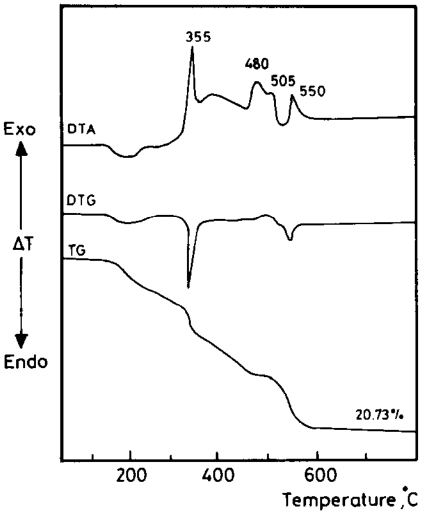


Fig. 5. The thermal curves of HINRd complex with Ni(II).

nicotinylamide fragment and displays 32.38% weight loss in the TG curve(III). On increase of the temperature from 390 to 570 ° C, a series of exothermic effects at 480 and 505 ° C, accompanied by weight loss, can be seen in the DTA curve. This weight loss is correlated with full decomposition of the complex and formation of a final stable residue of NiO. This remaining residue represents 20.73% of the initial weight of the complex (Table 2).

The experimental nickel : coordinated water : isonicotinylamide : rhodanine nucleus ratio, 1 : 2 : 0.97 : 1.0, is compatible with the theoretical value 1 : 2 : 1 : 1.

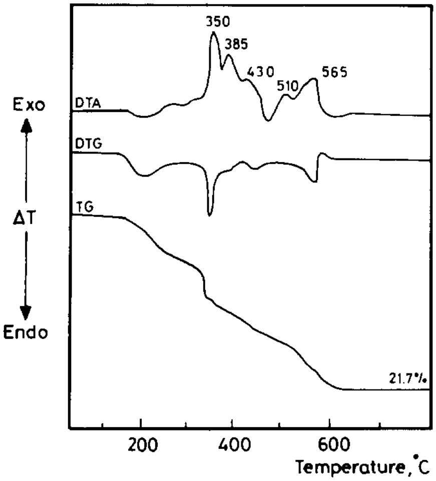


Fig. 6. The thermal curves of HINRd complex with Co(II).

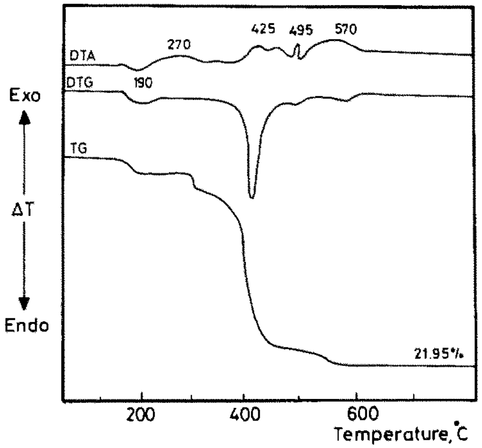


Fig. 7. The thermal curves of HINRd complex with Zn(II).

For the HINRd complex with cobaltous acetate (Fig. 6), the phenomena occurring are: the elimination of a water molecule, ending at 205 ° C, which relatively high dehydration temperature supports the opinion that this water molecule is most probably hydrogen bonded to the nitrogen atom of the pyridine nucleus and is not crystallization or coordination water; the second weight loss step (34.92%) at 350 ° C, an exothermic effect in the DTA curve, most probably correlated with the elimination of isonicotinylamide fragment (III); and the exothermic effects at 385, 430, 510 and 565 ° C, correlated with the full decomposition of the complex to the final product (21.7%) comprising mixed valence oxides (CoO/Co_2O_3) shown quantitatively in Table 2. The experimental value found for the cobalt : water : isonicotinylamide : rhodanine nucleus ratio, 1 : 1.02 : 1 : 1, is compatible with the theoretical combination ratio of 1 : 1 : 1 : 1.

The thermal behaviour of the HINRd complex with zinc acetate (Fig. 7) is somewhat different from those with Cd(II), Ni(II) and Co(II).

For $Zn(HINRd)(OH)_2 \cdot H_2O$, the DTA curve displays an endothermic peak at 190 ° C correlated with the elimination of a water molecule, hydrogen bonded to the nitrogen atom of the pyridine nucleus (5% weight loss). The pronounced thermal process which occurs between 365 and 590 ° C in the DTA curve suggests that some components are eliminated from the complex at a high rate, leaving behind ZnO as the final product representing 21.95% of the initial mass of the complex.

CONCLUSIONS

Generally, for all the complexes under investigation, the final products have been mathematically related to each formula weight of the starting metal complexes. Data obtained were found to be in good agreement with the suggested formulae (compositions given in Tables 1 and 2).

Accordingly, it is interesting to conclude that: (i) the two steps of thermal decomposition (**II** and **III**) including the relatively low temperature at which the first fragment begins to decompose, are attributed to the weak coordinating bonds of the first fragment with respect to the relatively strong covalent bonds of the remaining portion; this observation is not considered for $Cu(H_2BMINH)Cl_2 \cdot C_2H_5OH$, $Zn(HINRd)(OH)_2 \cdot H_2O$ and $Ni(BMINH) C_2H_5OH \cdot 2H_2O$ owing to their similar metal ligand coordinating or covalent bonds; (ii) the DTA curve of $Co(HBMINH)Ac \cdot 4H_2O$ complex displays an exothermic peak with a forward convex shape the presence of which could be usefully applied as a rapid and sensitive tool for the detection of acetate-containing complexes.

REFERENCES

1 M.M. Abou Sekkina and S.M. El-Helbaway, Thermochim. Acta, 81 (1984) 223.
2 M.M. Abou Sekkina and M.G. Abou El Azm, Thermochim. Acta, 77 (1984) 211.
3 K.M. Ibrahim, M.M. Bekheit, G.M. Abu El-Reash and M.M. Mostafa, Polyhedron, 5 (1986) 1635.
4 K.M. Ibrahim, M.M. Bekheit and G.M. Abu El-Reash, to be published.
5 T.H. Rakha, A.A. El Asmy, M.M. Mostafa and A. El Kourashy, Transition Met. Chem., 12 (1987) 125.
6 S.V.C. Rao, J. Indian Chem. Soc., 53 (1976) 49.