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THERMAL PROPERTIES OF HYDRAZIDO-CARBONATES OF COBALT AND NICKEL IN AN INERT ATMOSPHERE

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ABSTRACT

The thermal properties of different types of hydrazido-carbonates of cobalt and nickel in an inert atmosphere are presented. Their thermal stability and behaviour are discussed with regard to their composition and structure.

INTRODUCTION

Since the isolation of hydrazido-carbonic acid (N_2H_3COOH) [1], numerous salts and complexes of this acid with elements of the periodic table have been isolated and characterized [2–11]. Various types of compounds are known (Table 1), and in some cases their structures have been determined.

In the crystals of hydrazido-carbonates, in addition to the central cation and hydrazido-carbonato groups, water, hydrazine, hydrazinium (1 +) and a potassium cation can also be found. In these compounds the hydrazido-carbonato group acts in most cases as a bidentate or tridentate ligand [7,12]. With the central cation it forms a penta-atomic ring through bonds M–O(1) and M–N(4) (Fig. 1).

TABLE 1

Types of hydrazido-carbonate

A	$M(n)(N_2H_3COO)_n$	$n = 1, 2, 3$
B	$M(n)(N_2H_3COO)_n \cdot mH_2O$	$n = 1, 2, 3;\ m = 0.5, 1, 2, 3$
C	$M(n)(N_2H_3COO)_n \cdot H_2O \cdot N_2H_4$	$n = 2$
D	$M(n)(N_2H_3COO)_n \cdot mN_2H_4$	$n = 1, 2, 3;\ m = 1, 2$
E	$K[M(n)(N_2H_3COO)_{n+1}]$	$n = 2$
F	$N_2H_5[M(n)(N_2H_3COO)_{n+1}] \cdot mH_2O$	$n = 2, 3;\ m = 1, 3$

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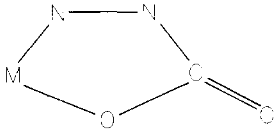

Fig. 1. Hydrazido-carbonato ring.

By forming bond M″–O(5) with the neighbouring cations, a tridentate hydrazido-carbonato ligand is formed. The number of hydrazido-carbonato groups can be equal to the charge of the central cation or can exceed it by one group. In this case the anionic complex of these ligands with a metal is obtained. In such compounds the crystals also contain hydrazinium (1 +) or potassium cations and in the former case also water. With a divalent cation three hydrazido-carbonato groups form an octahedron around it, so that all oxygen atoms lie in the same plane. Hydrazinium (1 +) *cis*-tris-hydrazido-carbonato metallates are known for iron, cobalt, nickel and zinc [7]. In the case of scandium four hydrazido-carbonato groups form a distorted quadratic antiprism around Sc^{3+} with a coordination number of eight [13]. With hydrazido-carbonates of bivalent metals, an octahedron is the usual form of coordinating polyhedron. In addition to bidentate or tridentate hydrazido-carbonato groups, water and hydrazinium (1 +) ions are also present in the crystals.

All these different types of compounds are so far known only for nickel(II) and partially for cobalt(II), where the compound C has not been isolated as yet. All these compounds exhibit thermal properties which are influenced by their composition, the nature of the central cation and the type of compound. In this paper, the thermal properties of cobalt(II) hydrazido-carbonates of types A, B, D, E and F and nickel(II) hydrazido-carbonates of types B, C and F are described and discussed.

Hydrazine has a significant impact on the thermal properties of these compounds due to its endothermic nature $\Delta H_f^{\ominus} = 50$ kJ mol^{-1}) [14]. It is thermally much less stable than ammonia and decomposes on heating in the absence of air or in an inert atmosphere into nitrogen and ammonia [15]

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \qquad \Delta H_0^{298} = -156.744\ \text{kJ mol}^{-1} \tag{1}$$

This reaction is catalysed by the presence of metals or their ions. Under special conditions it can proceed so as to produce, instead of ammonia, hydrogen and additional amounts of nitrogen

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad \Delta H_0^{298} = -95.186\ \text{kJ mol}^{-1} \tag{2}$$

Depending on the conditions and environment of the hydrazine, different combinations of both reactions are possible giving a general reaction scheme

$$3N_2H_4 \rightarrow (1 + 2x)N_2 + 4(1 - x)NH_3 + 6xH_2 \tag{3}$$

Hydrazine is present in these compounds either as a molecule which coordinates to the central cation as a monodentate or bidentate ligand, or as part of the hydrazido-carbonato anion.

Hydrazido-carbonic acid is unstable when heated. It starts to decompose first into its hydrazinium (1 +) salt and carbon dioxide [1]

$$2N_2H_3COOH \rightarrow N_2H_3COON_2H_5 + CO_2 \tag{4}$$

which on further heating decomposes into hydrazine and carbon dioxide.

EXPERIMENTAL

Samples of the above-mentioned compounds were prepared by reaction of aqueous solutions of hydrazido-carbonic acid with nickel or cobalt dichloride hexahydrate, or by further treatment of the prepared hydrazido-carbonates. A solution of hydrazido-carbonic acid was prepared by saturating an aqueous solution of hydrazine with carbon dioxide by bubbling this gas through it for 10 h. In the solution an equilibrium between this acid and its hydrazinium salt ($N_2H_3COON_2H_5$) is established.

$N_2H_5[Co(N_2H_3COO)_3] \cdot H_2O$ and the analogous nickel compound were prepared by dissolving cobalt or nickel dichloride hexahydrate in 25% hydrazine solution previously saturated with carbon dioxide [8,9].

$Co(N_2H_3COO)_2 \cdot 2H_2O$ and $Ni(N_2H_3COO)_2 \cdot 2H_2O$ were prepared by hydrolysis of finely ground crystals of hydrazinium (1 +) tris-hydrazido-carbonato cobaltate(II) or nickelate(II) hydrate at room temperature [16,17]. $Co(N_2H_3COO)_2$ was prepared from the same starting material as the former compound but the hydrolysis was carried out at 90–100 °C [16].

$Ni(N_2H_3COO)_2 \cdot H_2O \cdot N_2H_4$ was prepared as described in the literature [18].

$Co(N_2H_3COO)_2 \cdot N_2H_4$ was isolated by solvolysis of finely ground crystals of hydrazinium (1 +) tris-hydrazido-carbonato cobaltate(II) hydrate in a 10% solution of hydrazine [16]. $Co(N_2H_3COO)_2 \cdot 2N_2H_4$ was obtained by a similar procedure at room temperature and with higher concentrations of hydrazine (64%) [16]. This type of preparation of different hydrazido-carbonates by hydrolysis or solvolysis (in hydrazine solutions) has advantages over other methods since contamination of the product with anions of the starting compound is thus avoided.

$K[Co(N_2H_3COO)_3]$ was prepared according to published data [19].

Thermoanalytical studies (TG, DTG and DTA) were carried out on a Mettler TA 1 system. Sample weights were 100 mg. A heating rate of 4 °C min^{-1} and a dynamic atmosphere of argon with a flow rate of 5 l h^{-1} were used.

The chemical compositions of the starting materials and intermediates or end products were determined as follows: hydrazine, by potentiometric titration with a solution of potassium iodate in acidic media [20]; carbon dioxide, by evolution with hydrochloric acid and gravimetric determination

TABLE 2

Analytical data for cobalt and nickel hydrazido-carbonates

	Metal		N_2H_4		CO_2		H_2O [a]		K	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Co(N_2H_3COO)_2$	28.19	28.2	30.66	30.3	42.11	42.4	–	–	–	–
$Co(N_2H_3COO)_2 \cdot 2H_2O$	24.25	24.0	26.37	26.2	36.22	36.1	14.8	13.7	–	–
$Co(N_2H_3COO)_2 \cdot N_2H_4$	24.45	24.4	39.88	39.7	36.51	36.7	–	–	–	–
$Co(N_2H_3COO)_2 \cdot 2N_2H_4$	21.26	21.5	46.25	47.1	31.76	32.1	–	–	–	–
$K[Co(N_2H_3COO)_3]$	18.24	18.3	29.75	29.7	40.85	40.5	–	–	12.10	11.5
$N_2H_5[Co(N_2H_3COO)_3] \cdot H_2O$	17.58	17.5	38.25	37.6	39.40	39.9	5.3	5.0	–	–
$Ni(N_2H_3COO)_2 \cdot 2H_2O$	24.18	24.1	26.39	26.0	36.25	39.2	7.4	11.5	–	–
$Ni(N_2H_3COO)_2 \cdot H_2O \cdot N_2H_4$	22.68	22.9	37.14	37.0	34.00	34.4	6.9	6.5	–	–
$N_2H_5[Ni(N_2H_3COO)_3] \cdot H_2O$	17.53	17.7	38.27	38.5	39.42	39.9	5.3	4.5	–	–

[a] Calculated from the difference from 100%.

of the gas absorbed in lime; the amount of metal, by volumetric titration with EDTA [21].

The compositions of the starting materials prepared for the thermoanalytical studies are given in Table 2.

RESULTS AND DISCUSSION

The thermal properties of the investigated metal hydrazido-carbonates in an inert atmosphere reflect their composition, the properties of their constituents and the type of compound [22]. The thermal stabilities of the hydrazido-carbonates in an inert atmosphere are illustrated by the initial temperatures of decomposition as listed in Table 3.

Regarding their thermal stability in an inert argon atmosphere, cobalt hydrazido-carbonates can be divided into three groups. The first consists of the least thermally stable cobalt compounds, i.e. $Co(N_2H_3COO)_2 \cdot 2H_2O$ (Fig. 2) followed by $Co(N_2H_3COO)_2 \cdot 2N_2H_4$ and $N_2H_5[Co(N_2H_3COO)_3] \cdot H_2O$ (Fig. 3) with initial temperatures of thermal decomposition of 100, 110 and 115°C, respectively. In the second group is $Co(N_2H_3COO)_2 \cdot N_2H_4$ (Fig. 2) with an initial temperature of 155°C and in the third $K[Co(N_2H_3COO)_3]$ (Fig. 3) and $Co(N_2H_3COO)_2$ (Fig. 2) which start to decompose in argon at 230 and 240°C.

The thermal stabilities of these compounds can be explained by their composition and structure. This provides an insight and enables a rough prediction to be made of the composition and arrangement of the various parts of these molecules. Such complex crystals will start to decompose either by loss of constituent parts (dehydration), or by actual decomposition of their main constituents.

TABLE 3

Thermoanalytical data for hydrazido-carbonates

Compound	T_1	Reaction	T_2	DTA
$Co(N_2H_3COO)_2$	240	Decomposition	350	Endo
$Co(N_2H_3COO)_2 \cdot 2H_2O$	100	Dehydration	205	Endo
$Ni(N_2H_3COO)_2 \cdot 2H_2O$	151	Dehydration [a]	221	–
$Ni(N_2H_3COO)_2 \cdot H_2O \cdot N_2H_4$	105	Dehydration [a]	242	Endo
$Co(N_2H_3COO)_2 \cdot N_2H_4$	155	Decomposition	220	Exo
$Co(N_2H_3COO)_2 \cdot 2N_2H_4$	110	Decomposition	185	Exo
$K[Co(N_2H_3COO)_3]$	230	Decomposition	310	Exo
$N_2H_5[Co(N_2H_3COO)_3] \cdot H_2O$	115	Reaction (7)	192	Endo
$N_2H_5[Ni(N_2H_3COO)_3] \cdot H_2O$	130	Reaction (7) [a]	205	Endo

T_1, initial temperature; T_2, temperature of the end of the first decomposition step. [a] Decomposition proceeds; intermediate could not be obtained.

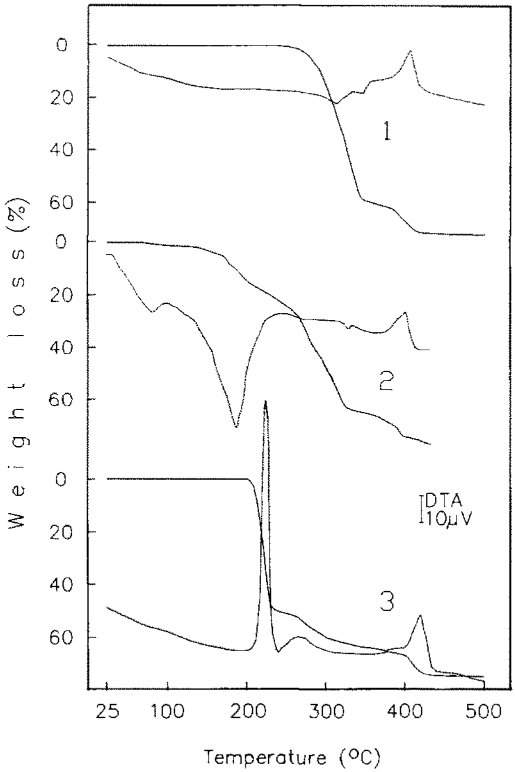

Fig. 2. TG and DTA curves of $Co(N_2H_3COO)_2$ (1), $Co(N_2H_3COO)_2 \cdot 2H_2O$ (2) and $Co(N_2H_3COO)_2 \cdot N_2H_4$ (3).

The first case can be observed in the dehydration of hydrazido-carbonate hydrates. Whether the water molecule can be released without causing the decomposition of the entire molecule also depends on the bonding in the crystal and the possibility of the rearrangement of other constituents to give a stable anhydrous compound.

The dihydrate $Co(N_2H_3COO)_2 \cdot 2H_2O$ is much less thermally stable than the anhydrous compound $Co(N_2H_3COO)_2$, the difference being 140 °C. The structure of the dihydrate has been determined [23], and from this it can be seen that water molecules are a part of the coordination polyhedron. This may be the reason why pure anhydrous cobalt hydrazido-carbonate cannot be prepared in this way since the dehydration is accompanied by the disruption of the penta-atomic rings of the hydrazido-carbonato groups. The mass loss at 205 °C confirms this: calculated for $Co(N_2H_3COO)_2$: 14.70%; found: 16.2%.

Similarly, hydrazine enters the coordination polyhedron around cobalt in both the hydrazinates $Co(N_2H_3COO)_2 \cdot 2N_2H_4$ and $Co(N_2H_3COO)_2 \cdot N_2H_4$. The first compound is isostructural with the same type of zinc

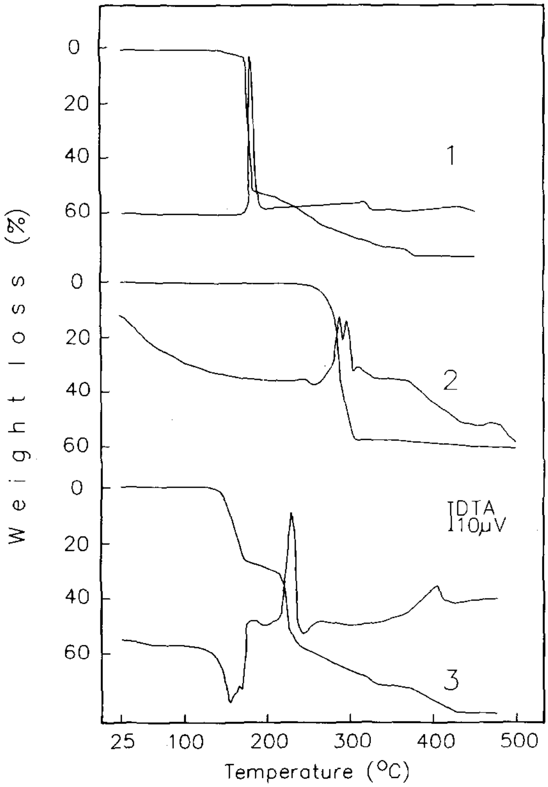

Fig. 3. TG and DTA curves of $Co(N_2H_3COO)_2 \cdot 2N_2H_4$ (1), $KCo(N_2H_3COO)_3$ (2) and $N_2H_5Co(N_2H_3COO)_3 \cdot H_2O$ (3).

compound [24], which consists of single molecules held together by weak hydrogen bonds. Coordination around the central cation is octahedral; the six corners are occupied by two penta-atomic rings of hydrazido-carbonato ions and two nitrogen atoms from two hydrazine molecules. The molecule of hydrazine is strongly bound and cannot be removed by heating of the sample. When a high enough temperature is achieved, hydrazine starts to decompose according to the reactions of disproportionation (1) or (3). This step is accompanied by a sharp exothermic DTA peak.

Although the crystal structure of $Co(N_2H_3COO)_2 \cdot N_2H_4$ is not known, it could be similar to the dihydrazinate, with hydrazine acting as a bidentate ligand which shifts the initial temperature to 155 °C.

$K[Co(N_2H_3COO)_3]$ and $Co(N_2H_3COO)_2$ are appreciably more stable than the cobalt compounds mentioned so far, with initial decomposition temperatures of 230 and 240 °C. The reason for this enhanced thermal stability is probably the fact that these compounds, with the exception of the central cation and potassium ion, contain only a hydrazido-carbonato group. It is known that the first step (reaction (5)) of the reaction between carbon dioxide and hydrazine which leads to formation of hydrazido-carbonic acid is exothermic [1]

$$2N_2H_4 + CO_2 \rightarrow N_2H_3COON_2H_5 \tag{5}$$

$$N_2H_3COON_2H_5 + CO_2 \rightarrow 2N_2H_3COOH \tag{6}$$

Although heats of reaction for these two processes have not yet been determined, hydrazine is probably sufficiently "stabilized" by this reaction so that the hydrazido-carbonato group is thermally much more stable than hydrazine.

In the case of $N_2H_5[Co(N_2H_3COO)_3] \cdot H_2O$, the structure consists of octahedra of hydrazido-carbonato groups around the central atom with hydrazinium (1 +) ions and water present, held together by weak hydrogen bonds [25]. This compound is therefore thermally less stable, with an initial decomposition temperature of 115 ° C. Thermal decomposition with increasing temperature proceeds through a definite intermediate step

$$N_2H_5[Co(N_2H_3COO)_3] \cdot H_2O \rightarrow Co(N_2H_3COO)_2 \cdot N_2H_4 + N_2H_4 + CO_2 + H_2O \tag{7}$$

This is confirmed by comparing the calculated and experimental weight losses (calculated 28.07%; found, 27.9%) and by chemical analysis of the residue obtained at 192 ° C (calculated: 39.88% N_2H_4; 24.45% Co; 36.51% CO_2; found: 39.6% N_2H_4; 24.5% Co; 36.7% CO_2).

The end product is cobalt in the form of a fine reactive powder, except in the case of $K[Co(N_2H_3COO)_3]$ when a mixture of cobalt and potassium carbonate in the molar ratio $Co : K_2CO_3 = 2 : 1$ is obtained. This was confirmed by comparing the calculated and obtained weight losses (calculated, 60.32%; found; 60.7%) and by chemical analysis of the end product obtained at 500 ° C (calculated: 46.03% Co; 34.37% CO_2; found: 45.9% Co; 34.0% CO_2).

Nickel hydrazido-carbonates show similar thermal properties to the cobalt compounds (Fig. 4). The least stable is $Ni(N_2H_3COO)_2 \cdot H_2O \cdot N_2H_4$ which starts to decompose at 105 ° C (comparable with the cobalt compound $Co(N_2H_3COO)_2 \cdot 2N_2H_4$ (110 ° C)). The other two nickel compounds exhibit thermal properties similar to their cobalt analogues, the main difference being the initial temperatures. In the case of nickel hydrazido-carbonate dihydrate, the initial temperature is shifted from 100 ° C to the higher temperature of 151 ° C. The reason for this probably lies in the fact that these two compounds have different structures [26].

$N_2H_5[Ni(N_2H_3COO)_3] \cdot H_2O$ exhibits similar thermal properties to its cobalt analogue, decomposing through the intermediate $Ni(N_2H_3COO)_2 \cdot N_2H_4$. A pure intermediate of this kind could not be isolated under the actual experimental conditions since before this step was complete, further decomposition of the sample occurred.

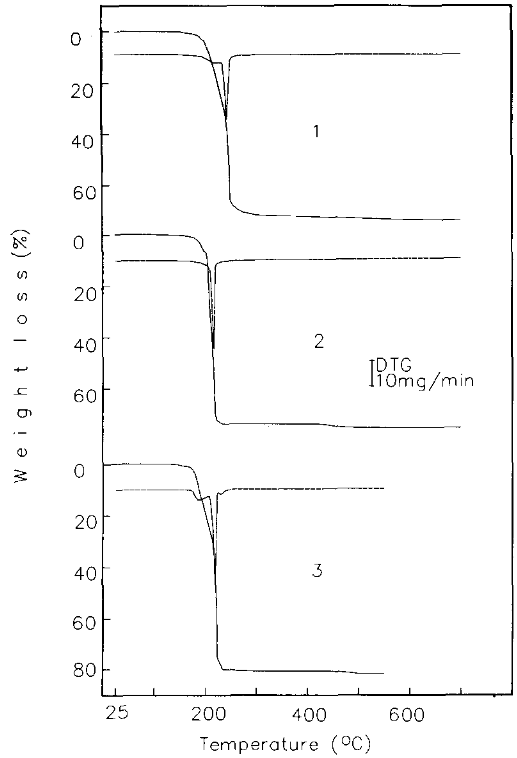

Fig. 4. TG and DTG curves of $Ni(N_2H_3COO)_2 \cdot 2H_2O$ (1), $Ni(N_2H_3COO)_2 \cdot N_2H_4 \cdot H_2O$ (2) and $N_2H_5Ni(N_2H_3COO)_3 \cdot H_2O$ (3).

The end product in all these thermoanalytical experiments is elemental nickel in the form of a fine reactive powder.

It is known that hydrazine and its derivatives are very sensitive to the catalytic influences of metals [15]. From the results it can be concluded that nickel catalyses more strongly the decomposition of the hydrazine or hydrazido-carbonic group.

The thermal decomposition is complete before or at 520 °C in all cases giving metal powders of cobalt or nickel as end products, which are very reactive and sensitive to oxidation by impurities in the argon. This is probably the reason why Patil et al. [27] could not obtain metallic end products when carrying out thermoanalytical experiments on some hydrazido-carbonates in nitrogen.

Whether the decomposition of the intermediates to metals is due to their composition and properties, or to the reducing atmosphere of ammonia and hydrogen which are formed by the decomposition of the hydrazine or the hydrazido group was determined by carrying out the experiments in vacuo. The samples, heated in an evacuated vessel, also gave very fine, pyrophoric metal powders as end products.

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