Journal of Thermal Analysis, Vol. 36 (1990) 847-853

THERMAL DECOMPOSITION OF Co(II), Ni(II), Cu(II) AND Zn(II) HIPPURATES

W. Brzyska and *M. Hakim*

DEPARTMENT OF INORGANIC AND GENERAL CHEMISTRY, INSTITUTE OF CHEMISTRY, MARIE CURIE SKLODOWSKA UNIVERSITY, 20-031 LUBLIN, POLAND

(Received February 5, 1988; in revised form June 5, 1989))

The hippurates of Co(II), Ni(II), Cu(II) and Zn(II) were isolated from the solution, their quantitative composition and the way of coordination of metal - ligand were determined and the conditions and products of thermal decomposition during heating in air atmosphere up to 1273 K were studied. The complexes of Ni(II), Cu(II) and Zn(II) heated lose some water molecules and then decompose to MO. The hippurate of Co(II) heated loses some water molecules and then docomposes to CoO with intermediate formation Co_3O_4.

The salts of hippuric acid are little known. Hippurates of NH_4^+, Na [1], Mg, Ca, Sr, Ba, Cu(II), Ag(I), Zn(II), Pb(II), Co(II) and Ni(II) were prepared as hydrated salts [2]. The hippurates of Zn(II), Co(II) and Ni(II) were prepared as pentahydrates and that of Cu(II) as trihydrate. The hippurate of Na was isolated also as anhydrous one [2]. The complexes of Zn(II) and Ni(II) with hippuric acid were studied in aqueous and non-aqueous media [3]. Polarographic behavior of Zn(II) and Ni(II) in presence of hippuric acid was investigated [3] and the stability constants of forming complexes species were evaluated.

As a continuation of our work on the thermal decomposition of aminocarboxylates of transition [4, 5, 6] and intratransition elements [5], we now report on the thermal decomposition of Co(II), Ni(II), Cu(II) and Zn(II) hippurates during heating in air atmosphere.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Table 1 Analytical data and solubilities in water of Co(II), Ni(II), Cu(II), Zn(II) hippurates

Complex	% Metal		% Carbon		% Hydrogen		% Nitrogen		Solubil.in water
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	10^{-3}mol.dm^{-3}
$CoL_2..9H_2O$	10.20	10.20	18.27	37.74	5.66	5.93	4.76	4.86	7.55
$NiL_2.18H_2O$	8.85	7.94	29.39	29.20	6.76	7.08	3.78	3.70	5.15
$CuL_2.6H_2O$	11.98	12.03	41.95	40.90	3.57	3.80	5.80	5.30	1.90
$ZnL_2.6H_2O$	12.17	12.30	40.80	40.80	5.07	5.30	4.84	5.20	5.58

Table 2 Thermal data of dehydration of Co(II), Ni(II), Cu(II) and Zn(II) hippurates

Complex	Temp.range of dyhydration K	Peak temp. of DTG K	Endothermic peak K	Loss of weight %		n,	E^x,
				Found	Calcd	H_2O	kJ.mol^{-1}
$CoL_2.9H_2O$	343-433	393	398	16.0	15.6	5	40.6
$NiL_2.18H_2O$	363-463	413	418	14.0	14.6	6	35.4
$CuL_2.6H_2O$	343-413	388	393	14.0	13.6	4	25.1
$ZnL_2.6H_2O$	333-413	363	360	10.0	10.2	3	51.7

E - Activation energy of dehydration reaction

Table 3 Data of thermal decomposition of Co(II), Ni(II), Cu(II) and Zn(II) hippurates

Com-plexes	Temp. range of decomposition K	Loss of weight, %		Prod-uct	Temp. range of decomp. K	Peak temperature of DTG K	Loss of weight, %		Endotherm. peaks, K	Exotherm peaks, K	T_k
		Found	Calcd.				Found	Calcd.			
$CoL_2.4H_2O$	513-1018	86.0	85.4	Co_3O_4	1018-1173	543, 663, 1173	87.0	87.0	553, 1173	703	1173
$NiL_2.12H_2O$	493-1073			-		523, 643	90.0	89.9	-	533, 733	1073
$CuL_2.2H_2O$	483-973			-		513, 803	85.0	84.9	503, 723	523, 783	973
$ZnL_2.3H_2O$	543-923			-		573, 713	84.8	84.6	503, 813	773	923

Experimental

Hippurates of Co(II), Ni(II), Cu(II) and Zn(II) were prepared by adding ammonium hippurate (pH 4.0) to a hot solution of these cation nitrates and crystallization at room temperature. The precipitate formed was filtered off, washed with water to remove NH_4^+ ions and dried at 303 K to a constant weight.

The content of carbon, hydrogen and nitrogen was determined by elemental analysis. The content of Co(II), Ni(II), Cu(II) and Zn(II) was determined from TG curve and by ignition the complexes to oxides CoO, NiO, CuO and ZnO. The content of water was determined from TG curve and by isothermal heating complexes at define temperature. The analysis data are given in Table 1.

The IR spectra of hippuric acid and isolated hippurates were recorded over the range 4000-400 cm^{-1} with Q-1500 spectrophotometer.

The solubilities in water at 293 K of the prepared complexes were determined. The saturation solutions have been prepared under isothermal conditions. After the equilibrium established the content of M^{2+} ions have been determined in the samples by polarographic method on OH-102 Radelkis polarograph. The content of Cu^{2+} ions was determined directly in the prepared solution, whereas the content of Co(II), Ni(II), Cu(II) and Zn(II) after mineralization of samples and desolving in HCl solution. On the basis of M^{2+} content the solubility of complexes has been calculated.

Next, the thermal stabilities of Co(II), Ni(II), Cu(II) and Zn(II) hippurates were studied by using TG, DTG and DTA techniques. The measurements were made with a derivatograph (MOM, Hungary). The samples of 100 mg were heated in platine crucibles in air atmosphere at heating rate 10 deg. min^{-1}, up to 1273 K.

From the thermal curves, the data on the thermal decomposition of prepared hippurates were evalueted and presented in Tables 2 and 3. The solid products were calculated from TG curves and verified by recording the IR and X spectra. The activation energy of dehydration reaction of prepared complexes was calculated from thermal curves by means of Pletniev and Fotiyev method [7].

Results

The hippurates of Co(II), Ni(II), Cu(II) and Zn(II) were prepared as crystalline solids sparingly soluble in water. The complex of Co(II) is pinkcolour, Ni(II)-green, Cu(II)-blue and that of Zn(II)-white. On the basis of elemental analysis it was found that prepared hippurates formed the hydrates with the ratio of metal to ligand of 1:2 (Table 1). The analysis of IR spectra confirms the suggested composition of complexes. The IR spectra of prepared complexes are similar each other. In the IR spectra of prepared hippurates the broad absorption band with maximum at 3410-3400 cm^{-1} arising from vibration of OH group of water and narrow band at 1630 cm^{-1} of water molecule vibration make their appearance. These bands confirm the presence of crystallization water in the outer coordination sphere.

The absence of absorption band at 1730 cm^{-1} arising COOH group indicates that hydrogen ions in the hippuric acid molecules are substituted by M^{2+} ions. In the IR spectra of the prepared complexes appear strong absorption bands of asymmetric vibration of OCO^- group (ν_{as}) at 1580-1575 cm^{-1} and symmetric ones (ν_s) at 1400-1395^{-1}. In the IR spectra of Co(II), Ni(II), and Cu(II) hippurates there are two strong bands of N-H vibrations at 3340-3320 and 3260 cm^{-1} whereas in the spectrum of Zn(II) hippurate there is only one band at 3280 cm^{-1}. In the spectra of all prepared complexes absorption bands of N–H at 3080-3030 cm^{-1} and N-H at 1610 cm^{-1} make their appearance. The band appearing at 1610 cm^{-1} has both N-H and ring vibrational character. The bands at 560-540 cm^{-1} arise from vibrations of metal-oxygen bond. In the chelate ring of these complexes may occur the conjugation of M–O, C–O and C–C bonds, and hence there will be no pure M–O stretching vibration. The magnitude of the separation, $\Delta\nu$, between the frequencies due to ν_{as} OCO^- and ν_s OCO^- in preparation hippurates indicates the lower degree of ionic bond in these complexes as compared to those of sodium salt. Having a higher ionic potential than sodium salt, M^{2+} ions influence more strongly the ligand causing its more significant deformation. On the basis of displacement of absorption band of asymmetric vibration of carboxylate group to lower frequency and the symmetrical one, and on the basis of $\Delta\nu$ values, the carboxylic group in complexes under study is found to be bidentate ligand.

The position of ν N–H group which does not change or changes only slighty, in comparison to corresponding absorption band of the acid indicates the existence of the hydrogen bond N–H$\cdots$O.

The hippurates of Co(II), Ni(II), Cu(II) and Zn(II) are crystalline solids of low symmetry and big unit cells. The complexes of Co(II), Ni(II), and Cu(II) have the high degree of crystallinity, and that of Zn(II)- very low one. The prepared hippurates are sparingly soluble in water (Table 1). Their solubilities are of the order 10^{-3} mole. dm^{-3} and inerease in the order:

$$Cu < Ni < Zn < Co$$

with decreasing of ionic potential. The solubility of prepared hippurates are similar to solubility of rare earth hippurates [8].

The hydrated hippurates of Co(II), Ni(II), Cu(II) and Zn(II) are stable to 333-343 K and then are decomposed in two or three steps (Tables 2, 3). The hydrated complexes of Ni(II), Cu(II) and Zn(II) lose some water molecules at temperature range 333-463 K to the accompaniment of a strong endothermic effect and next decompose to oxides MO with intermediate formation very unstable products, which are not identificated. Hippurate of Co(II) decompose in three steps. Nonehydrated complex heated loses 5 water molecules and then tetrahydrated one is decomposed at the temperature range 513-1018 K to Co_3O_4, which undergoes at 1018-1173 K into CoO. The begining of decomposition is connected with weak endothermic effects. The hydrates formed after losing of some water molecules are stable to 483-543 K and then are dehydrated with simultaneously decomposition. The water molecules in prepared complexes are bonded in various way.

This is probably outer and inner sphere water. The activation energy of dehydration reactions has values from 25.1 kJ for Ni(II) hippurate to 51.7 kJ for Co(II) one and increases with the decreasing of ionic potential of metal ion.

The temperature at decomposition of prepared hippurates increases in the order:

$$Cu < Ni < Co < Zn$$

and the temperature of MO formation (T_k) increases in the order:

$$Zn < Cu < Ni < Co$$

with decreasing of atomic number of metal. The oxide ZnO is formed at the lowest temperature (923 K) while CoO is formed at the higest one (1173).

References

1 Beilsteins Handbuch der organischen Chemie, Bd IX, p. 225, Verlag von I. Springer, Berlin 1926.
2 Beilsteins Handbuch der organischen Chemie, E II. 9, p. 174, Verlag von I. Springer, Berlin 1949.
3 J. K. Gupta and M. C. Gupta, Indian J. Chem, 8 (1970) 264.
4 W. Brzyska and R. Kurpiel-Gorgol, J. Thermal Anal., 32 (1987) 671.
5 W. Brzyska and Z. Rzaczynska, J. Thermal Anal., 60 (1986) 27.
6 W. Brzyska and R. Kurpiel-Gorgol. J. Thermal Anal., - in press.

7 R. N. Pletniev and A. A. Fotiyev, Tr. Inst. Khimii Uralsk. Nauchn. Centra, 23 (1970) 144.
8 W. Brzyska and M. Hakim, Pol. J. Chem., - in press.

Zusammenfassung — Aus Lösung wurden die Co(II)-, Ni(II)-, Cu(II)- und Zn(II)- Salze der Hippursäure gewonnen, ihre quantitative Zusammensetzung sowie die Art der Koordination der Metall-Ligandenbindung bestimmt. Weiterhin wurden die Bedingungen und Produkte der thermischen Zersetzung beim Erhitzen in einer Luftatmosphäre bis 1273 K untersucht. Die Komplexe von Ni(II), Cu(II) und Zn(II) verlieren beim Erhitzen ein paar Moleküle Wasser und zersetzen sich anschließend zu MO. Co(II)-hippurat gibt beim Erhitzen einige Moleküle Wasser ab und zersetzt sich dann über die Zwischenstufe Co_3O_4 zu CoO.