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Biomimetic Complexes of Cd(II), Mn(II), and Zn(II) with 1,1-Diaminobutane–Schiff Base. EGA/MS Study of the Thermally Induced Decomposition[1]

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Abstract—Frequently, in addition to X-ray and spectroscopic approaches, thermal analysis is the method of choice for comprehensive characterization of precipitated metal complexes. However, thermogravimetry itself is not sufficient enough for explaining complex decomposition or releasing steps. For correct elucidation of the decomposition mechanism of biomimetic Cd(II), Mn(II), and Zn(II) complexes with 1,1-diaminobutane–Schiff base, evolved gas analysis by mass spectrometry (EGA/MS) was used to define the thermally induced steps. Those were synthesized and characterized by hyphenated thermogravimetry-mass spectrometry (TG–MS) that allowed to interpret the decomposition steps.

Keywords: 1,1-diaminobutane–Schiff base, biomimetic complexes, cadmium complexes, manganese complexes, zinc complexes, evolved gas analysis, EGA/MS, TG–MS

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INTRODUCTION

Complexes containing Shiff base ligands and transition metal ions are intensively studied due to their versatile structures, biomimetic potential modelling and wide industrial applications. Schiff bases are able to form coordination bonds with many metal ions via the azomethine or phenolic groups. Due to their easy formation and strong metal-binding ability, those have been used for synthesis of various metal complexes. Over the recent years coordination compounds of biologically active ligands [1–4] have received close attention.

Due to significant influence of chelation upon biological properties of compounds, the Schiff bases complexes potential applications have been tested [5, 6] and their antibacterial, antifungal, anticancer, and herbicidal activities [7–12] were detected. The ability of microorganisms to become resistant to major therapies used against them has long been recognized and became more pronounced. Recently, the number of diseases, caused by multidrug resistant gram-positive microorganisms, has been continuously increasing. The growing antimicrobial resistance (AMR) presents major threats to public health because it reduces the effectiveness of antimicrobial treatment leading to higher mortality and health care expenditure [13, 14]. Thus, recent studies pay high attention to new Schiff bases containing SNO donor atoms and their pharmacologically active complexes.

Besides X-ray and spectroscopic methods, a thermoanalytical characterization was highly efficient in making the more complete approach to thermally induced decomposition mechanisms [15–17]. However, thermogravimetry (TG) itself is no longer sufficient to explain complex releasing steps. The experience of our group demonstrated high efficiency of thermoanalytical data combined with FTIR and/or MS spectroscopies. The hyphenation allows to characterize correctly releasing or decomposition steps [18–22] and to propose decomposition mechanisms for precipitated complexes [23–30].

In a recent study several complexes with *N,N'*-bis-(2-hydroxybenzylidene)-1,1-diaminobutane ligand (BHBDAB) were precipitated and characterized [31]. This was followed by synthesis of similar or new complexes by the same method [31]. Evolved Gas Analysis by Mass spectrometry (EGA/MS) was

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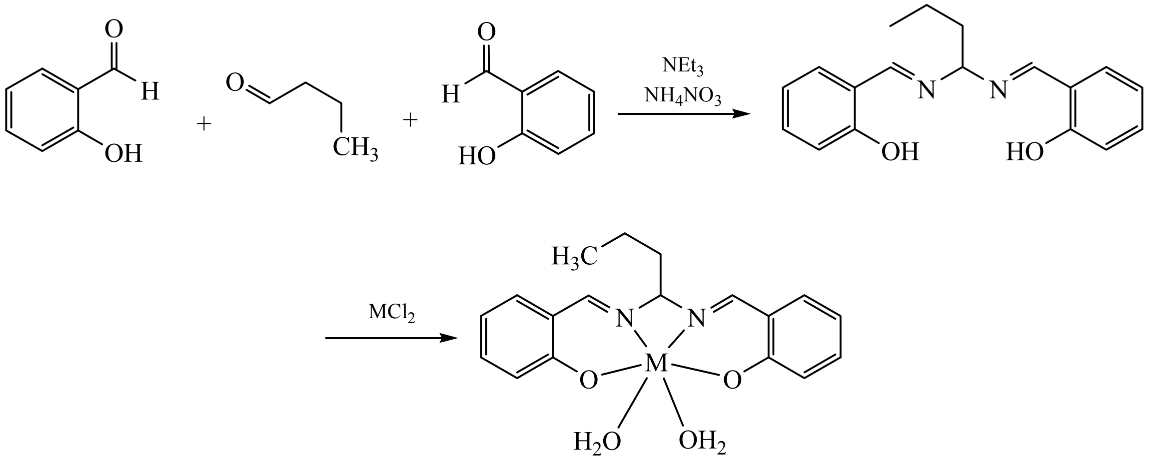
[1] The text was submitted by the authors in English.

Scheme 1. Synthesis of the complexes.



applied to prove the thermally induced behavior. The precipitated compounds were characterized by hyphenated TG–MS that allowed to describe each thermally induced step.

EXPERIMENTAL

Cd(II), Mn(II) and Zn(II) chlorides, ammonium nitrate, salicylaldehyde, and butanal were supplied by Aldrich and Fluka. The solvents were purchased from Merck and used without further purification. The earlier study [31] approach was applied to the synthesis of the ligand and precipitation of the complexes of general formula M(BHBDAB)$(H_2O)_2$, where M = Cd(II), Mn(II) or Zn(II) (Scheme 1).

Precipitation of the complexes was followed by elemental analysis on a VarioEl III CHN Analyzer. FTIR spectra were recorded on a Perkin Elmer 1760X spectrophotometer. The metal concentration was determined by ICP-OES (Varian ICP/VISTA MPX) equipped with an ultrasonic nebulizer (U 5000 AT+, Cetac Technologies Inc.). Analytical blanks were performed. A subtraction of blanks (calculated as the mean value of six replicated measurements) was applied in all cases. To control nebulizer efficiency, an internal standard (Yttrium 100 µg/L at a wavelength 371.030 nm) was used.

Thermoanalytical curves were recorded on a Perkin-Elmer TGA7 instrument. The samples, ca. 7–8 mg, were heated in platinum crucibles within temperature range 20–850°C, in the atmosphere of Ar or air (mixture of N_2 with O_2, 80 and 20%, v/v, respectively) at a flow rate of 100 mL/min and a scanning rate of 5 deg/min (best resolution rate).

MS of the gases evolved in the course of the thermoanalytical experiments were recorded by a STD 2960 simultaneous DTA–TGA instrument (TA Instruments Inc., USA) using sealed crucibles with a pinhole on the top. The gaseous species were analyzed on a ThermoStar GDS 200 (Balzers Instrument) quadrupole Mass Spectrometer equipped with Chaneltron detector (EI, 70eV), by passing those through a heated 100% methyl deactivated fused silica capillary tubing. Two different TG instruments recorded overlapped curves, so ensuring the reproducibility of the thermo-analytical experiments. Such experimental approach was constantly applied to achieve comparable data, with the aim of proposing decomposition characteristic behavior among complexes with similar ligand structures [32–36].

Table 1. Elemental analysis data for the precipitated complexes

Complex	Found, %				Calculated, %			
	C	H	N	M^a	C	H	N	25.3
Cd(BHBDAB)$(H_2O)_2$	48.3	4.7	6.0	25.0	48.9	4.9	6.3	14.1
Mn(BHBDAB)$(H_2O)_2$	56.2	5.6	7.1	14.2	56.2	5.7	7.3	16.5
Zn(BHBDAB)$(H_2O)_2$	54.3	5.6	7.1	16.3	54.7	5.6	7.1	16.5

[a] Cd, Mn and Zn (M) were determined by ICP-OES.

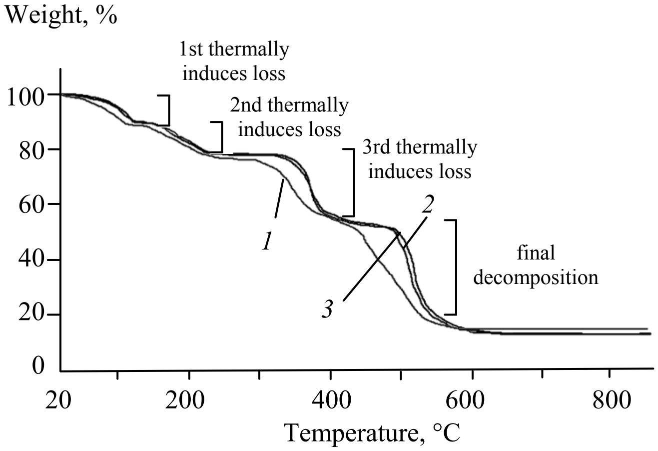


Fig. 1. Thermoanalytical curves of (*1*) cadmium(II), (*2*) manganese(II), and (*3*) zinc(II) chloride complexes; air flow rate 100 mL/min, heating rate 5 deg/min.

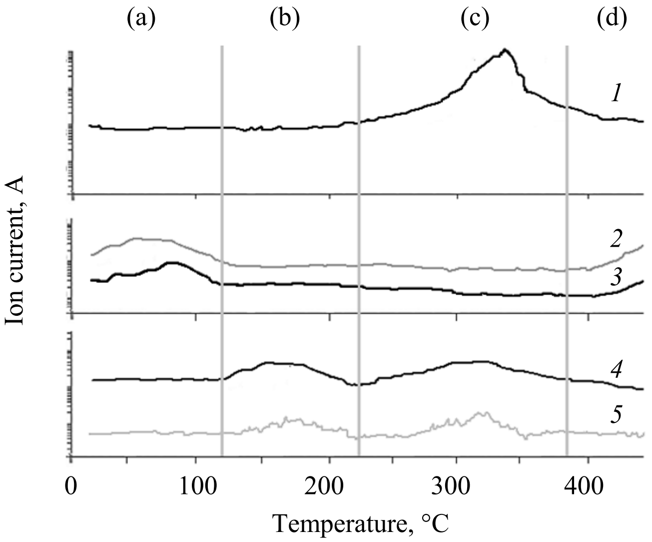


Fig. 2. EGA/MS *m*/*z* traces for the (a) first, (b) second, (c) third, and (d) final thermal decomposition steps of complexes as functions of temperature. (*1*) $m/z = 29$, $H_2C{=}NH^+$, (*2*) $m/z = 18$, H_2O, (*3*) $m/z = 17$, HO^+, (*4*) $m/z = 28$, $CH_2{=}CH_2^+$, (*5*) $m/z = 42$, $CH_3CH{=}CH_2$.

RESULTS AND DISCUSSION

According to the elemental analysis (Table 1), the complexes did not contain two external water molecules even upon the experimental conditions of the previous report [31] being strictly followed. It could be due to the drying process that removed all unstructured water molecules. Such result did not come as a surprise because in the earlier study [31] the thermogravimetric curves exhibited incongruence with the calculated weight loss. Probably Alaghaz [31] obtained different complexes in the course of preparing crystals for X-ray powder diffraction.

FTIR spectra confirmed the complex formation by the shift of the main common absorption bands (KBr), ν, cm^{-1}: 1560, 1316 and 1265, whereas in the study [31], the bands at 1373–1380 cm^{-1} for all complexes (CH_3 stretching and the aliphatic protons) were not affected by complexation.

Decomposition mechanism of the precipitated complexes was elucidated on the basis of thermally induced releasing steps studied comparatively by EGA/MS coupled with TG. In Fig. 1, the thermoanalytical profiles of the complexes are overlapped to compare the releasing steps when the purging flow was air.

The thermal decomposition proceeded via four main steps that were similar for all complexes and did not depend on the nature of coordinated metals. Actually, there were recorded same decomposition steps but different thermal stability. Similar thermal behavior has been reported earlier by our research group [24, 28, 37–39].

The percent weight loss (Table 1) was probably due to the first release of two coordinated water molecules followed by the tail of the ligand. This hypothesis was based on the calculated molecular weight loss and the absence of nitrogen-containing fragments in the mass spectra of the evolved gas.

EGA/MS confirmed the release of two water molecules (fragments at $m/z = 17$ and 18 accompanied by the tail $m/z = 28$) (Fig. 2). Such pattern was not influenced by the gas flow (air or Ar). Consequently, the release of CO could be excluded because $m/z = 28$ was also detected under inert flow conditions which supported the proposed decomposition path.

The third releasing process was deduced from purging the analyzer furnace with N_2. The recorded fragments at $m/z = 28$ and 29 (Fig. 2) and calculated percent weight loss indicated rupture of the ligand ring (Fig. 3), and the temporary consequent rearrangement.

The fourth thermally induced step led to complete decomposition of the residual compound and formation of the metal oxide. This step demonstrated MS fragments related to water, nitrogen and carbon dioxides upon purging the furnace by the air. Inert gas

Table 2. Temperature range of the main thermal steps and the corresponding percent weight loss

Complex	TG weigt loss, %							
	found, %				calculated, %			
	1st step	2nd step	3rd step	4th step	1st step	2nd step	3rd step	4th step
Cd(BHBDAB)(H_2O)$_2$	9.0	10.0	25.0	35.8	9.2	10.8	25.2	35.6
Mn(BHBDAB)(H_2O)$_2$	9.2	10.2	25.1	35.5	9.2	10.8	25.2	35.6
Zn(BHBDAB)(H_2O)$_2$	9.0	10.4	25.0	34.6	9.1	10.6	24.8	34.9

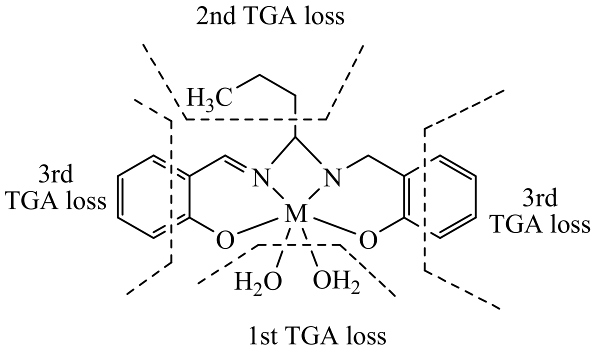


Fig. 3. General decomposition mechanism

flow (N_2 or Ar) did not lead to a constant final residue at 800°C.

The proposed decomposition mechanism was supported by correlation between the MS fragmentation and the calculated and experimental percent weight loss data (Table 2).

CONCLUSIONS

The thermally induced decomposition mechanism of Cd(II), Mn(II) and Zn(II) complexes with *N,N'*-bis(2-hydroxybenzylidene)-1,1-diaminobutane was studied by on-line coupling mass spectrometer to a thermogravimetric analyzer. The resulting weight loss and the *m/z* traces from the EGA/MS allowed to propose the decomposition path and confirmed the thermally induced mechanism.

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