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# TG–MS and TG–FTIR studies of imidazole-substituted coordination compounds: Co(II) and Ni(II)-complexes of bis(1-methylimidazol-2-yl)ketone

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#### 1. Introduction

Coordination compounds with nitrogen donor ligands like substituted-imidazoles have been thoroughly investigated during the last years. These compounds can be good models to simulate several industrial applications, like the behavior of manganese compounds containing enzymes as catalysts for the polymerization of olefins [1–12] and for washing and bleaching purposes. The improvement of classical washing and bleaching processes is both economically and ecologically relevant. The use of catalytically active transition metal complexes, which can activate hydrogen peroxide, might be a means of achieving these aims.

Several complexes with polydentate N-donor ligands have been patented for this purpose [1–3]. Cobalt or Nickel complexes are also important as model compounds for metal-containing enzymes such as superoxide dismutase, catalases or extradiolcleaving catechol dioxygenases. In order to mimic the histidines, many model complexes comprise bi- or tridentate N-donor ligands such as 2,2'-bipyridine, hydrotris(pyrazol-1-yl)borate or triazacyclononane [4–7]. Cobalt (II), Manganese(II) or Ni(II) complexes containing N-donor ligands have also been tested as polymerization catalysts for olefines, especially ethene. The hitherto published

#### ABSTRACT

Co(II) and Ni(II) coordination compounds with bis(1-methylimidazol-2-yl)ketone (BIK) of general formula  $M(BIK)_2X_2$  (M=Co or Ni; X=Cl or NO<sub>3</sub>) were synthesized and characterized by elemental analysis, by UV-vis and FTIR spectroscopies. Following our previous thermoanalytical studies on imidazole-substituted coordination compounds, the thermal behavior of the synthesized complexes was investigated by TG and DTG techniques: the thermal profile is always characterized by three substantial consecutive releasing steps for all the three complexes and the releasing supposed behavior is confirmed by EGA analysis (TG-MS and TG-FTIR). In particular, the first step is ascribed to the release of the two anions, followed by the loss of four methyl groups (side chains of the ligand) and two bridge-carbonyl groups. The residual Cobalt or Nickel tetra-imidazole complex decomposes in a final step to give the metal oxide as the final residue.

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results are promising, though still far from those of established catalyst systems [8–12].

In this view, thermoanalytical characterizations are useful to complete the information related to the metal-binding sites and to relate their physico-chemical properties. In addition, the Evolved Gas Analysis allows to confirm the proposed decomposition steps. Several papers have been published by our group in this field [13–22,24]. A thermoanalytical study of bis(imidazol-2yl)methane (BIM) complexes with cobalt, copper and nickel has already been reported by our group, since BIM is the simplest polyimidazole ligand useful to model multihistidine coordination [17].

Bis(1-methylimidazol-2-yl)ketone (BIK) (Fig. 1) has been known to be a versatile N,N ligand for many transition metals since its first synthesis in 1977 [25].

In this work, following the experimental conditions reported in the literature and in our previous work [24], the synthesis and the thermoanalytical study of bis(1-methylimidazl-2yl)ketone(BIK) complexes with divalent Copper or Nickel having a general formula  $M(BIK)_2X_2$  are reported (M=Co or Ni; X=Cl or NO<sub>3</sub>). The thermal stability and the decomposition steps were determined by thermogravimetry (TG) and derivative thermogravimetry (DTG). The released products, due to the thermal decomposition, were analyzed by on-line coupling a mass spectrometer and a FTIR spectrometer to the thermobalance; the so obtained evolved gas analysis (EGA–MS and EGA–FTIR) allowed to prove the proposed decomposition steps.



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Scheme 1. Synthesis of the complexes. M = Co or Ni; X = Cl or NO<sub>3</sub>.



Fig. 1. The ligand bis(1-methylimidazol-2-yl)ketone (BIK).

#### 2. Experimental and methods

#### 2.1. Materials

For all the complexes of general formula  $M(BIK)_2X_2$ , a 20 mL methanol solution of 900 mg of BIK (about 4.8 mmol) was added to 2.4 mmol methanol solutions of respectively  $CoCl_2$ ,  $NiCl_2$ ,  $Co(NO_3)_2$  or  $Ni(NO_3)_2$ . After few minutes of warm stirring, the solvent was gently removed to precipitate the complexes. A similar procedure has also been reported in the literature and previously applied for the synthesis of the manganese-BIK complexes [23,24]. The reaction is shown in Scheme 1.

#### 2.2. Instrumental

Elemental analysis was performed by a VarioEl III CHN Analyzer; UV–vis by a Perkin Elmer Lambda Series and FTIR measurements by a Perkin Elmer 1760X instrument. TG curves were recorded using a Perkin-Elmer TGA7 equipment. The samples investigated of approximately 7–8 mg were heated in platinum crucibles in the temperature range between 20 and 850 °C, under an atmosphere of pure nitrogen or air (gaseous mixture of nitrogen and oxygen with 80 and 20%, v/v, respectively) under a flow rate of 100 mL min<sup>-1</sup>. The thermal behavior was investigated using TG data at 10 °C min<sup>-1</sup> because of its best resolution.

Mass spectra of the gases evolved during the experiments were recorded by a simultaneous TG/DTA apparatus (STD 2960 simultaneous DTA-TGA, TA Instruments Inc., USA) using sealed crucibles with a pinhole on the top. The gaseous species were analyzed by a ThermoStar GDS 200 (Balzers Instrument) quadrupole mass spectrometer equipped with Chaneltron detector, through a heated 100% methyl deactivated fused silica capillary tubing. FTIR spectra gases evolved during the experiments were recorded by a simultaneous Perkin Elmer system obtained by coupling the TGA7 and the 1760 FTIR before cited.

#### 3. Results and discussion

All the complexes were easily precipitated after mixing the starting solutions; the complexes resulted with a good stoichiometry even if the yields were much lower than the supposed (around 45%) [23,24].

Elemental analysis data of the complexes considered in this study is summarized in Table 1. As a result of the good agreement between experimental and calculated data a general formula  $M(BIK)_2X_2$  (where M = Co or Ni; X = Cl or NO<sub>3</sub>) can be hypothesized. The Ni(BIK)<sub>2</sub>Cl<sub>2</sub> and Co(BIK)<sub>2</sub>Cl<sub>2</sub> complexes were also characterized by UV–vis and FTIR spectroscopies to be compared with the corresponding literature data [23,24].

All the complexes showed IR bands (KBr) related to C=O at 1633 cm<sup>-1</sup> (m), 1478 cm<sup>-1</sup> (w), 1463 cm<sup>-1</sup> (w), and to C=N at 1416 cm<sup>-1</sup> (s), 1292 cm<sup>-1</sup> (w), 1173 cm<sup>-1</sup> (w). The UV-vis spectrum in acetonitrile showed a  $\lambda_{max}$  (log*e*)=323 (4.51) nm. The ligand BIK absorbs ultraviolet light at 318 nm (log*e*=4.22). This strong absorption results almost exclusively from an electron transition from the HOMO – 1 into the LUMO [23,24].

Looking at the thermal behavior, with respect to the BIM complexes, where only one main thermal decomposition step is present [17], the BIK complexes are characterized by a first releasing step of the anions, followed by the loss of four methyl groups (side chains) and two bridge-carbonyl groups. The residual tetraimidazole cobalt or nickel compound decompose in a final step to give the metal oxide as the final residue.

The TG curves of the two  $Co(BIK)_2Cl_2$  and  $Ni(BIK)_2Cl_2$  complexes are reported in Fig. 2, while the TG curves of the two  $Co(BIK)_2(NO_3)_2$ and  $Ni(BIK)_2(NO_3)_2$  complexes are reported in Fig. 3, with their first derivative curves. All the TG profiles evidence the described three steps occurring in the temperature ranges 20–200 °C, 200–340 °C and 340–450 °C, respectively.

Table 2 reports the calculated and the found mass loss for each complex, and clearly shows that the experimental and the calculated results are in good agreement.

The following scheme summarizes the proposed TG releasing steps ( $M = Co \text{ or } Ni; X = Cl \text{ or } NO_3$ ):

$$M(BIK)_2X_2 \xrightarrow{-2X} M(BIK)_2 \xrightarrow{-2CO-4Me} M(Im)_4 \xrightarrow{-4Imid} MC$$

The EGA analysis performed by coupling the TG analyzer either to MS or to FTIR spectrometers allowed to confirm the proposed general decomposition mechanism.

In Fig. 4a, the mass spectra recorded in the TGA steps of the complexes decomposition by TG–MS coupled analysis is reported: in

#### Table 1

Results of elemental analysis. Col	alt and Nickel have been	determined by ICP-OES.
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Complex	mplex C %		Н %		N %		Metal (Ni o	r Co)%
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
Co(BIK)Cl <sub>2</sub>	42.0	42.4	4.1	3.9	27.3	27.5	11.9	11.6
Ni(BIK)Cl <sub>2</sub>	42.1	42.4	4.1	3.9	27.5	27.5	11.7	11.5
Co(BIK)(NO <sub>3</sub> ) <sub>2</sub>	38.2	38.4	3.7	3.6	25.2	24.9	10.3	10.5
Ni(BIK)(NO <sub>3</sub> ) <sub>2</sub>	38.0	38.4	3.9	3.6	25.1	24.9	10.2	10.4



**Fig. 2.** TG and DTG curves of  $Co(BIK)_2Cl_2$  (red curves) and Ni(BIK)\_2Cl\_2 (blue curves) at a heating rate of  $10 \circ C \min^{-1}$  (100 mLmin<sup>-1</sup> air flow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 3. TG and DTG curves of Co(BIK)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (grey curves) and Ni(BIK)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (green curves) at a heating rate of 10 °C min<sup>-1</sup> (100 mL min<sup>-1</sup> air flow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 2

Experimental mass loss percentages determined by TG and comparison with calculated ones, obtained by taking into account the proposed reaction mechanisms.

Compound	Exp. loss 1st TGA step (calculated)	Exp. loss 2nd TGA step (calculated)	res after 3rd TGA step (calculated)
Co(BIK) <sub>2</sub> Cl <sub>2</sub>	-13.9% (-2Cl=-13.76%)	$-23.2\%$ ( $-4 \times CH_3$ ; $-2 \times CO = -22.79\%$ )	13.8% (res CoO = 14.73%)
Ni(BIK) <sub>2</sub> Cl <sub>2</sub>	-14.0% ( $-2Cl = -13.85%$ )	$-23.0\%$ ( $-4 \times CH_3$ ; $-2 \times CO = -22.78\%$ )	14.0% (res NiO = 14.67%)
$Co(BIK)_2(NO_3)_2$	$-23.5\%$ ( $-2NO_3 = -22.13\%$ )	$-20.5\%$ ( $-4 \times CH_3$ ; $-2 \times CO = -20.58\%$ )	13.9% (res CoO = 13.30%)
Ni(BIK) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	$-23.6\%$ ( $-2 \text{ NO}_3 = -22.13\%$ )	$-21.1\%$ ( $-4 \times CH_3$ ; $-2 \times CO = -20.59\%$ )	13.8% (res NiO = 13.26%)



Fig. 4. Evolved Gas Analysis (EGA) plots of the characteristic MS fragments and IR spectra: (a) EGA–MS of Ni and Co complexes; (b) EGA–FTIR of Ni and Co complexes – second TG step (temperature range 200–340 °C).

the plot of the ion current related to the first TG step, fragments at m/z 30 (NO<sup>+</sup>), 44 (N<sub>2</sub>O<sup>+</sup>) and 46 (NO<sub>2</sub><sup>+</sup>) prove the release of the nitrate ion, while the trace related to HCl (m/z = 36) prove the release of the chloride ion. In the temperature range 220–320 °C the fragments with m/z 44 (CO<sub>2</sub><sup>+</sup>), 22 (CO<sub>2</sub><sup>2+</sup>), 18 (H<sub>2</sub>O<sup>+</sup>) and 17 (OH<sup>+</sup>) support the proposed release of CO (oxidated to CO<sub>2</sub>) and the oxidation of the methyl groups to water and carbon dioxide. The m/z = 26, detected when nitrogen flow purges the TGA furnace, is attributed to C<sub>2</sub>H<sub>2</sub><sup>+</sup> and support the release of the two CH<sub>3</sub> that rearrange in the vapor phase.

TG-FTIR evolved gas analysis confirmed the mechanism: as expected, no bands were detected in the first TGA step of the chloride complex decomposition, since the release of Cl<sub>2</sub> does not contribute with IR bands; water and carbon dioxide characterize the spectra during the following TGA step, as shown in Fig. 4b, when the purging flow is air.

By the EGA–MS and EGA–FTIR results of Fig. 4, the proposed general mechanism of decomposition that our group suggested in several recent studies is again respected. As already shown for the BIM complexes, also the BIK complexes follow the same thermal decomposition path, with the loss of the counter ions as first process, followed by the release of all the substitutions to give the imidazole complex that decomposes in the final step.

The experimental results confirm that the thermal stability of the complexes based on substituted imidazoles are only function of the metal coordination characteristics and of the side chains.

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