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Biomimetic polyimidazole complexes: A thermoanalytical study of Co(II)-, Ni(II)- and Cu(II)-bis(imidazol-2-yl)methane complexes

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Abstract

Imidazole rings of histidine residues often form part of the metal-binding site in metalloproteins, so ligands with the 2-imidazolyl units are good models for mimicking biological metal-binding sites because the histidine imidazole ring is often attached via the 2-position to the side chain when the imidazole is coordinated to a metal. Thermoanalytical studies on biomimetic molecules are useful to complete the informations on the mechanism of action of the metal-binding sites of metalloproteins and to relate their chemico-physical properties. The synthesis, the spectroscopic characterization and the thermoanalytical study of bis(imidazol-2-yl)methane (BIM) complexes with divalent cobalt, nickel and copper, with a general formula $M(BIM)_2Cl_2$, are reported: the thermal stability and the decomposition steps were determined by thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). The released products, due to the thermal decomposition, were analysed by on-line coupling a FTIR spectrometer to the thermobalance; the so obtained evolved gas analysis (EGA) allowed to prove the proposed decomposition steps.

Keywords: Complexes; Bis(imidazol-2-yl)methane; Imidazole derivatives; TGA; DSC; Coupled TG-FTIR; EGA

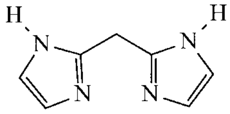
1. Introduction

Copper metalloproteins are involved in various biological functions such as electron transfer, oxygen transport, or substrate oxidation [1–5]. These functions are the consequence of the redox properties of the copper ion modulated by the protein ligands and of the selection of substrates by the active site.

Imidazole rings of histidine residues form part of the metal-binding site in metalloproteins [6–8]. The ubiquitous histidine ligation in metalloenzymes has stimulated syntheses of imidazole-containing multidentate ligands for biomimetic studies. Many bi-, tri- and tetradentate metal chelating ligands containing substituted imidazole have been developed [9,10]: ligands with the 2-imidazolyl units are good models for mimicking biological metal-binding sites because the histidine imidazole ring is often attached via the 2-position to the side chain when the imidazole is coordinated to a metal.

In this view, thermoanalytical studies on biomimetic molecules are useful to complete the information on the mechanism of action of the metal-binding sites of metalloproteins and to relate their physico-chemical properties [11–17].

Bis(imidazol-2-yl)methane (BIM) is the simplest polyimidazole ligand useful to model multihistidine coordination, as also reported by Place et al. [18].



Bis(imidazol-2-yl)Methane

(BIM)

In this work, the synthesis of the $Cu(BIM)_2Cl_2$ complex is reported. Its thermal stability and the decomposition mechanisms were studied by thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) and compared to

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cobalt and nickel complexes synthesized with the same procedure.

For each TG process, the released products, due to the thermal decomposition, were analysed by on-line coupling a FTIR spectrometer to the thermobalance; the so obtained evolved gas analysis (EGA) [19,20] allowed to prove the proposed decomposition steps.

The results are discussed on the basis of the different instrumental characterizations reported in the literature.

2. Experimental

2.1. Syntheses of the complexes

All the complexes of general formula $M(BIM)_2Cl_2$ (where M = Co(II), Ni(II) or Cu(II)) were synthesized by following the procedure reported in literature [18] with few modifications.

BIM was obtained as reported by Collman et al. [21]. The metal chloride salts were purchased from Sigma–Aldrich.

In detail, a 20 mL methanol solution of 1058 g of BIM (7.14 mmol) was added to 3.57 mmol methanol solutions of cobalt(II)-, nickel(II)- or copper(II)-chloride. After few minutes of stirring, the complexes spontaneously precipitated to give powders of $M(BIM)_2Cl_2$ (where M = Co(II), Ni(II) or Cu(II)).

2.1.1. Elemental analysis (metal by ICP-OES)

$Co(BIM)_2Cl_2$: C 39.4% (39.4), H 3.5% (3.7), N 26.3% (26.2), Co 13.90% (13.8); $Ni(BIM)_2Cl_2$: C 39.5% (39.4), H 3.7% (3.7), N 26.9% (26.2), Ni 14.10% (13.8); $Cu(BIM)_2Cl_2$ C 39.0% (39.0), H 3.8% (3.7), N 26.3% (26.0), Cu 15.00% (14.7).

2.2. Instrumental

UV–vis spectra were recorded by using a Perkin Elmer Lambda 11 spectrophotometer.

The thermoanalytical curves were obtained by using a Perkin Elmer TGA7 thermobalance (range 20–1000 °C) and a Perkin Elmer DSC7 calorimeter; the atmosphere was either pure nitrogen or air, at a flow rate of $100\,mL\,min^{-1}$; the heating rate was varied between 5 and $40\,°C\,min^{-1}$, with the best resolution achieved at a scanning rate of $10\,°C\,min^{-1}$.

To obtain the IR spectra of the gases evolved during the thermogravimetric analysis, the thermobalance was coupled with a Perkin Elmer FTIR spectrometer, model 1760X. The TGA7 was linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, the temperatures of the cell and of the transfer line being independently selected.

3. Results and discussion

The synthesis of BIM is reported in two articles by Joseph et al. [22] and Collman et al. [21]. The complexes were initially synthesized by both the procedures to determine the differences: since the yield resulted very similar, the second approach was preferred and is so cited in Section 2.

The complexes present a weak absorption in the visible region, with a large Gaussian shape centred at 600–615 nm. A similar absorption is also reported for the complex $Cu(BIM)_2(ClO_4)_2$ [18].

To verify the structure of the precipitated new $Cu(BIM)_2Cl_2$, it was solved by X-ray crystal structure to be compared with $Cu(BIM)_2(ClO_4)_2$ compound [18]. To this end, a diluted methanol solution was slowly evaporated (usually more than 2 days) resulting in square crystals. Both the chloride and the perchlorate complexes show the copper(II) ion in a square plane

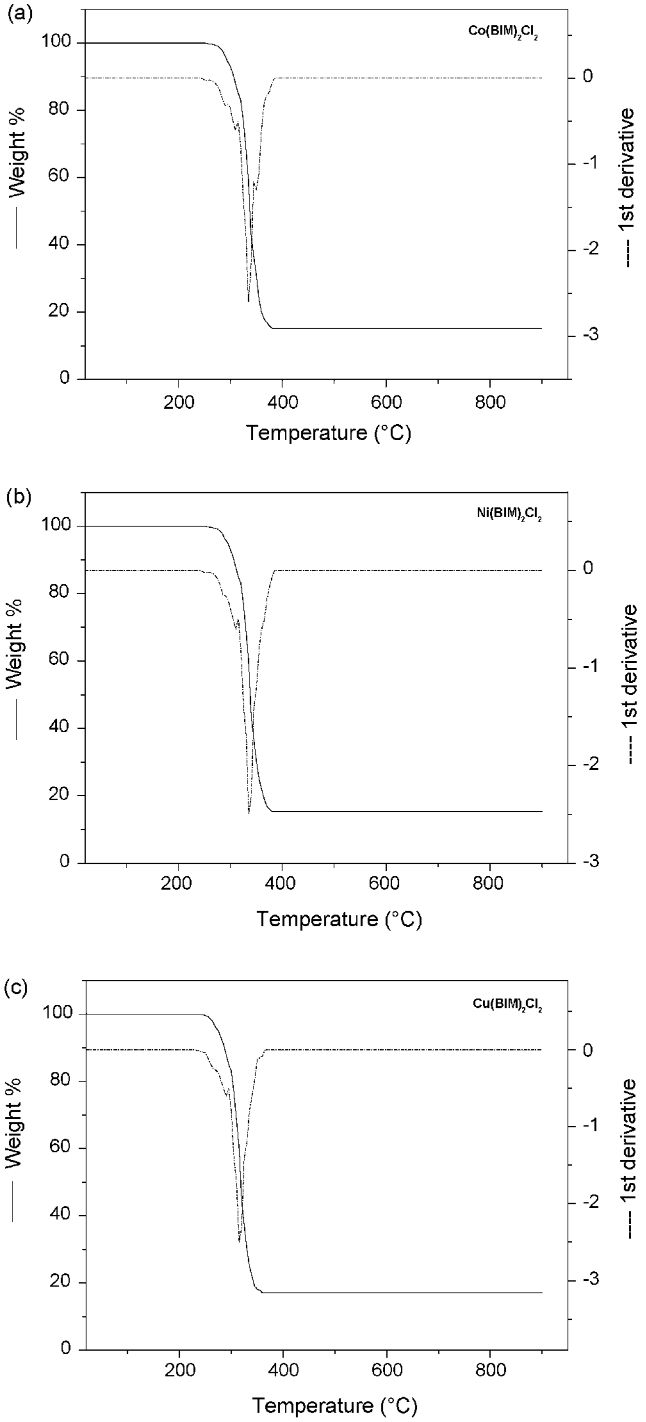
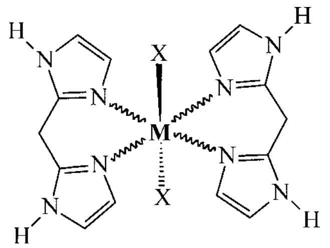


Fig. 1. TG (—) and DTG (------) curves of $Co(BIM)_2Cl_2$ (a), $Ni(BIM)_2Cl_2$ (b) and $Cu(BIM)_2Cl_2$ (c) complexes. Heating rate: $10\,°C\,min^{-1}$. Air flow at $100\,mL\,min^{-1}$ rate.

of four nitrogens from imidazoles, with bonding interactions with two chlorides or two oxygens in apical positions. The copper is at the center of a symmetry of the complex molecule and lies in the plane defined by the four nitrogens. The BIM ligand can in fact accommodate a planar arrangement of the four binding nitrogens around the copper. The tetragonal symmetry of both $Cu(BIM)_2Cl_2$ and $Cu(BIM)_2(ClO_4)_2$ stabilizes the complexes.



Structure of $Cu(BIM)_2Cl_2$

No difference was found among the Cu–N bond lengths of the chloride and perchlorate complexes. Looking at the counter ions, the Cu–Cl bonds are constantly shorter (a difference of 0.12 Å) with respect to the Cu–O bonds (in the case of the perchlorate ions) and suggest a stronger interaction Cu–Cl than Cu–O, with a higher stability of the $Cu(BIM)_2Cl_2$ complex structure. These results are in agreement with previous reported data [18–23].

The stability can be confirmed by the thermal profile recorded for all the $M(BIM)_2Cl_2$ complexes. In fact, only one main thermal decomposition step is present in the TG profiles of all the complexes (air flow), as shown in Fig. 1. The complexes are stable, showing a TG plateau, up to 265 °C, when the break-down of each complex starts. The first derivative of the thermogravimetric curve allows to distinguish between the initial release of the two chloride ions and the subsequent decomposition to give the metal oxides.

When the purging flow is changed to inert gas (nitrogen or argon), the thermal profile is not significantly affected, with a shift of few degrees to higher temperature of the decomposition step. Although in absence of oxygen, because of the high stability of the complexes, a highly exothermal decomposition take place after the break-down of the structure due to the loss of the chloride ions.

By the analysis of the evolved gases, performed by on-line coupling a FTIR spectrometer to the thermobalance, the proposed decomposition step can be confirmed. As can be seen in the stacked plot of the spectra recorded in the temperature range 250–350 °C (Fig. 2), the initial absence of IR bands (250–290 °C) is due to the release of both the Cl-ions with the consequent formation of Cl_2 in the gas phase. In the temperature range 290–370 °C, corresponding to the second releasing process enhanced in the DTG curve, the IR bands are due to CO_2, H_2O and NH_3 as consequence of the break-down of the ligand molecules. The metal oxide is the final residue. The evolved gas analysis so confirms the proposed thermal decomposition pathway deduced by calculating the molecular weight loss from the TG traces.

On the basis of the thermal profiles shown in Fig. 1, the following thermal stability scale can be proposed, with

$$Cu(BIM)_2Cl_2 < Co(BIM)_2Cl_2 \cong Ni(BIM)_2Cl_2.$$

In addition, these complexes showed the ability to reversibly bind one methanol molecule. When the complexes are left at

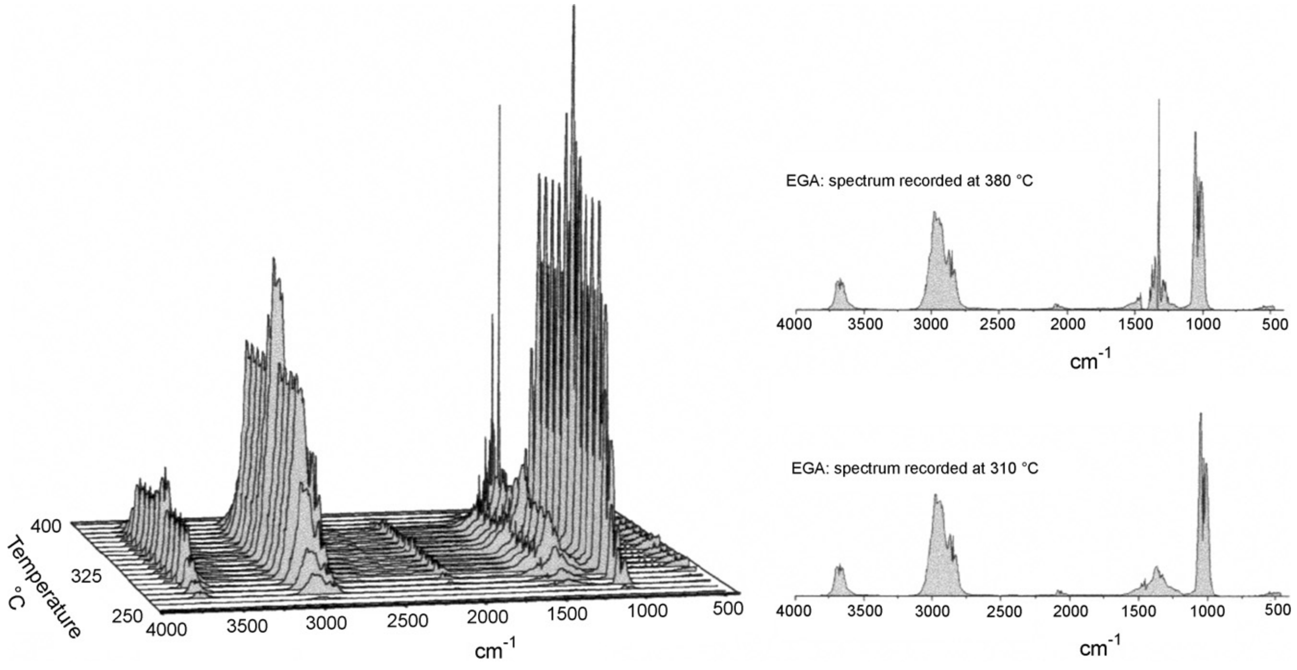


Fig. 2. Infrared spectra of the TG evolved gases for the decomposition of $M(BIM)_2Cl_2$ complexes in the temperature range 250–400 °C. Air flow at 100 mL min^{-1} rate. Resolution: 8 cm^{-1}, 10 scans per spectrum.

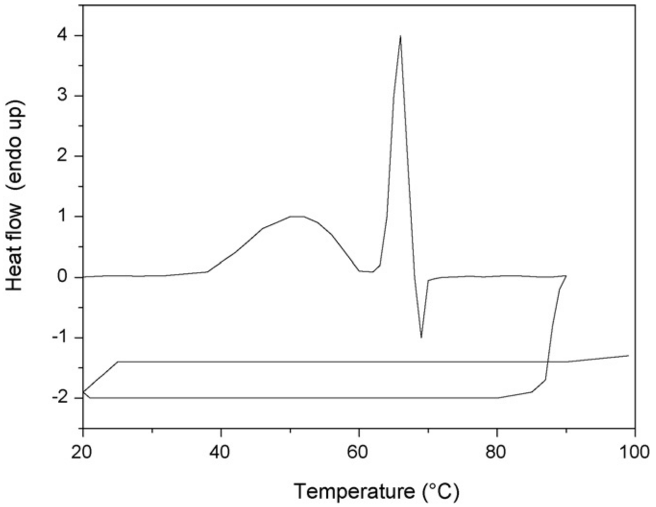


Fig. 3. DSC curve of the $Co(BIM)_2Cl_2$. Closed pan. Scanning rate: 10 °C min^{-1}.

least 2 days in a controlled 20% methanol vapours enriched environment, the DSC curve (Fig. 3) shows a peak in the temperature range 40–60 °C that disappears if a second heating run is immediately performed. In the DSC curve it can also be noted an endothermic peak, with maximum at 66 °C, not shown by the original complexes. The peak is due to a rearrangement of the new different structure that is formed when the methanol molecule is present. Unfortunately, it has not been possible so far to obtain structural informations related to this second structure.

References

[1] R. Lontre (Ed.), Copper Proteins and Copper Enzymes, vols. I–III, CRC Press, Boca Raton, FL, 1984.
[2] F. Jiang, J. McCracken, J. Peisach, J. Am. Chem. Soc. 112 (1990) 9035.
[3] H. Beinert, J. Inorg. Biochem. 44 (1991) 173.
[4] B.P. Murphy, Coord. Chem. Rev. 124 (1993) 63.
[5] M.J. Colaneri, J. Peisach, J. Am. Chem. Soc. 117 (1995) 6308.
[6] R.H. Holm, P. Kennepohl, E.I. Solomon, Chem. Rev. 96 (1996) 2239.
[7] E. Rimura, T. Koike, Adv. Inorg. Chem. 44 (1997) 229.
[8] M. Kobayashi, S. Shimizu, Eur. J. Biochem. 261 (1999) 1.
[9] S. Elgafi, L.D. Field, B.A. Messerle, T.W. Hambley, P. Turner, J. Chem. Soc. Dalton Trans. (1997) 2341.
[10] F. Tani, Y. Matsumoto, Y. Tachi, T. Sasaki, Y. Naruta, Chem. Commun. (1998) 1731.
[11] T.N. Sorrell, Tetrahedron 45 (1989) 63.
[12] K.D. Karlin, Science 261 (1993) 701.
[13] S. Materazzi, E. Vasca, Thermochim. Acta 373 (2001) 7.
[14] S. Materazzi, K. Kurdziel, U. Tentolini, A. Bacaloni, S. Aquili, Thermochim. Acta 395 (2003) 137.
[15] S. Materazzi, G. D'Ascenzo, S. Aquili, K.M. Kadish, J.L. Bear, Thermochim. Acta 397 (2003) 129.
[16] S. Materazzi, S. Aquili, C. Bianchetti, G. D'Ascenzo, K.M. Kadish, J.L. Bear, Thermochim. Acta 409 (2004) 145.
[17] S. Materazzi, S. Aquili, S. De Angelis Curtis, S. Vecchio, K. Kurdziel, F. Sagone, Thermochim. Acta 421 (2004) 19.
[18] C. Place, J.L. Zimmermann, E. Mulliez, G. Guillot, C. Bois, J.C. Chottard, Inorg. Chem. 37 (1998) 4030.
[19] S. Materazzi, A. Gentili, R. Curini, Talanta 68 (2006) 489.
[20] S. Materazzi, A. Gentili, R. Curini, Talanta 69 (2006) 781.
[21] J.P. Collman, M. Zhong, Z. Wang, Org. Lett. 1 (1999) 949.
[22] M. Joseph, T. Leigh, M.L. Swain, Synthesis 7 (1977) 459.
[23] S. Abuskhuna, M. McCann, J. Briody, M. Devereux, V. McKee, Polyhedron 23 (2004) 1731.