

Article

Modeling Solid State Stability for Speciation: A Ten-Year Long Study

Roberta Risoluti ¹, Giuseppina Gullifa ¹, Elena Carcassi ¹ , Francesca Buiarelli ¹, Li W. Wo ² and Stefano Materazzi ^{1,*} 

¹ Department of Chemistry, "Sapienza" University of Rome, p.le A.Moro 5, 00185 Roma, Italy

² Department of Chemistry, Illinois State University, 100 N University St, Normal, IL 61761, USA

* Correspondence: stefano.materazzi@uniroma1.it; Tel.: +39-0649913616; Fax: +39-06490631

Received: 23 June 2019; Accepted: 13 August 2019; Published: 20 August 2019



Abstract: Speciation studies are based on fundamental models that relate the properties of biomimetic coordination compounds to the stability of the complexes. In addition to the classic approach based on solution studies, solid state properties have been recently proposed as supporting tools to understand the bioavailability of the involved metal. A ten-year long systematic study of several different complexes of imidazole substituted ligands with transition metal ions led our group to the definition of a model based on experimental evidences. This model revealed to be a useful tool to predict the stability of such coordination complexes and is based on the induced behavior under thermal stress. Several different solid state complexes were characterized by Thermally Induced Evolved Gas Analysis by Mass Spectrometry (TI-EGA-MS). This hyphenated technique provides fundamental information to determine the solid state properties and to create a model that relates stability to coordination. In this research, the model resulting from our ten-year long systematic study of complexes of transition metal ions with imidazole substituted ligands is described. In view of a systematic addition of information, new complexes of Cu(II), Zn(II), or Cd(II) with 2-propyl-4,5-imidazoledicarboxylic acid were precipitated, characterized, and studied by means of Thermally Induced Evolved Gas Analysis performed by mass spectrometry (TI-EGA-MS). The hyphenated approach was applied to enrich the information related to thermally induced steps, to confirm the supposed decomposition mechanism, and to determine the thermal stability of the studied complexes. Results, again, allowed supporting the theory that only two main characteristic and common thermally induced decomposition behaviors join the imidazole substituted complexes studied by our group. These two behaviors could be considered as typical trends and the model allowed to predict coordination behavior and to provide speciation information.

Keywords: speciation; biomimetic complexes; evolved gas analysis; TI-EGA-MS

1. Introduction

Speciation studies can be related by setting up fundamental models based on properties of biomimetic coordination compounds that provide the stability of the complexes in order to understand the bioavailability of the involved metal.

Speciation models are mainly based on the classic approach by studies in different solution conditions. It is also well known that the thermal stability of a complex in the solid state is inversely proportional to the stability of the same complex in aqueous solution.

Metal complexes containing imidazoledicarboxylate ligands have been extensively studied because of their interesting properties. They are recognized to be realistic models as biomimetic simulators because of their characteristics, such as versatile structures useful for flexible tailoring. Additional interest has been demonstrated because of promising applications in gas storage, catalysis,

optoelectronics, sensors, magnetism, luminescence, environment, and porous materials [1–33]. In consulting the literature, it is usual to find characterizations of new coordination compounds or complexes that report the synthesis, the elemental analysis, IR spectroscopic, and sometimes NMR or X-ray resulting information. More frequently, additional information is obtained from the solid state precipitates by means of thermal behavior. It is now globally recognized that the thermal stress induced on the complexes is able to provide kinetic and chemical decomposition information of the examined samples. This approach in itself is not sufficient to explain complex releasing steps. The most recent approach on-line couples FTIR or MS spectroscopies to increase the information and correctly characterizes the releasing (or decomposition) steps. The obtained data from the Thermally Induced Evolved Gas Analysis (TI-EGA) are becoming valuable supporting information that proposes a more complete characterization of the study of thermally induced decomposition mechanisms [34–41]. Our group reported these advantages in several reviews [42,43], enhancing the very different fields of application. This hyphenated approach is recognized as a very useful tool to propose decomposition mechanisms for precipitated complexes [44–48]. To step ahead, our group recently suggested new trends in thermal analysis [49–55] also comparing a new approach by portable microNIR, both oriented on the application of chemometrics [56,57].

A ten-year long systematic study of several different complexes of imidazole substituted ligands with transition metal ions led our group to the definition of a model based on experimental evidences. This model is revealed to be a useful tool to predict the stability of such coordination complexes and is based on the induced behavior under thermal stress. Several different solid state complexes were characterized by Thermally Induced Evolved Gas Analysis by Mass Spectrometry (TI-EGA-MS). This hyphenated technique provides fundamental information to determine the solid state properties and to create a model that relates stability to coordination.

The results of our ten-year long systematic study on several different complexes of substituted imidazole ligands with transition metal ions gave us the experimental evidence of two characteristic reproducible decomposition pathways. A predictive model was consequently proposed by our group. The TI-EGA-MS results allowed us to propose, for all these complexes, preliminary low-temperature thermally induced steps related to the loss of water molecules and counter ions, already present, followed by two different reproducible discriminating trends:

- The rupture of side chains, to give a five- or six-member ring as intermediate, compatibly with the percent weight loss and the TI-EGA-MS information. This behavior was recorded with ligands, such as *N,N'*-bis-(2-hydroxybenzylidene)-1,1-diaminobutane, 2-aminomethyl-benzimidazole, imidazole-4,5-dicarboxylic acid, and similar structures;
- The total loss of substitutions, with an imidazole 1:2 or 1:4 complex remaining as intermediate, before the last decomposition step involving the metal oxide. This behavior was recorded with ligands, such as (1-methylimidazol-2-yl)ketone, dopamine, and derived structures. All these studies are described in the references [57–68] and are the experimental evidences on which the proposed model is based. This thermally induced behavior, and the consequently derived model, is proposed as a tool to provide stability information on the complexes to be related to speciation studies.

The robustness of this predictive model needs additional examples to be continuously inserted. This study of new solid state complexes of Cu(II), Zn(II), and Cd(II) with 2-propyl-4,5-imidazoledicarboxylic acid was carried out with two main goals: i) To predict the stability from the solid state characteristics and ii) to add experimental evidences to the model.

Complexes were precipitated and characterized following previously reported procedure to be correctly compared. On the basis of the resulting characteristics, a predicted behavior and consequent stability was predicted by the model. The model prediction was successfully confirmed by the results of the Thermally Induced Mass Spectrometry Evolved Gas Analysis (TI-EGA-MS). Results, again, showed that between the two main common thermally induced decomposition behaviors, the one

predicted by the model joined the substituted imidazole complexes studied by our group and could be considered as typical trends for these structures.

2. Results and Discussion

The results from the elemental analysis of the precipitated complexes are reported in Table 1. Calculated and experimentally measured element percents are in good agreement.

Table 1. Elemental analysis results for the precipitated complexes. Cu, Zn, or Cd (Metal%) were determined by ICP-OES.

Complex	C/%		H/%		N/%		Metal/%	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
Cu(H ₂ PIDC) ₂ (H ₂ O) ₂	39.1	39.3	4.7	4.5	11.8	11.4	12.2	12.1
Zn(H ₂ PIDC) ₂ (H ₂ O) ₂	39.3	39.3	4.7	4.5	11.5	11.4	11.9	12.1
Cd(H ₂ PIDC) ₂ (H ₂ O) ₂	27.2	27.4	4.5	4.0	7.9	8.0	21.1	21.3

As for similar complexes, reported by Yang and coworkers [69], FTIR spectra confirmed the main common absorption band (KBr, cm⁻¹): 2975 (m), 1720 (s), 1540 (s), 1390 (s), 1280 (s), 1100 (m), 860 (m), 775 (m), 695 (w), 660 (m), 510 (m).

The Solid State Model, on the basis of these characteristics, predicted these complexes belonging to the first group described in the introduction.

Thermally induced releasing steps of the precipitated Cu(H₂PIDC)₂(H₂O)₂, Zn(H₂PIDC)₂(H₂O)₂, and Cd(H₂PIDC)₂(H₂O)₂ were comparatively studied by thermally induced evolved gas analysis by mass spectrometry (TI-EGA-MS) to confirm the decomposition mechanism proposed by the model. In Figure 1, the thermoanalytical profiles of the three complexes, registered while heating the precipitates, are overlapped to compare the releasing steps under the oxidant (air) purging flow.

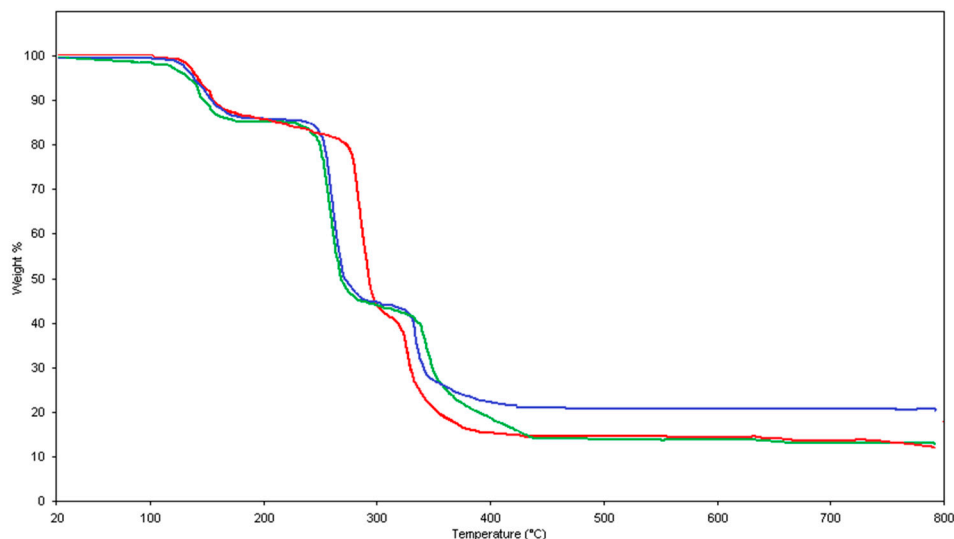


Figure 1. Thermally induced releasing profiles of the Cu(H₂PIDC)₂(H₂O)₂ (blue curve), Cd(H₂PIDC)₂(H₂O)₂ (red curve), and Zn(H₂PIDC)₂(H₂O)₂ (green curve): Air flow at 100 mL min⁻¹; heating rate 5 °C min⁻¹.

As previously reported for similar complexes, the thermally induced behavior was confirmed to be based on three main steps (see Table 1) with a first release of the water molecules and of only one side chain of the ligand. This hypothesis can be based on the molecular structure of this complex that shows one side chain in the external position, consequently easier to be removed.

The consequent Evolved Gas Analysis by Mass Spectrometry confirmed the release of the two water molecules by detecting fragments at $m/z = 17$ and 18, and of the side chain by $m/z = 28$, in the

temperature range of 100–200 °C, as shown in Figure 2. The behavior was not influenced when the oxidant flow (air) was changed to inert flow (N₂).

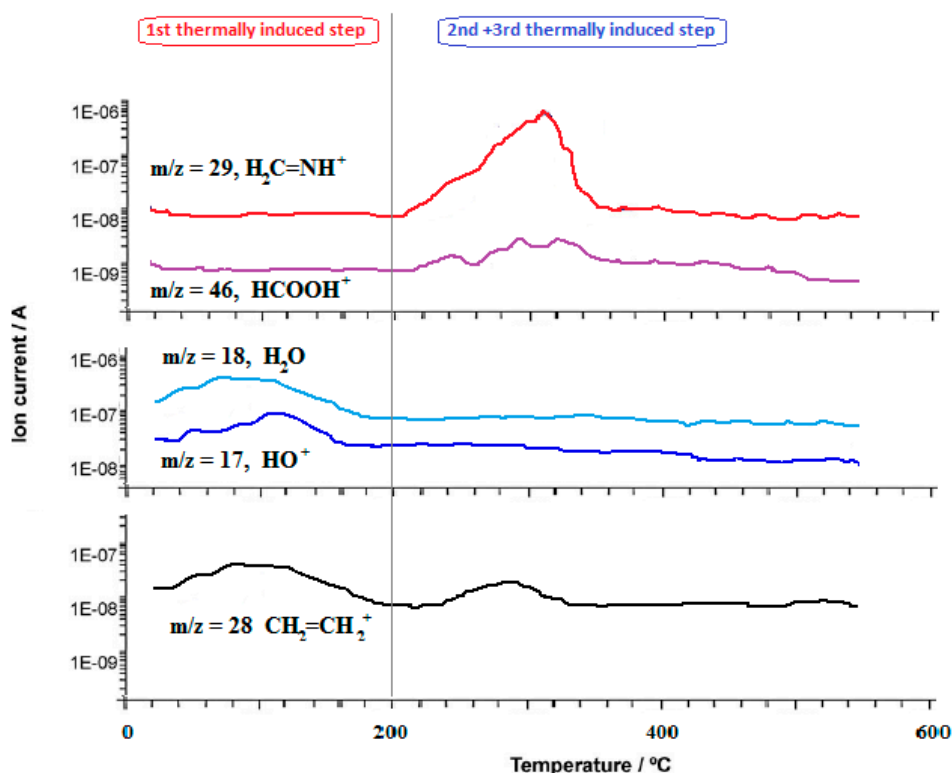


Figure 2. Representative curves of Thermally Induced Evolved Gas Analysis by Mass Spectrometry: m/z traces commonly recorded as a function of the temperature for all the analyzed complexes.

In the second releasing process (200–300 °C), the presence of fragments at $m/z = 28, 29,$ and 46 when nitrogen is the reacting flow (Figure 2) and the calculated percent weight loss, proved the rupture of the ligand ring, as depicted in Figure 3, and the temporary consequent rearrangement. The final third thermally induced step (300–500 °C) led to the complete decomposition of the residual compound to obtain the metal oxide.

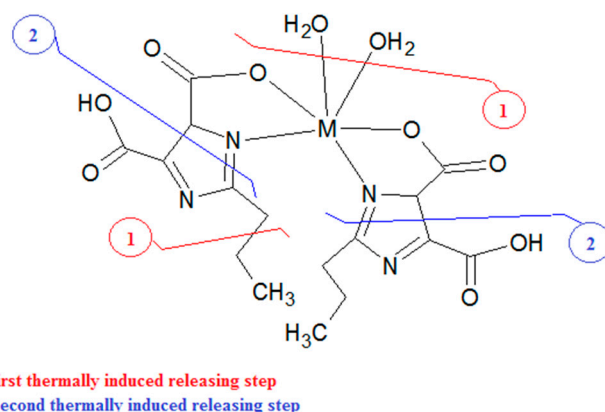


Figure 3. Scheme of the general decomposition mechanism.

By matching the MS fragmentation and the correspondence between percent weight loss calculated and percent weight loss experimentally recorded (Table 2), the proposed decomposition mechanism is clearly supported.

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

Complex	First TG Step 100–190 °C Weight Loss %		Second TG Step 230–300 °C Weight Loss %		Third TG Step 300–450 °C Weight Loss %	
	Found	Calculated	Found	Calculated	Found	Calculated
	Cu(H ₂ PIDC) ₂ (H ₂ O) ₂	13.3	13.1	45.0	45.8	25.7
Zn(H ₂ PIDC) ₂ (H ₂ O) ₂	13.0	13.1	46.9	45.8	24.0	26.0
Cd(H ₂ PIDC) ₂ (H ₂ O) ₂	11.6	11.2	43.0	43.3	24.3	24.2

The thermal behavior of the complexes was also verified by an inert purging flow (nitrogen) to check the differences when the pyrolysis took place instead of oxidation. Only the final step showed a different shape due to the uncompleted reaction to give the metal oxides.

No effects due to the inert atmosphere were detected up to 300 °C.

Consequently, the results clearly showed that the studied complexes of transition metal ions with 2-propyl-4,5-imidazoledicarboxylic acid belong to the first group described in the introduction.

The model correctly predicted the corresponding group.

3. Experimental and Methods

3.1. Materials

The ligand 2-propyl-4,5-imidazoledicarboxylic acid (H₃PIDC) and the copper, zinc, and cadmium salts were purchased from Sigma-Aldrich-Merck Co. (St. Louis, MO, USA). All the reagents were of A.R. grade and used without further purification. The conditions already reported for the previously published similar complexes were strictly followed.

3.2. Instrumental

Elemental and spectroscopic analyses, thermoanalytical characterization, and consequent Thermally Induced Evolved Gas Analysis by Mass Spectrometry (TI-EGA-MS) were performed as previously reported [68,70,71].

4. Conclusions

This study of newly synthesized transition metal complexes is aimed to contribute to a larger systematic investigation to support the two-way characteristic decomposition path that is strictly related to the structural stability of the precipitated complexes.

The ten-year long based model correctly predicted the characteristics of the precipitated complexes, anticipating what was experimentally confirmed.

Author Contributions: Conceptualization, R.R. and S.M.; methodology, R.R. and F.B.; software, R.R. and G.G.; validation, R.R. and E.C.; formal analysis, G.G., L.W.W. and E.C.; investigation, G.G., L.W.W. and F.B.; data curation, R.R. and S.M.; writing—original draft preparation, R.R. and S.M.; writing—review and editing, R.R. and S.M.; visualization, S.M.; supervision, R.R. and S.M.; project administration, S.M.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Rajendiran, T.M.; Kirk, M.L.; Setyawati, I.A.; Caudle, M.T.; Kampf, J.W.; Pecoraro, V.W. Isolation of the first ferromagnetically coupled Mn(III/IV) complex. *Chem. Commun.* **2003**, 824–825. [[CrossRef](#)]
- Bayon, J.C.; Net, G.; Rasmussen, P.G.; Kolowich, J.B. Dinuclear rhodium and iridium complexes of dicarboxylimidazolates; crystal structure of [NBu₄][(cod)Rh(dcbi)Rh(cod)]·2Pr¹OH. *J. Chem. Soc. Dalton Trans.* **1987**, 3003–3007. [[CrossRef](#)]

3. Zou, R.-Q.; Sakurai, H.; Xu, Q. Preparation, Adsorption Properties, and Catalytic Activity of 3D Porous Metal–Organic Frameworks Composed of Cubic Building Blocks and Alkali-Metal Ions. *Angew. Chem. Int. Ed.* **2006**, *45*, 2542. [[CrossRef](#)] [[PubMed](#)]
4. Marchetti, L.; Sabbieti, M.G.; Materazzi, S.; Hurley, M.M.; Menghi, G. Effects of phthalate esters on actin cytoskeleton of Py1a rat osteoblasts. *Histol. Histopathol.* **2002**, *17*, 1061–1066. [[CrossRef](#)] [[PubMed](#)]
5. Liu, Y.; Cheng, D.; Li, Y.-X.; Zhang, J.-D.; Yang, H.-X. A new one-dimensional Cd^{II} coordination polymer incorporating 2,2'-(1,2-phenylene)bis(1H-imidazole-4,5-dicarboxylate). *Acta Crystallogr. Sect. C Struct. Chem.* **2018**, *74*, 1128–1132. [[CrossRef](#)] [[PubMed](#)]
6. Liu, Y.; Kravtsov, V.C.; Eddaoudi, M. Template-Directed Assembly of Zeolite-like Metal–Organic Frameworks (ZMOFs): A usf-ZMOF with an Unprecedented Zeolite Topology. *Angew. Chem. Int. Ed.* **2008**, *47*, 8446. [[CrossRef](#)]
7. Wang, W.; Wang, R.; Liu, L.; Wu, B. Coordination Frameworks Containing Magnetic Single Chain of Imidazoledicarboxylate-Bridged Cobalt(II)/Nickel(II): Syntheses, Structures, and Magnetic Properties. *Cryst. Growth Des.* **2018**, *18*, 3449–3457. [[CrossRef](#)]
8. Wang, R.; Liu, L.; Lv, L.; Wang, X.; Chen, R.; Wu, B. Synthesis, Structural Diversity, and Properties of Cd Metal–Organic Frameworks Based on 2-(5-Bromo-pyridin-3-yl)-1H-imidazole-4,5-dicarboxylate and N-Heterocyclic Ancillary Ligands. *Cryst. Growth Des.* **2017**, *17*, 3616–3624. [[CrossRef](#)]
9. Wang, S.; Zhang, L.; Li, G.; Huo, Q.; Liu, Y. Assembly of two 3-D metal–organic frameworks from Cd(II) and 4,5-imidazoledicarboxylic acid or 2-ethyl-4,5-imidazoledicarboxylic acid. *Cryst. Eng. Comm.* **2008**, *10*, 1662. [[CrossRef](#)]
10. Bai, X.-Y.; Ji, W.-J.; Li, S.-N.; Jiang, Y.-C.; Hu, M.-C.; Zhai, Q.-G. Nonlinear Optical Rod Indium-Imidazoledicarboxylate Framework as Room-Temperature Gas Sensor for Butanol Isomers. *Cryst. Growth Des.* **2017**, *17*, 423–427. [[CrossRef](#)]
11. Catauro, M.; Tranquillo, E.; Risoluti, R.; Vecchio Cipriotti, S. Sol-Gel Synthesis, Spectroscopic and Thermal Behavior Study of SiO₂/PEG Composites Containing Different Amount of Chlorogenic Acid. *Polymers* **2018**, *10*, 682. [[CrossRef](#)] [[PubMed](#)]
12. Gangu, K.K.; Maddila, S.; Mukkamala, S.B.; Jonnalagadda, S.B. Synthesis, characterisation and catalytic activity of 4, 5-imidazoledicarboxylate ligated Co(II) and Cd(II) metal-organic coordination complexes. *J. Mol. Struct.* **2017**, *1143*, 153–162. [[CrossRef](#)]
13. Catauro, M.; Naviglio, D.; Risoluti, R.; Vecchio Cipriotti, S. Sol-gel synthesis and thermal behavior of bioactive ferrous citrate-silica hybrid materials. *J. Therm. Anal. Calorim.* **2018**, *133*, 1085–1092. [[CrossRef](#)]
14. Fei, H.; Lin, Y.; Xu, T. Cobalt imidazoledicarboxylate coordination complex microspheres: Stable intercalation materials for lithium and sodium-ion batteries. *Ionics* **2017**, *23*, 1949–1954. [[CrossRef](#)]
15. Song, Y.; Lin, C.-S.; Wei, Q.; Wu, Z.-F.; Huang, X.-Y. Three-Dimensional Non-Centrosymmetric Ba(II)/Li(I)–Imidazolecarboxylate Coordination Polymers: Second Harmonic Generation and Blue Fluorescence. *Cryst. Growth Des.* **2016**, *16*, 6654–6662. [[CrossRef](#)]
16. Jing, X.-M.; Xiao, L.-W.; Wei, L.; Dai, F.-C.; Ren, L.-L. Solvent directed assembly of two zinc(II)-2-(4-pyridyl)-4,5-imidazoledicarboxylate frameworks. *Inorg. Chem. Commun.* **2016**, *71*, 78–81. [[CrossRef](#)]
17. Perrino, C.; Marconi, E.; Tofful, L.; Farao, C.; Materazzi, S.; Canepari, S. Thermal stability of inorganic and organic compounds in atmospheric particulate matter. *Atmos. Environ.* **2012**, *54*, 36. [[CrossRef](#)]
18. Jia, Y.; Li, Y.; Zhou, R.; Song, J. The Advance of Imidazoledicarboxylate Derivatives-Based Coordination Polymers. *Prog. Chem.* **2016**, *28*, 482–496. [[CrossRef](#)]
19. Pang, Q.; Tu, B.; Ning, E.; Li, Q.; Zhao, D. Distinct Packings of Supramolecular Building Blocks in Metal–Organic Frameworks Based on Imidazoledicarboxylic Acid. *Inorg. Chem.* **2015**, *54*, 9678–9680. [[CrossRef](#)] [[PubMed](#)]
20. Liu, Y.; Kravtsov, V.; Walsh, R.D.; Poddar, P.; Srikanthc, H.; Eddaoudi, M. Directed assembly of metal–organic cubes from deliberately predesigned molecular building blocks. *Chem. Commun.* **2004**, 2806–2807. [[CrossRef](#)] [[PubMed](#)]
21. Dai, C.; Zhou, X.; Jing, X.; Li, G.; Huo, Q.; Liu, Y. Assembly of two Cu-based coordination polymers from 2-(pyridine-3-yl)-1H-4,5-imidazoledicarboxylate ligand. *Inorg. Chem. Commun.* **2015**, *52*, 69–72. [[CrossRef](#)]
22. Sabbieti, M.G.; Agas, D.; Santoni, G.; Materazzi, S.; Menghi, G.; Marchetti, L. Involvement of p53 in phthalate effects on mouse and rat osteoblasts. *J. Cell. Biochem.* **2009**, *107*, 316–327. [[CrossRef](#)] [[PubMed](#)]

23. Li, S.-M.; Cao, W.; Zheng, X.-J.; Jin, L.-P. Self-assembly and characterization of Ca–Zn heterometallic MOFs with 4,5-imidazoledicarboxylate. *Polyhedron* **2014**, *83*, 122–129. [[CrossRef](#)]
24. Liu, L.; Zhang, Z.; Zhao, Z.; Niu, S.; Song, A.; Peng, Y. Syntheses, Crystal Structures, and Luminescent Properties of Two Cadmium(II) Complexes with CdS Network and (3,4)-Connected Topology. *Anorg. Allg. Chem.* **2014**, *640*, 2520–2524. [[CrossRef](#)]
25. Sergi, M.; Gentili, A.; Perret, D.; Marchese, S.; Materazzi, S.; Curini, R. MSPD Extraction of Sulphonamides from Meat followed by LC Tandem MS Determination. *Chromatographia* **2007**, *65*, 757–761. [[CrossRef](#)]
26. Luo, Z.-R.; Yin, X.-H.; Zhao, J.-H.; Gao, P. Coordination Polymers with the Ligand (2-propyl-4,5-imidazoledicarboxylic acid): Synthesis, Structural Characteristics, and Properties Studies. *Synth. React. Inorg. Met. Org. Nano Met. Chem.* **2013**, *43*, 662–670. [[CrossRef](#)]
27. Yue, S.; Li, N.; Bian, J.; Hou, T.; Ma, J. Synthesis, crystal structure and luminescent properties of transition metals complexes based on imidazole derivatives. *Synth. Met.* **2012**, *162*, 247. [[CrossRef](#)]
28. Gentili, A.; Caretti, F.; D’Ascenzo, G.; Mainero Rocca, L.; Marchese, S.; Materazzi, S.; Perret, D. Simultaneous Determination of Trichothecenes A, B, and D in Maize Food Products by LC-MS-MS. *Chromatographia* **2007**, *66*, 669–676. [[CrossRef](#)]
29. Liu, Y.; Kravtsov, V.; Larsena, R.; Eddaoudi, M. Molecular building blocks approach to the assembly of zeolite-like metal–organic frameworks (ZMOFs) with extra-large cavities. *Chem. Commun.* **2006**, 1488–1490. [[CrossRef](#)]
30. Migliorati, V.; Ballirano, P.; Gontrani, L.; Materazzi, S.; Ceccacci, F.; Caminiti, R. A Combined Theoretical and Experimental Study of Solid Octyl and Decylammonium Chlorides and of Their Aqueous Solutions. *J. Phys. Chem. B* **2013**, *117*, 7806. [[CrossRef](#)]
31. Nouar, F.; Eckert, J.; Eubank, J.F.; Forster, P.; Eddaoudi, M. Zeolite-like Metal–Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H₂-(rho-ZMOF) Interaction Studies. *J. Am. Chem. Soc.* **2009**, *131*, 2864. [[CrossRef](#)] [[PubMed](#)]
32. Rumyantseva, M.; Nasriddinov, A.; Vladimirova, S.; Tokarev, S.; Fedorova, O.; Krylov, I.; Drozdov, K.; Baranchikov, A.; Gaskov, A. Photosensitive Organic-Inorganic Hybrid Materials for Room Temperature Gas Sensor Applications. *Nanomaterials* **2018**, *8*, 671. [[CrossRef](#)] [[PubMed](#)]
33. Silva, M.O.D.; Carneiro, M.L.B.; Siqueira, J.L.N.; Bão, S.N.; Souza, A.R. Development of a Promising Antitumor Compound Based on Rhodium(II) Succinate Associated with Iron Oxide Nanoparticles Coated with Lauric Acid/Albumin Hybrid: Synthesis, Colloidal Stability and Cytotoxic Effect in Breast Carcinoma Cells. *J. Nanosci. Nanotechnol.* **2018**, *18*, 3832–3843. [[CrossRef](#)] [[PubMed](#)]
34. Shahbazi, S.; Stratz, S.A.; Auxier, J.D.; Hanson, D.E.; Marsh, M.L.; Hall, H.L. Characterization and thermogravimetric analysis of lanthanide hexafluoroacetylacetonate chelates. *J. Radioanal. Nucl. Chem.* **2017**, *311*, 617–626. [[CrossRef](#)] [[PubMed](#)]
35. Liu, N.; Guo, X.; Navrotsky, A.; Shi, L.; Wu, D. Thermodynamic complexity of sulfated zirconia catalysts. *J. Catal.* **2016**, *342*, 158–163. [[CrossRef](#)]
36. Veselá, P.; Slovák, V.; Zelenka, T.; Koštejn, M.; Mucha, M. The influence of pyrolytic temperature on sorption ability of carbon xerogel based on 3-aminophenol-formaldehyde polymer for Cu(II) ions and phenol. *J. Anal. Appl. Pyrolysis* **2016**, *121*, 29–40. [[CrossRef](#)]
37. Baksi, A.; Cocke, D.L.; Gomes, A.; Gossage, J.; Riggs, M.; Beall, G.; McWhinney, H. Characterization of Copper-Manganese-Aluminum-Magnesium Mixed Oxyhydroxide and Oxide Catalysts for Redox Reactions. *Charact. Miner. Met. Mater.* **2016**, *2016*, 151–158. [[CrossRef](#)]
38. Aiello, D.; Materazzi, S.; Risoluti, R.; Thangavel, H.; Di Donna, L.; Mazzotti, F.; Casadonte, F.; Siciliano, C.; Sindona, G.; Napoli, A. A major allergen in rainbow trout (*Oncorhynchus mykiss*): Complete sequences of parvalbumin by MALDI tandem mass spectrometry. *Mol. BioSyst.* **2015**, *11*, 2373–2382. [[CrossRef](#)]
39. Oliani, W.L.; Komatsu, L.G.H.; Lugao, A.B.; Rangari, V.K.; Parra, D.F. Natural Aging Effects in HMS-Polypropylene Synthesized by Gamma Radiation in Acetylene Atmosphere. In *TMS Annual Meeting & Exhibition*; Springer: Cham, Switzerland, 2016; pp. 151–158.
40. Duemichen, E.; Braun, U.; Senz, R.; Fabian, G.; Sturm, H. Assessment of a new method for the analysis of decomposition gases of polymers by a combining thermogravimetric solid-phase extraction and thermal desorption gas chromatography mass spectrometry. *J. Chromatogr. A* **2014**, *1354*, 117–128. [[CrossRef](#)]

41. Dovgaliuk, I.; Ban, V.; Sadikin, Y.; Černý, R.; Aranda, L.; Casati, N.; Devillers, M.; Filinchuk, Y. The First Halide-Free Bimetallic Aluminum Borohydride: Synthesis, Structure, Stability, and Decomposition Pathway. *J. Phys. Chem. C* **2014**, *118*, 145–153. [[CrossRef](#)]
42. Szymańska, I.B.; Piszczek, P.; Szłyk, E. Gas phase studies of new copper(I) carboxylates compounds with vinylsilanes and their application in Chemical Vapor Deposition (CVD). *Polyhedron* **2009**, *28*, 721–728. [[CrossRef](#)]
43. Risoluti, R.; Fabiano, M.A.; Gullifa, G.; Vecchio Cipriotti, S.; Materazzi, S. FTIR-evolved gas analysis in recent thermoanalytical investigations. *Appl. Spectr. Rev.* **2017**, *52*, 39. [[CrossRef](#)]
44. Materazzi, S.; Risoluti, R. Evolved Gas Analysis by Mass Spectrometry. *Appl. Spectr. Rev.* **2014**, *49*, 635. [[CrossRef](#)]
45. Humphrie, T.D.; Sheppard, D.A.; Li, G.; Rowles, M.R. Complex hydrides as thermal energy storage materials: Characterisation and thermal decomposition of $\text{Na}_2\text{Mg}_2\text{NiH}_6$. *J. Mater. Chem. A* **2018**, *6*, 9099–9108. [[CrossRef](#)]
46. Lin, Y.; Zheng, M.; Ye, C.; Power, I.M. Thermogravimetric analysis–mass spectrometry (TGA–MS) of hydromagnesite from Dujiali Lake in Tibet, China. *J. Therm. Anal. Calorim.* **2018**, *133*, 1429–1437. [[CrossRef](#)]
47. Fernández-Alonso, S.; Corrales, T.; Pablos, J.L.; Catalina, F. A Switchable fluorescence solid sensor for Hg^{2+} detection in aqueous media based on a photocrosslinked membrane functionalized with (benzimidazolyl)methyl-piperazine derivative of 1,8-naphthalimide. *Sens. Actuators B Chem.* **2018**, *270*, 256–262. [[CrossRef](#)]
48. Kumar, A.; Chae, P.S. Fluorescence tunable thiophene-bis(benzimidazole)-based probes for cascade trace detection of Hg^{2+} and lysine: A molecular switch mimic. *J. Nanosci. Nanotechnol.* **2018**, *18*, 3832–3843. [[CrossRef](#)]
49. Zhang, H.; Zheng, J.; Chao, Y.; Zhang, K.; Zhu, Z. Surface engineering of FeCo-based electrocatalysts supported on carbon paper by incorporating non-noble metals for water oxidation. *New J. Chem.* **2018**, *42*, 7254–7261. [[CrossRef](#)]
50. Materazzi, S.; Risoluti, R.; Gullifa, G.; Fabiano, M.A.; Frati, P.; Santurro, A.; Scopetti, M.; Fineschi, V. New frontiers in thermal analysis. A TG/Chemometrics approach for postmortem interval estimation in vitreous humor. *J. Therm. Anal. Calorim.* **2017**, *130*, 549–557. [[CrossRef](#)]
51. Risoluti, R.; Materazzi, S.; Sorrentino, F.; Maffei, L.; Caprari, P. Thermogravimetric analysis coupled with chemometrics as a powerful predictive tool for β -thalassemia screening. *Talanta* **2016**, *159*, 425. [[CrossRef](#)] [[PubMed](#)]
52. Risoluti, R.; Gregori, A.; Schiavone, S.; Materazzi, S. “Click and Screen” Technology for the Detection of Explosives on Human Hands by a Portable MicroNIR–Chemometrics Platform. *Anal. Chem.* **2018**, *90*, 4288. [[CrossRef](#)] [[PubMed](#)]
53. Materazzi, S.; Peluso, G.; Ripani, L.; Risoluti, R. High-throughput prediction of AKB48 in emerging illicit products by NIR spectroscopy and chemometrics. *Microchem. J.* **2017**, *134*, 277. [[CrossRef](#)]
54. Materazzi, S.; Risoluti, R.; Pinci, S.; Romolo, F.S. New insights in forensic chemistry: NIR/Chemometrics analysis of toners for questioned documents examination. *Talanta* **2017**, *174*, 673. [[CrossRef](#)] [[PubMed](#)]
55. Materazzi, S.; Gregori, A.; Ripani, L.; Apriceno, A.; Risoluti, R. Cocaine profiling: Implementation of a predictive model by ATR-FTIR coupled with chemometrics in forensic chemistry. *Talanta* **2017**, *166*, 328. [[CrossRef](#)] [[PubMed](#)]
56. Risoluti, R.; Materazzi, S.; Gregori, A.; Ripani, L. Early detection of emerging street drugs by near infrared spectroscopy and chemometrics. *Talanta* **2016**, *153*, 407. [[CrossRef](#)] [[PubMed](#)]
57. Materazzi, S.; Risoluti, R.; Napoli, A. EGA-MS study to characterize the thermally induced decomposition of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,1-diaminobutane-Schiff base. *Thermochim. Acta* **2015**, *606*, 90. [[CrossRef](#)]
58. Materazzi, S.; Risoluti, R.; Finamore, J.; Napoli, A. Divalent Transition Metal Complexes of 2-(Pyridin-2-yl)imidazole: Evolved Gas Analysis Predicting Model to Provide Characteristic Coordination. *Microchem. J.* **2014**, *115*, 27. [[CrossRef](#)]
59. Materazzi, S.; Napoli, A.; Finamore, J.; Risoluti, R.; D’Arienzo, S. Characterization of thermally induced mechanisms by mass spectrometry-evolved gas analysis (EGA-MS): A study of divalent cobalt and zinc biomimetic complexes with *N*-heterocyclic dicarboxylic ligands. *Int. J. Mass Spectrom.* **2014**, *365/366*, 372. [[CrossRef](#)]

60. Materazzi, S.; Foti, C.; Crea, F.; Risoluti, R.; Finamore, J. Biomimetic complexes of divalent cobalt and zinc with N-heterocyclic dicarboxylic ligands. *Thermochim. Acta* **2014**, *580*, 7. [[CrossRef](#)]
61. Papadopoulos, C.; Cristóvão, B.; Ferenc, W.; Hatzidimitriou, A.; Vecchio Cipriotti, S.; Risoluti, R.; Lalia-Kantouri, M. Thermoanalytical, magnetic and structural investigation of neutral Co(II) complexes with 2,2'-dipyridylamine and salicylaldehydes. *J. Therm. Anal. Calorim.* **2016**, *123*, 717. [[CrossRef](#)]
62. Risoluti, R.; Piazzese, D.; Napoli, A.; Materazzi, S. Study of [2-(2'-pyridyl)imidazole] complexes to confirm two main characteristic thermoanalytical behaviors of transition metal complexes based on imidazole derivatives. *J. Anal. Appl. Pyrolysis* **2016**, *117*, 82. [[CrossRef](#)]
63. Risoluti, R.; Gullifa, G.; Fabiano, M.A.; Iona, R.; Zuccatosta, F.; Wo, L.W.; Materazzi, S. Divalent Transition Metal Complexes of 2-(Pyridin-2-yl)imidazole: Evolved Gas Analysis Predicting Model to Provide Characteristic Coordination. *Russ. J. Gen. Chem.* **2017**, *87*, 2915. [[CrossRef](#)]
64. Risoluti, R.; Gullifa, G.; Fabiano, M.A.; Wo, L.W.; Materazzi, S. Biomimetic complexes of Cd(II), Mn(II), and Zn(II) with 1,1-diaminobutane–Schiff base. EGA/MS study of the thermally induced decomposition. *Russ. J. Gen. Chem.* **2017**, *87*, 564. [[CrossRef](#)]
65. Risoluti, R.; Gullifa, G.; Fabiano, M.A.; Wo, L.W.; Materazzi, S. Biomimetic complexes of Cd(II), Mn(II), and Zn(II) with 2-aminomethylbenzimidazole. EGA/MS characterization of the thermally induced decomposition. *Russ. J. Gen. Chem.* **2017**, *87*, 300. [[CrossRef](#)]
66. Risoluti, R.; Gullifa, G.; Fabiano, M.A.; Materazzi, S. Biomimetic complexes of Co(II), Mn(II), and Ni(II) with 2-propyl-4,5-imidazoledicarboxylic acid. EGA–MS characterization of the thermally induced decomposition. *Russ. J. Gen. Chem.* **2015**, *85*, 2374. [[CrossRef](#)]
67. Materazzi, S.; Curini, R.; D'Ascenzo, G. Thermoanalytical study of benzimidazole complexes with transition metal ions: Copper (II) complexes. *Thermochim. Acta* **1996**, *286*, 1–15. [[CrossRef](#)]
68. Materazzi, S.; Vecchio, S.; Wo, L.W.; De Angelis Curtis, S. TG–MS and TG–FTIR studies of imidazole-substituted coordination compounds: Co(II) and Ni(II)-complexes of bis(1-methylimidazol-2-yl)ketone. *Thermochim. Acta* **2012**, *543*, 183. [[CrossRef](#)]
69. De Angelis Curtis, S.; Kurdziel, K.; Materazzi, S.; Vecchio, S. Crystal structure and thermoanalytical study of a manganese(II) complex with 1-allylimidazole. *J. Therm. Anal. Calorim.* **2008**, *92*, 109. [[CrossRef](#)]
70. Yang, Z.; Chen, N.; Wang, C.; Yan, L.; Li, G. Syntheses, Crystal Structures, and Properties of Four Complexes Constructed from 2-Propyl-1H-Imidazole-4,5- Dicarboxylic Acid. *Synth. React. Inorg. Met. Org. Nano Met. Chem.* **2012**, *42*, 336. [[CrossRef](#)]
71. Bretti, C.; Crea, F.; De Stefano, C.; Foti, C.; Materazzi, S.; Vianelli, G. Thermodynamic Properties of Dopamine in Aqueous Solution. Acid–Base Properties, Distribution, and Activity Coefficients in NaCl Aqueous Solutions at Different Ionic Strengths and Temperatures. *J. Chem. Eng. Data* **2013**, *58*, 2835–2847. [[CrossRef](#)]

Sample Availability: Samples of the compounds are not available from the authors.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).