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# Imidazolidine Ring Cleavage upon Complexation with First Row Transition Metals

Khaled Cheaib, Christian Herrero, Régis Guillot, Frédéric Banse,\* Jean-Pierre Mahy,\* Frédéric Avenier\*

Abstract: The reaction of a cyclic di-aminal ligand, obtained from the reaction of N,N'-bis(2-pyridylmethyl) ethane-1,2-diamine as a secondary diamine and isophthalaldehyde, with different first row transition metal ions such as Fe(III), Zn(II), Cu(II) and Cu(I) was explored using UV-visible kinetic studies, and cyclic voltammetry. The 3D structure of the resulting metal complexes were determined by X-Ray diffraction analysis. We demonstrate that the ring cleavage reaction of the imidazolidine ligand upon complexation with various metal ions depends on the Lewis acidity of the metal ions, as well as on the coordinative requirements of the metal centers. With a soft acid such as Cu(I), the di-aminal ligand was unmodified and stabilized tricoordinated planar cuprous ions. In contrast, in the presence of harder acids, such as Fe(III), Zn(II) and Cu(II), the diaminal ligand undergoes hydrolysis/cleavage to yield complexes of the tetradentate N,N-bis(2-pyridylmethyl) ethane-1,2-diamine ligand. Interestingly, it was also observed that the ring cleavage reaction in presence of Fe(III) led to the formation of Fe(II) complexes. However, we demonstrate that these two events are independent from each other.

#### Introduction

Imidazolidines, also known aminals or as tetrahydroimidazoles,<sup>1</sup> have attracted much attention due to their usefulness in diverse applications. They have indeed proven their importance in biological systems and pharmaceutical processes,<sup>2-6</sup> and their potential as protective groups in organic synthesis7 as well as sacrificial chiral ligands in asymmetric catalysis.8 In these latter cases, their attractiveness is largely due to their dynamic behavior in solution. Indeed, while they are stable under basic conditions, they can be hydrolyzed under acidic ones9 and these properties involving reversible formation of aminals have been nicely exploited in dynamic combinatorial chemistry for the controlled release of bioactive volatiles.<sup>10,11</sup> Studying the reactivity of this class of compounds is thus of great interest in order to control their fate and improve their use in various applications.

 Khaled Cheaib, Christian Herrero, Régis Guillot, Frédéric Banse, Jean-Pierre Mahy, Frédéric Avenier Institut de Chimie Moléculaire et des Matériaux d'Orsay (UMR CNRS 8182) Univ. Paris Sud, Université Paris Saclay 91405 Orsay Cedex, France.
 E-mail: <u>frederic.banse@u-psud.fr</u>; <u>frederic.avenier@u-psud.fr</u>;

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The principal method of synthesis of imidazolidines involves the reaction of aldehydes with aliphatic 1,2-diamines in which both amine groups are secondary. If the polyamine contains primary and secondary amine groups, the condensation products are either exclusively imidazolidines, or mixtures of imidazolidines and of the corresponding isomeric acyclic Schiff base, with relative ratios depending on the aldehyde and diamine substituents.<sup>1</sup>

Upon complexation with metal ions, both imidazolidine ring formation and opening have been observed in several systems (Scheme 1). The template effect of metal ions in the opening of the imidazolidine ring was investigated with ligands issued from the condensation of one primary and one secondary amine with an aldehyde by two different research groups. Boča et al. (L1, Scheme 1) first reported that imidazolidine ring-closing and ringopening were related to the competition that exists between the Lewis acidity of the metal ion and that of the sp<sup>2</sup>-hybridized imine carbon site.12 The complete opening of the aminal ring could be induced by hard Lewis acids (e. g. Fe(III)) whereas an only partial ring opening could be observed with softer Lewis acids (e. g. Cu(II)).12 In contrast, Tuchagues et al. (L2, Scheme 1) postulated that the size of the metal ion played an important role in shifting the equilibrium toward one tautomeric form or the other.<sup>13</sup> They showed that low spin Fe(II) was small enough to induce a template effect resulting in the opening of the ring, while Ni(II) was too large to be coordinated by the pentadentate open form, therefore stabilizing the tetradentate aminal ring isomer.

In 2009, on the basis of electrochemical data and UV-Visible spectroscopy studies, Sosa-Torres et al. (L3, Scheme 1) detailed the oxidative dehydrogenation of the aminal ring (obtained from a secondary diamine) upon complexation with Fe(III).<sup>14,15</sup> In this case, in addition to the ring opening, the ferric ion was reduced to Fe(II) and the secondary amine located on the ligand skeleton was oxidized to the corresponding imine.

Similar ligands, synthesized from secondary diamines as starting material, (L4, Scheme 1) were extensively studied in order to build metal complexes with specific magnetic properties.<sup>16-23</sup> In the presence of metal ions, cleavage was observed instead of ring opening,<sup>21-23</sup> but this ligand hydrolysis could be inhibited in the presence of exogenous bridging ligands.<sup>17,21</sup>

In the course of our research on dinuclear complexes,<sup>24-26</sup> the synthesis of new polydentate nitrogen ligands led us to explore the reaction of the cyclic di-aminal ligand L (obtained from the reaction of a dialdehyde, isophthalaldehyde, and a secondary diamine, *N*,*N'*-bis(2-pyridylmethyl)-ethane-1,2-diamine) with different first row transition metal ions such as Fe(III), Zn(II), Cu(II) and Cu(I).

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Scheme 1. Imidazolidine ring opening and ring cleavage reactions reported in the literature.<sup>12-23</sup> Counter anions and exogenous ligands are omitted for clarity

In this paper, we demonstrate that the ring cleavage reaction of the imidazolidine ligand upon complexation with various metal ions depends on the Lewis acidity and on the coordination requirements of the metal ions. Interestingly, we also observe that the ring cleavage reaction in presence of Fe(III) leads to the formation of Fe(II) complexes. However, we demonstrate that these two events are independent from each other.

#### **Results and Discussion**

# Complexation of Fe(III), Cu(II) and Zn(II) ions with ring cleavage of the aminal group

The bis-ring imidazolidine ligand L was synthesized by condensation of isophthalaldehyde with two equivalents of N,N'bis(2-pyridylmethyl)-ethane-1,2-diamine (H<sub>2</sub>L') (Scheme S1, Figures S1 to S3). Its reaction with two equivalents of Fe<sup>III</sup>(CIO<sub>4</sub>)<sub>3</sub>•6 H<sub>2</sub>O in acetonitrile under aerobic conditions, induced a progressive color change from red to purple. Slow diffusion of diethyl ether into this solution led to the formation of a red powder in good yield (58%, see Supporting Information, synthesis of C1 method A, Scheme S1). After recrystallization, X-ray diffraction analysis indicated the formation of [Fe<sup>II</sup>(H<sub>2</sub>L')(CH<sub>3</sub>CN)<sub>2</sub>](CIO<sub>4</sub>)<sub>2</sub> revealing that the iron center of complex C1 was in its reduced form (Figure 1 and Scheme 2). The reduction of iron(III) into iron(II) was accompanied by ring cleavage of the aminal rings. Interestingly, C1 could also be obtained with a similar yield (51%) by the direct reaction of H<sub>2</sub>L' with an Fe<sup>II</sup> salt (Supporting Information, synthesis of C1, method B, Scheme S4). The fact that the yields of C1 formation following the two methods are similar indicates that C1 formation from L and an Fe<sup>III</sup> salt is not a parasite reaction.

Complex C1 crystallized in the centrosymmetric monoclinic space group C2/c as a mononuclear Fe<sup>II</sup> species with the ferrous

ion in a distorted octahedral geometry (Figure 1). As shown in Figure 1, H<sub>2</sub>L' acts as a tetradentate neutral ligand in *cis*- $\alpha$  coordination mode (Scheme S2). The pyridyl nitrogens

 $(N_1 \text{ and } N_2)$  occupy the axial coordination positions whereas the secondary amine nitrogens ( $N_3$  and  $N_4$ ) are in the equatorial plane. The octahedral environment of the ferrous ion is completed by the coordination of two CH<sub>3</sub>CN molecules and two ClO<sub>4</sub><sup>-</sup> anions balancing the charge of the cation. The short Fe-N bond distances (average distance of 1.971(2) Å) obtained from the diffraction data are in accordance with a low-spin electronic configuration (S=0) for this complex in the solid state, in agreement with crystallographic data reported by Ray et al.<sup>27</sup>



**Scheme 2.** Reduction/cleavage reaction of L in the presence of 2 equiv. Fe<sup>III</sup> (hydrolysis of the L promoted by Fe<sup>III</sup>).

Upon dissolution in acetonitrile, the UV-Vis spectrum of **C1** (Figure 2A, black trace) shows a charge transfer band at 315 nm ( $\varepsilon \Box ca.$  7000 M<sup>-1</sup>cm<sup>-1</sup>) with a shoulder at 360 nm ( $\varepsilon \Box ca.$  4500 M<sup>-1</sup>cm<sup>-1</sup>) and a low intensity band at 490 nm ( $\varepsilon \Box ca.$  500 M<sup>-1</sup>cm<sup>-1</sup>). This spectrum slowly evolves over 20 hours to give a new charge transfer band at 360 nm that develops at the expense of the band at 315 nm, together with the appearance of a broad absorption at 530 nm. During this slow process, an isosbestic point appears at 335 nm suggesting the existence of two species in equilibrium. This observation is supported by electrochemical studies that reveals the presence of two reversible redox waves with very close potential E<sub>1/2</sub> values of

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0.975 V and 1.135 V vs SCE (Figure 2B). Tetraazadentate ligands can coordinate to an octahedral iron center in three different topologies, *cis*- $\alpha$ , *cis*- $\beta$ , and *trans* forms (Scheme S2).<sup>28</sup> Similar tetradentate ligands, the cyclohexyl derivatives BPMCN and BQCN, have been shown to give Fe(II) complexes with either a *cis*- $\alpha$  or *cis*- $\beta$  geometry, depending on the synthetic

route used.<sup>29-31</sup> Additionally, it was also demonstrated that the

structure observed in the solid-state did not represent the only



Figure 1. Structure of the molecular cation of C1 determined by X-ray diffraction analysis.

geometry in solution, as dynamic equilibria between complexes with different geometries (*cis*- $\alpha$ , *cis*- $\beta$ , and *trans*) were observed in solution.<sup>32,33</sup> In the case of C1, Britovsek et al. have reported <sup>1</sup>H NMR evidences of rearrangements between geometrical isomers.<sup>28</sup> This fluxional behaviour may be related to the low spin (S=0) to high spin (S=2) spin crossover observed in acetonitrile solution.<sup>28</sup> Therefore, one can assume that the final UV-Vis spectrum (Figure 2A, red trace) corresponds either to the trans or the cis- $\beta$  isomer, whereas the initial one (Figure 2A, black trace) is characteristic of the  $cis-\alpha$  complex characterized by X-ray crystallography. By analogy with electronic absorption spectra of similar amine/pyridine Fe(II) complexes, the two sets of bands observed can be assigned to ligand-centred  $\pi$ - $\pi^*$ transitions ( $\lambda_{max}$  < 270 nm) and to metal-to-ligand charge transfer transitions (MLCT, *λ*<sub>max</sub>= 368 nm, ε□ca. 6500 M<sup>-1</sup>cm<sup>-1</sup> and 530 nm ɛ□ca. 2000 M<sup>-1</sup>cm<sup>-1</sup>).34 The MLCT extinction coefficient values are intermediate between low spin (S=0) and high spin (S=2) Fe<sup>II</sup> complexes,<sup>35</sup> which supports the existence of a spin state equilibrium for C1 in solution.



Figure 2. (A) Evolution as a function of time of the UV-Visible spectrum of C1 0.2 mM in CH<sub>3</sub>CN (black trace, t=0; red trace, t= 20 h). (B) Cyclic voltammetry

of C1 after time evolution (corresponding to the red trace on panel A); 1mM in 0.1 M TBAPF\_6 / CH\_3CN, 100 mV.s^{-1}

In order to better understand why complex C1 was formed when the ligand L was mixed with 2 equivalents of Fe<sup>III</sup>(CIO<sub>4</sub>)<sub>3</sub>•6 H<sub>2</sub>O in acetonitrile, the reaction was followed by UV-Visible spectroscopy (Figure 3A). The initial mixture of L + 2 equiv. Fe(III) did not exhibit any feature in the visible, except for tails of intense UV absorptions (Figure 3A, black trace). Then, the characteristic absorption band of C1 at 530 nm increased gradually during the course of the reaction (Figure 3A and 3B, red traces). Interestingly, the reaction seemed to proceed in two stages, as suggested by the time evolution of the spectra in the UV region (Figure 3B, black trace). One may assign the first phase of the evolution to the redox/cleavage reaction of Fe(III) and L to yield C1. This irreversible reaction proceeds without any isosbestic point (from bold black to blue trace; Figure 3A). The second stage would correspond to the equilibrium between the different isomers of C1 in solution (from blue to red), which is clearly evidenced by the isosbestic point observed at 335 nm. The final spectrum (Figure 3A, red trace), is identical to that observed for the isolated complex C1 in solution (Figure 2A, red trace). The characteristic 530 nm absorption band in the final spectrum (red trace) displayed an electronic extinction coefficient (ca. 2000 M<sup>-1</sup>.cm<sup>-1</sup>) that matches the absorptivity of C1 in its steady state equilibrium. This indicates that the reaction



Figure 3. (A) Evolution of the cleavage/reduction reaction of L promoted by Fe(III) (0.05 mM L and 0.1 mM Fe<sup>III</sup>(CIO<sub>4</sub>)<sub>3</sub>•6 H<sub>2</sub>O in CH<sub>3</sub>CN) monitored by UV-Visible spectroscopy. Black trace: initial spectrum, blue to red trace: equilibrium between both forms of C1 evidenced by the isosbestic point observed at 335 nm. (B) Time traces at 320 nm (black trace) and 530 nm red trace).

was almost quantitative, *i.e.* L was quantitatively transformed into H<sub>2</sub>L' while Fe(III) was completely reduced to Fe(II). Control experiments confirmed that light and dioxygen had no effect on the redox/ring cleavage process. Once evolution of the absorption spectrum stopped, the solution was filtered off on silica and the structure of the organic compound remaining in solution was found to be that of isophthalaldehyde, as shown by <sup>1</sup>H NMR (Figure S4). This confirmed that the interaction of the bis-imidazolidine (L) with iron led to its hydrolysis, yielding C1 and the starting isophthalaldehyde fragment (Scheme 2). In contrast, in the absence of a metal salt, L was stable in acetonitrile, methanol or chloroform as no trace of

decomposition could be observed both by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as well as ESI MS analysis (Figures S1 to S3).

# Concerning ligand hydrolysis and the effect of different metal ions.

In order to understand the ring cleavage reaction of L promoted by Fe(III), different first row transition metals were used, such as Zn(II) as redox inactive and Cu(II) and Cu(I) as redox active metal ions. Addition of two equivalents of MII(OTf)2 (M= Zn or Cu) in acetonitrile or methanol solution to one equivalent of L induced the hydrolytic cleavage of the aminal ring and the formation of M<sup>II</sup>(H<sub>2</sub>L') complexes (C2 M=Zn, and C3 M=Cu, Scheme S3). The isophthalaldehyde fragment and the monotopic tetradentate protonated ligand (H<sub>2</sub>L') were thus generated in a similar way to that described above with Fe(III). In addition, the yield in isolated C2 (65%) and C3 (55%) were similar or better than that in C1 indicating that these two complexes were obtained as main products. The structures of C2 and C3 are shown in Figure 4. Zinc complex C2 adopts a similar geometry to that of the ferrous complex C1. The Zn(II) cation is in a distorted octahedral [ZnN<sub>4</sub>O<sub>2</sub>] environment, surrounded by H<sub>2</sub>L' acting as a tetradentate ligand in a  $cis-\alpha$ mode. The coordination sphere is completed by two water molecules (Figure 4, left).

Alternatively, by adding Cu(II) to ligand L, a different geometry of  $H_2L'$  was stabilized for complex **C3** in the solid state. It adopted a trans coordination mode around the metal center (Figure 4, right) with the cupric ion coordinated by four N atoms



Figure 4. Structure of the molecular cations of C2 (left) and C3 (right) determined by X-ray diffraction analysis.

of the ancillary ligand and two *trans* triflate anions in the axial positions. The resulting molecular complex had an octahedral coordination geometry with the main tetragonal distortion departing from an ideal geometry due to a strong Jahn–Teller effect. Apical bond lengths (Cu1–O6, 2.46 Å, and Cu1–O2, 2.53 Å) were very long by comparison to the equatorial Cu-N bond lengths (*ca.* 2 Å). The mean Cu(II)–O (triflate) bond length computed from 128 hits in the CSD was approximately 2.55 Å, which confirmed that triflate ions were weakly bonded in **C3**.<sup>36</sup>

#### Complexation of Cu(I) ions with retention of ligand integrity

When Cu(I) was used as a metal precursor, the bisimidazolidine ligand (L) remained stable and did not undergo any ring cleavage. The reaction of one equivalent of L with two equivalents of Cu<sup>I</sup>(OTf) under argon atmosphere, resulted in the formation of a colourless compound (Figure 5A). Recrystallization of this compound led to the formation of single crystals suitable for X-Ray diffraction analysis. The resulting structure displayed in Figure 5B shows the formation of complex **C4** ([Cu<sub>2</sub>(L)](OTf)<sub>2</sub>) that bears two crystallographically independent cuprous ions.



Figure 5. (A) Synthesis and schematic representation of the formation of C4. (B) Structure of the molecular cation of C4 determined by X-ray diffraction analysis.

Each Cu(I) is three fold coordinated to two pyridyl nitrogens (N1, N2 for Cu1 and N5, N6 for Cu2) and one imidazolidine nitrogen (N3 for Cu1 and N4 for Cu2) in a distorted trigonal planar geometry. In contrast, N7 and N8 are not coordinated to a copper center, as shown by Cu1—N8 and Cu2—N7 distances of 3.714(4) and 3.609(4) Å, respectively. Cu-Nimidazolidine bond lengths (Cu1—N3 2.213(4) Å and Cu2—N4 2.210(4) Å) fall in the range of Cu-N<sub>amine</sub> distances for which copper adopts the same trigonal geometry.<sup>37,38</sup> Consequently, C27—N4 (1.499(6) Å) and C30—N3 (1.480(6) Å) are significantly elongated compared to C-N<sub>imidazolidine</sub> in which the N atom is uncoordinated (C30—N7 1.454(6) Å and C27—N8 1.461(6) Å). These structural data reveal a weakening of the C27—N4 and C30—N3 bonds induced by coordination to the metal center, in agreement with their elongation.

In light of these observations, the cleavage of the imidazolidine rings during complexation may be discussed in terms of the Lewis acidity of the metal ion and stability of the final complexes with respect to that of the starting  $(L + 2 M^{z+})$ compounds. Upon coordination to the metal center, L chelates the metal center as observed in complex C4. This results in an elongation of two of the C-N<sub>imidazolidine</sub> bonds revealing a polarization of these and an increased electrophilic character of the sp<sup>3</sup>-hybridized imidazolidine carbon atoms. These  $C^{\delta^+}$  atoms become more prone to nucleophilic attack by adventitious water molecules, which leads to the hydrolysis of the aminal ring. Thus, it is likely that a soft Lewis acid, such as Cu(I), does not induce a strong enough polarization and does not promote hydrolysis of the imidazolidine rings whereas harder Lewis acids, such as Fe(III), Cu(II) and Zn(II), readily do it. Additionally, the coordinative requirements of Cu(I) allow the stabilization of the

closed form of the ligand (L). In contrast, hydrolysis/cleavage from L to  $H_2L'$  leads to a stronger Lewis base due to a gain of denticity of the ligand, for which Fe(III), Cu(II) and Zn(II) have higher affinity. Furthermore, the chelation of the metal ion by  $H_2L'$  leads to three five membered metallocycles and thus, additional stabilization of the final species, while coordination by L, with only one five membered metallocycle, provides a much weaker chelate effect (Scheme 3).

# Concerning the reduction of $\mathrm{Fe}^{\mathrm{III}}$ into $\mathrm{Fe}^{\mathrm{II}}$ during the imidazolidine ring cleavage.

Control experiments (under argon atmosphere and protected from light) confirmed that there was no effect of light and/or dioxygen on the redox/ring cleavage process. In order to better understand the reduction of Fe(III) and its possible relation to the ring cleavage process, complexation of one equivalent of  $Fe^{III}(CIO_4)_3$ ·6H<sub>2</sub>O with the tetradentate ligand H<sub>2</sub>L' was carried out under aerobic conditions (Scheme S5). In this case, spontaneous reduction took place and the ferrous complex C1 was obtained. It is worth noting that water molecules present in solution were not oxidized to dioxygen. Indeed, no evolution of dioxygen could be detected when the reaction was followed using a Clark electrode, and no ligand oxidation could be observed as well. In C1, both the C-N<sub>amine</sub> average bond lengths (1.484(3) Å) and the C-C bond length of the ethylenediamine fragment (1.511(4) Å) are consistent with a single bond character.



Scheme 3. Chelating characteristics of the ligands H<sub>2</sub>L' and L

Spontaneous reduction of the Fe(III) under aerobic conditions is quite rare in iron coordination chemistry. A few examples of spontaneous reduction of a ferric ion chelated with bis(methylimidazolyl)ketone,<sup>39</sup> salicyloyl hydrazonodithiolane,<sup>40</sup> hydrazide,<sup>41</sup> or Schiff base ligands<sup>42-44</sup> have been identified in the literature, but the mechanism of the reduction has not been reported. Nevertheless, Sosa-Torres et al. reported that oxidative dehydrogenation of polyamine ligands in the presence of Fe<sup>III</sup> led to the Fe<sup>II</sup> complexes of the corresponding imine ligands.<sup>14,45</sup> In our case, we were unable to isolate any Fe(III) intermediate complex using Fe(ClO<sub>4</sub>)<sub>3</sub>•6H<sub>2</sub>O as metal salt (Scheme S5). However, the stoichiometric addition of FeCl<sub>3</sub> to methanolic solutions of H<sub>2</sub>L' afforded a high spin ferric complex C5 [Fe<sup>III</sup>(H<sub>2</sub>L')Cl<sub>2</sub>]Cl (Figure S5 and Scheme S5) in high yield (ca. 80 %). Addition of 3 equivalents of silver perchlorate to an acetonitrile solution of C5 allowed to remove chloride ions which

led to the formation of C1 after one night, as revealed by UVvisible measurements. This was confirmed by X-ray diffraction analysis after isolation and recrystallization of the complex (Scheme S5). Thus, these observations indicate that reduction of Fe<sup>III</sup> into Fe<sup>II</sup> is not dependent on any oxidative transformation of H<sub>2</sub>L'. While the Fe<sup>III</sup>(H<sub>2</sub>L') complexes are stable in the presence of chloride as exogenous ligands, they are unstable in their absence. This is consistent with the redox properties observed for both C5, and a stoichiometric mixture of H<sub>2</sub>L' and Fe(ClO<sub>4</sub>)<sub>3</sub>•6H<sub>2</sub>O, when investigated by cyclic voltammetry (Figure 6). Besides the characteristic irreversible anodic wave of the chloride counter ions at high potential, the Fe(III) complex C5 presents a reversible wave at 0.270 V vs SCE. This value is similar to the one reported for [Fe(BPMEN)Cl<sub>2</sub>]<sup>+</sup> by Girerd et al (0.18 V vs SCE).<sup>46</sup> Regarding the H<sub>2</sub>L'/Fe(III) stoichiometric mixture, it displays, after the time evolution discussed above, two reversible redox signals with high positive E<sub>1/2</sub> values (1.197 V and 1.095 V vs SCE) which are characteristic of complex C1 (Figure 2B and Figure 6). These values are in agreement with a good stabilization of the Fe(II) center in C1 and suggest the facile reduction of Fe(III) in the absence of chlorides.

To get insight into the reduction of Fe<sup>III</sup> when complexed to H<sub>2</sub>L', we performed additional experiments in MeOH. Similarly to what happened in acetonitrile, slow evolution into a ferrous purple complex with spectral features similar to C1 was observed by UV-visible spectrocopy, indicating that the nature of the solvent was not a critical parameter. In order to determine if the reduction of Fe(III) happened via a radical mechanism, EPR experiments using PBN as a spin trap were carried out in CH<sub>3</sub>CN/EtOH as solvent (Scheme S6). No conclusive radical trapping information could be obtained, but interestingly, a small amount of a dinuclear Fe(III) complex bridged by an acetate ion was isolated as single crystals (C6, Figure S6). This result indicated that EtOH was oxidized into its corresponding acid during the process, which suggested that solvent could serve as electron donor for Fe(III) reduction during the hydrolysis/cleavage of L to yield the stable complex C1. Additionally, considering that C1 was formed starting from L and a ferric salt, or from H<sub>2</sub>L' and a ferric salt one can conclude that the hydrolysis/cleavage of L and the reduction of Fe(III) are most likely independent from each other.



Figure 6. Cyclic voltammograms of 0.25 mM H<sub>2</sub>L' + 0.5 mM Fe<sup>III</sup>(CIO<sub>4</sub>)<sub>3</sub>•6H<sub>2</sub>O after complete reduction (green) and of 1 mM C5 (red). The cyclic voltammogram of 1 mM C1 after time evolution is shown as the blue trace. Room temperature, 0.1 M TBAPF<sub>6</sub> / CH<sub>3</sub>CN, 100 mV.s<sup>-1</sup>.

The in-depth understanding of the formation of **C6** is out of the scope of this paper. It is indeed a slow process that implies oxidation of the solvent into products that we have not been able to identify yet, except in the case of EtOH. However, one may suggest that upon the reduction of formally four Fe<sup>III</sup>, one EtOH molecule was oxidized to the corresponding acetate (Scheme S6). Owing to the bridging character of acetate, such process would give rise to the formation of dinuclear iron(II) species, which are known to readily react with  $O_2$ ,<sup>47-49</sup> and then would lead to the formation of the dinuclear ferric complex **C6**.

### Conclusions

The fate of the complexes obtained by coordination of metal ions to the imidazolidine ligand L depends on the nature of the metal and its coordinative preference. With a soft Lewis acid such as Cu(I), L is preserved and acts as a tridentate bitopic ligand, even though two of the C-N bonds of the imidazolidine moeties appear weakened upon coordination to the metal cation. When using harder Lewis acids such as Fe(III), Zn(II), and Cu(II), L undergoes hydrolysis/cleavage to yield the tetradentate amine/pyridine ligand H<sub>2</sub>L'. This reaction on the L ligand can be seen as the result of both a stronger polarization, and thus an increased weakening of the C-N bond upon coordination to a harder acid, and to the formation of more stable complexes between H<sub>2</sub>L' and Fe(III), Zn(II), or Cu(II). Independently to ring cleavage of the aminal, the Fe<sup>III</sup>(H<sub>2</sub>L') complex is slowly reduced, most probably by the solvent, leading to the formation of its Fe(II) counterpart which exhibits a strong redox stability, as determined by cyclic voltametry.

#### **Experimental Section**

**abbreviations:** BPMCN, *N*,*N*-bis(2-pyridylmethyl)-*N*,*N*-dimethyl-*trans*-1,2-diaminocyclohexane; BQCN, *N*,*N*-bis(8-quinolyl)-*N*,*N*-dimethyl-*trans*-1,2-diaminocyclohexane; PBN (Phenyl *N*-t-butylnitrone); BPMEN, *N*,*N*-dimethyl-N,N'-bis(pyridylmethyl)ethylenediamine)

Chemicals were purchased from Aldrich and TCI and were used without purification. All solvents except for DCM, CH<sub>3</sub>CN and MeOH were purchased from Aldrich or VWR and were used as received. NMR spectra were taken either on a Brucker AV 250 MHz or on a Brucker 300 MHz spectrometer using the residual protonated solvent as internal standard. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) and coupling constants (J) are reported in hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), and doublet of doublet of doublet (ddd). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were taken on a Thermo Scientific TSQ, or a Bruker microTOF in the positive mode of detection (ESI+).

**Electronic absorption spectroscopy.** All experiments were carried out with a Varian Cary 300-bio or a Cary 60 spectrophotometer in quartz cuvette with one cm optical path length.

**Electrochemistry.** All electrochemical experiments were run under an argon atmosphere. Cyclic voltammetry measurements were recorded using an Autolab potentiostat controlled with a Nova 1.10 software package. The counter electrode used was a Pt wire and the working electrode was a glassy carbon disk carefully polished before each voltammogram with 1  $\mu$ m diamond paste, sonicated in an ethanol bath, and washed with ethanol. The reference electrode used was a SCE electrode isolated from the rest of the solution by a fritted bridge. Experiments were run in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

X-ray diffraction. X-ray diffraction data for compounds C1 and C6 were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoKa radiation. X-ray diffraction data for compounds C2, C3, C4 and C5 were collected by using a Kappa VENTURE PHOTON 100 Bruker diffractometer with IµS microfocus graphite-monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flash frozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-971 and refined against F2 by full-matrix leastsquares techniques using SHELXL-2014 or 20162 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX. CCDC 1530705-1530710 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via

http://www.ccdc.cam.ac.uk/Community/Requestastructure.

1,3-bis(1,3-bis(pyridin-2-ylmethyl)imidazolidin-2-yl)benzene (L). N,Nbis(2pyridylmethyl) ethane-1,2-diamine<sup>4</sup> ( $H_2L'$ ) (2 g, 8.25 mmol) was dissolved in 35 mL of diethyl ether. To this solution was added isophthaladehyde (553 mg, 4.126 mmol) dissolved in 15 mL of diethyl ether. The mixture was allowed to react overnight. The product (L) was precipitated as a white powder and was then filtered on a fritted glass and washed with diethyl ether. The filtrate was concentrated and recrystallized in a minimum amount of diethyl ether. L: 2.2 g, 91% yield. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 8.41 (d, 4H, J= 4.2 Hz, Py-H); δ 7.88 (s, 1H, phenyl-H); δ 7.58 (d, 2H, J= 4.2 Hz, phenyl-H); δ 7.48 (t, 4H, J= 7.5 Hz, Py-H);  $\delta$  7.32 (broad, 5H, phenyl-H and Py-H);  $\delta$  7.03 (t, 4H, J= 6.2 Hz, Py-H); δ 4.05 (s, 2H, N-CH-N); δ 3.86 (d, 4H, <sup>2</sup>J=14.4Hz, Py-CH2) δ 3.51 (d, 4H, <sup>2</sup>J=14.4Hz, Py-CH2); δ 3.31 (m, 4H, N-CH2-CH2-N); δ 2.68 (m, 4H, N-CH2-CH2-N). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 159.4, 148.6, 140, 136.2, 130.6, 129.8, 128.2, 122.7, 121.7, 88.9, 58.8, 51.2. HRMS (ESI+),  $\label{eq:masses} [M+H]^{+}{=}~583.3298. \ Calculated~for~C_{36}H_{39}N_8 = 583.3219.$ 

[Fe<sup>II</sup>(H<sub>2</sub>L')(CH<sub>3</sub>CN)](CIO<sub>4</sub>)<sub>2</sub> (C1) has been synthesised via two different methods. *Method A.* A solution of Fe<sup>III</sup>(CIO<sub>4</sub>)<sub>3</sub>•6 H<sub>2</sub>O (80 mg, 0.17 mmol) in 2 mL of acetonitrile was slowly added to L (50 mg, 0.085 mmol) and stirred for 6 hours at room temperature under aerobic conditions. The color of the solution changed from red to purple. The solvent was evaporated under reduced pressure and the resulting pasty complex was dissolved in small amount of CH<sub>3</sub>CN/DCM (0.1 mL / 2 mL) and precipitated with Et<sub>2</sub>O. The red solid was filtered, washed with diethyl

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ether and dried under vacuum. C1: 57 mg, Yield: 58 %. Crystals of C1 that were suitable for X-Ray diffraction were grown by diffusing diethyl ether into an acetonitrile solution of C1. Method B. In a glovebox, a solution of Fe<sup>II</sup>Cl<sub>2</sub> (34.5 mg, 0.27 mmol) in acetonitrile (2 mL) was added to a stirred solution of H<sub>2</sub>L' (66 mg, 0.27 mmol) in acetonitrile (2 mL). After stirring for 15 min, the mixture was then treated with 2 mL of an acetonitrile solution of AgClO<sub>4</sub> (112 mg, 0.54 mmol), resulting in the formation of a white precipitate of AgCl, which was filtered away after allowing the mixture to stir. The filtrate was then dried under vacuum, redissolved in CH\_3CN/DCM (0.1 mL / 2 mL) and precipitated with Et\_2O, yielding the desired complex as a red powder. C1: 80 mg, Yield 51%. HRMS (ESI+), m/z [Fe<sup>II</sup>(H<sub>2</sub>L')(OH)]+= 333.056. Calculated for  $C_{14}H_{21}FeN_4O_2$  = 333.10. Crystals of C1 that were suitable for X-Ray diffraction were grown by diffusing diethyl ether into an acetonitrile solution of C1. Caution! Perchlorate salts are potentially explosive and should be handled with care.

$$\label{eq:linear} \begin{split} & [\text{Zn}(\text{H}_2\text{L}')(\text{H}_2\text{O})_2](\text{OTf})_2 \ (\text{C2}). \mbox{A solution of } Zn(\text{OTf})_2; \ 6\text{H}_2\text{O} \ (31 \mbox{ mg}, \ 0.085 \mbox{mmol}) \mbox{ in 2 mL of acetonitrile was slowly added to L (25 \mbox{ mg}, \ 0.043 \mbox{ mmol}) \mbox{ and stirred for 2 hours at room temperature under aerobic conditions. \mbox{The solvent was evaporated under reduced pressure and the resulting light yellow powder was redissolved in 0.5 mL of DCM and precipitated with EtzO. The light yellow solid was filtered, washed with diethyl ether and dried in vacuum. C2: 44 \mbox{ mg}, \ Yield: \ 65\%. \ HRMS \ (ESI^+), \ m/z \ [Zn^{II}(\text{H}_2\text{L}')(\text{OTf})]^+ = \ 455.01. \ Calculated \ for \ ZnC_{15}H_{18}F_3N_4O_3S \ 455.03. \ Crystals \ of \ C2 \ that were suitable \ for \ X-Ray diffraction were grown \ by slow evaporation of a DCM/EtzO \ (1/1) \ solution of \ C2. \ \end{tabular}$$

Cu(H<sub>2</sub>L')(OTf)<sub>2</sub> (C3). A solution of Cu(OTf)<sub>2</sub> (37.2 mg, 0.1 mmol) in 2 mL of acetonitrile was slowly added to L (30 mg, 0.05 mmol) and stirred for 36 hours at room temperature under aerobic conditions. The solution was filtered through a filter paper and the solvent was removed under reduced pressure. The blue powder of the desired complex was filtered, washed with Et<sub>2</sub>O and dried under vacuum. C3: 34.1 mg, yield: 55 % HRMS (ESI<sup>+</sup>), m/z [Cu<sup>II</sup>(H<sub>2</sub>L')(OTf)]<sup>+</sup>= 454.035. Calculated for C<sub>15</sub>H<sub>18</sub>CuF<sub>3</sub>N<sub>4</sub>O<sub>3</sub>S = 454.04 Crystals of C3 that were suitable for X-Ray diffraction were grown by diffusing diethyl ether into a DCM/CH<sub>3</sub>CN solution of C3.

[Cu<sub>2</sub>(L)](OTf)<sub>2</sub> (C4). The ligand L and [Cu<sup>1</sup>(OTf)]<sub>2</sub>;Ce<sub>B</sub>H<sub>5</sub>CH<sub>3</sub> being insoluble in acetonitrile, the synthesis has been carried out in a toluene/DCM (1/1 v/v) mixture. Note that attempts to synthesize C4 in MeOH led to Cu<sup>1</sup> oxidation into Cu<sup>11</sup>. In a glovebox, a brown solution of [Cu<sup>1</sup>(OTf)]<sub>2</sub>; Ce<sub>B</sub>H<sub>5</sub>CH<sub>3</sub> (26.6 mg, 0.051 mmol) in toluene (2 mL) was added dropwise to a light yellow stirred solution of L (30 mg, 0.051 mmol) in DCM (2 mL). After stirring for three hours the desired complex was precipitated as a silver crystalline powder C4. After 30 min of centrifugation the filtrate was removed, the silver powder was washed with diethyl ether and dried under vacuum. C4: 36 mg, Yield: 70%. Crystals of C4 that were suitable for X-Ray diffraction were grown by diffusion of diethyl ether into an acetone solution of C4.

 $\label{eq:horsestation} \begin{array}{l} \mbox{[FeII]}(H_2L')(CI)_2]CI (C5). \mbox{ A solution of FeCI}_3 (9.9 mg, 0.061 mmol) in 2 mL of MeOH was slowly added to a solution of H_2L' (15 mg, 0.061 mmol) in MeOH (1mL) and stirred for 2 hours at room temperature under aerobic conditions. C5 was isolated as a yellow crystals suitable for X-Ray diffraction by slow evaporation of the previous solution. C5: 19 mg, yield: 80%. Crystals were washed with Et_2O and dried under vacuum. \end{array}$ 

**[Fe<sup>III</sup><sub>2</sub>(μ-O)(μ-OAc)(H<sub>2</sub>L')](CIO<sub>4</sub>)<sub>3</sub> (C6).** A solution of Fe<sup>III</sup>(CIO<sub>4</sub>)<sub>3</sub>•6H<sub>2</sub>O (22.1 mg, 0.048 mmol) in 3 mL of EtOH was slowly added to a solution of H<sub>2</sub>L' (11.6 mg, 0.048 mmol) and *N-tert*-Butyl-α-phenylnitrone (22.8 mg, 0.144 mmol) in 2 mL of EtOH. A precipitation took place. 2 mL of acetonitrile were added in order to solubilize the mixture and the resulting

homogeneous solution was then stirred overnight. Crystals of **C6** were obtained by slow evaporation of the solution mixture. The quantity of crystals obtained was not enough to determine the yield of product formation.

**Supporting Information**, including schemes S1 to S6, figures S1 to S6 and tables S1 to S2, is available from the link on the first page of this paper.

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# **FULL PAPER**

Reaction of the imidazolidine ligand upon complexation with various first row transition metals (Fe(III), Zn(II), Cu(II) and Cu(I)) depends on the Lewis acidity of the metal ions, as well as on the coordinative requirements of the metal centers.



#### Imidazolidine complexation

Khaled Cheaib, Christian Herrero, Régis Guillot, Frédéric Banse, Jean-Pierre Mahy, Frédéric Avenier

Imidazolidine Ring Cleavage upon Complexation with First Row Transition Metals

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