EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

SHORT COMMUNICATION

DOI:10.1002/ejic.201402140

Electrochemical Implication of a Hydrogen-Bonded Imidazole on a Redox-Active-Bound Phenolate Group

Sanae El Ghachtouli,[a][‡] Benedikt Lassalle-Kaiser,[b][‡‡] Régis Guillot,[a] and Ally Aukauloo*[a,b]

Keywords: Redox chemistry / Electrochemistry / Zinc / N,O ligands / Radicals

We report the synthesis of a pentadentate N_4O ligand with an imidazole group in the *ortho* position of the phenol group. The syntheses and crystallographic structures are reported for zinc(II) complexes by using the previously reported *tert*-butyl-substituted ligand and the imidazole-substituted ligand in two different protonation states. We describe the influence of the *ortho* substituent (*tert*-butyl, imidazole, and imidazolium) on the electrochemical behavior of the zinc(II) complexes. The substitution of the *tert*-butyl group in the *ortho* position by an imidazole group shifts the oxidation potential of the phenolate by more than 300 mV. The *o*-*tert*-butyl-substituted ligand allows the formation of a stable radical phenoxylzinc(II) complex upon electrochemical oxidation, but it is unstable in the case of the imidazole-substituted complex. The imidazole-substituted ligand can be reversibly protonated without altering the electrochemical properties of the phenolate group.

Introduction

Redox-active ligands have played an important role in the development of modern coordination chemistry.[1] These non-innocent ligands play an active role in the electronic structure of metal complexes and have led to recurring controversies concerning the attribution of oxidation states.[2] Only recent advanced spectroscopic methods have allowed the electronic states of such metal–radical species to be deciphered.[3] Since it was established that metalloradical species play an active role in the functioning of several metalloenzymes,[4] chemists have devoted considerable effort to the design and characterization of such species. In some particular cases, the electronic properties of these metalloradical species have been modulated by subtle effects in the coordination sphere of the metal ion.[5] For instance, coordination of an exogenous ligand, second-coordination-sphere substituents, or weak interactions (such as hydrogen bonding) can shift the locus of the lone electron from the metal to the ligand.[6] The control of the reactivity of such metalloradical species requires the understanding of their electronic properties. In a recent review, Crabtree et al.[7] discussed the unique catalytic properties of a variety of metal–radical species. It makes no doubt that the participation of the ligand in the catalytic scheme of metal complexes has opened new perspectives in the field of molecular catalysis. In particular, phenolate-containing ligands surrounding metal ions have been shown to participate in the redox activity of metal complexes.[8] For example, previous studies have shown that phenoxyl radicals can be stabilized by deprotonation of an imidazole substituent in the *para* position of the phenyl ring,[9] whereas ligand sets with a donor *O*-phenol group and an *N*-imidazole function in the *ortho* position bound to a metal center were found to generate stable metalloradical species.

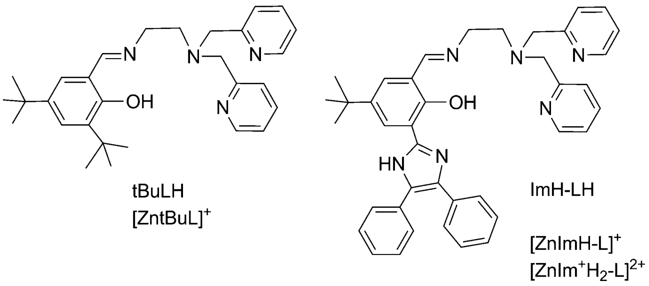
In a previous study, we reported the synthesis and properties of a pentadentate ligand bearing a half-salen motif coordinating a manganese ion.[10] We showed how second-coordination-sphere water molecules play an active role in stabilizing high-oxidation-state species of this complex. The working hypothesis was that the water molecules in the second coordination sphere help in assisting the deprotonation of the metal-bound water molecule. In a subsequent study, to further investigate the proton-coupled electron-transfer process of a water molecule ligated to a manganese ion, we developed a derivative of the pentadentate ligand LH holding a benzimidazole fragment disposed in the *ortho* position of the phenol group to develop a hydrogen-bonding interaction with the water molecule at the metal center. Unexpectedly we noticed that this modified version of ligand LH led to stabilization of the Mn^{II} complex, and the one-electron oxidation process was irreversible in contrast to that of the

---

[a] Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR-CNRS 8182, Université de Paris-Sud XI,
91405 Orsay, France
E-mail: ally.aukauloo@u-psud.fr
http://www.icmmo.u-psud.fr/Labos/LCI/cv/aa.php
[b] CEA, iBiTec-S, Service de Bioénergétique Biologie Structurale et Mécanismes (SB2SM),
91191 Gif-sur-Yvette, France
[‡] Current address: Laboratoire Interface Matériaux Environnement, Faculté des Sciences Aïn Chock, Casablanca 20100, Maroc
[‡‡] Current address: Synchrotron SOLEIL, Saint-Aubin, 91191 Gif-sur-Yvette, France

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402140.

*t*BuLMn complex. On the basis of these intriguing results, we report in the present study on the influence of a secondary imidazole fragment in the *ortho* position of a phenol group, for which the imidazole is not coordinated to the metal ion but forms a hydrogen bond with the metal-bound phenolate moiety. For this, we prepared the new ligand ImH-LH (Scheme 1), together with the corresponding Zn^{II} complexes. The zinc(II) complexes serve as a diamagnetic reference to study the non-innocent redox properties of the imidazole–phenol dyad. Crystallographic structures of the zinc complexes are described and electrochemical studies indicate that the presence of the pending imidazole group in the *ortho* position of the phenolate function leads to a decrease in the stability of the radical species.



Scheme 1. Ligands and complexes of interest in this study.

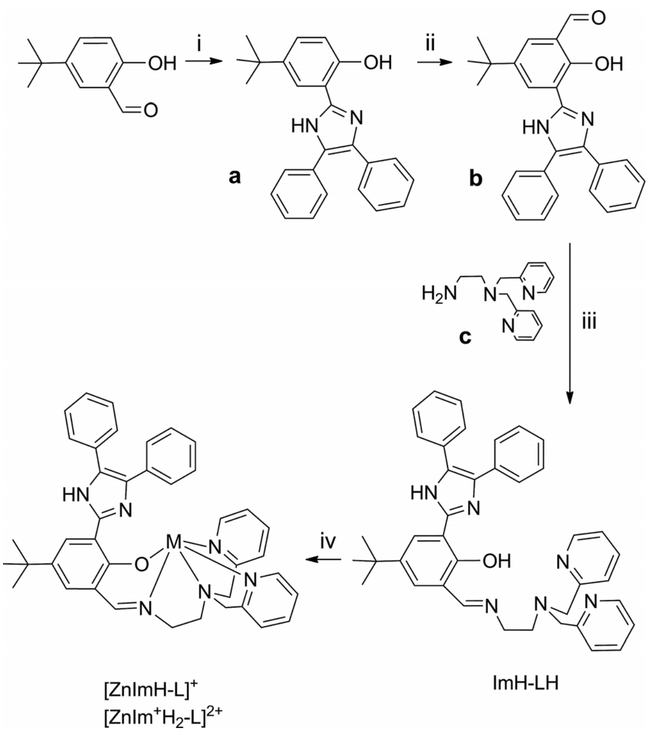
Results and Discussion

Synthesis of the Ligands

The *t*BuLH ligand (Scheme 1) was synthesized according to a published procedure.[10b] The ImH-LH ligand (Scheme 2) was obtained in good yield by condensation of 2-hydroxy-3-(4,5-diphenylimidazole)-5-*tert*-butylbenzaldehyde (**b**) with *N*,*N*-bis(2-pyridylmethyl)ethane-1,2-diamine (**c**) in ethanol. The diphenyl imidazole fragment in the *ortho* position of the phenol group (see compound **a**) was obtained by condensation of 5-*tert*-butyl-2-hydroxybenzaldehyde with benzil (1:1) in glacial acetic acid in the presence of an excess amount of ammonium acetate. The aldehyde function in **b** was introduced following the Duff reaction by treatment of **a** with hexamethyltetramine (HMT) in trifluoroacetic acid (TFA) followed by hydrolysis in basic medium.[11] The product was isolated as a yellow powder.

Synthesis of Complexes

The zinc(II) monomeric complexes [Zn(*t*BuL)](BF_4) and [Zn(ImH-L)](ClO_4) were synthesized by treating stoichiometric amounts of the ligand with $Zn(BF_4)_2$ and $Zn(ClO_4)_2$ salts in methanol and in the presence of Et_3N (1 equiv.) for deprotonation of the phenol group. It is expected that metalation of ImH-LH in the absence of a base occurs through the action of the pending imidazole group, which deprotonates the phenol group.



Scheme 2. Reagents: (i) benzil (1 equiv.)/NH_4OAc (10 equiv.)/AcOH/reflux 3 h; (ii) HMT/TFA reflux overnight; (iii) **c**/ethanol; (iv) methanol, $Zn(ClO_4)_2 \cdot 6H_2O$, Et_3N for $[Zn(ImH\text{-}L)]^+$ and methanol, $Zn(ClO_4)_2 \cdot 6H_2O$ for $[Zn(Im^+H_2\text{-}L)]^{2+}$.

X-ray Diffraction

For each complex synthesized, crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into an ethanol solution of the complex. For all three zinc complexes, the structure demonstrates an N_4O coordination sphere around the Zn^{II} ion (Figure 1). The coordination scheme is best described as a distorted trigonal bipyramid with the two pyridine rings and the nitrogen atom of the imine group located in the trigonal plane. The phenolate oxygen atom and tertiary amine nitrogen atom occupy axial positions.

In the case of the [Zn(*t*BuL)](BF_4) complex (Figure 1, a), the mean Zn–N bond length is about 2 Å. The three nitrogen atoms (N1, N2, N3) define a plane, and the zinc ion is found at 0.218 Å outside the basal plane. The length of the Zn–O1 bond is 1.94 Å and is noticeably smaller than the other axial Zn–N2 bonds (2.24 Å). For both the $[Zn(ImH\text{-}L)]^+$ and $[Zn(Im^+H_2\text{-}L)]^{2+}$ cations (Figure 1, b,c), the average metric distances of the Zn–N and Zn–O bonds are similar to those of the [Zn(*t*BuL)] complex. Interestingly, the presence of a hydrogen bond between the imidazole or imidazolium protons and the phenolate oxygen atom in the $[Zn(ImH\text{-}L)]^+$ or $[Zn(Im^+H_2\text{-}L)]^{2+}$ cations, respectively, do not alter the Zn–O distance.

Electrochemical and Spectroelectrochemical Studies of $[Zn(tBuL)]^+$

The electrochemical behavior of the complexes was studied in acetonitrile by cyclic voltammetry (CV). The CV

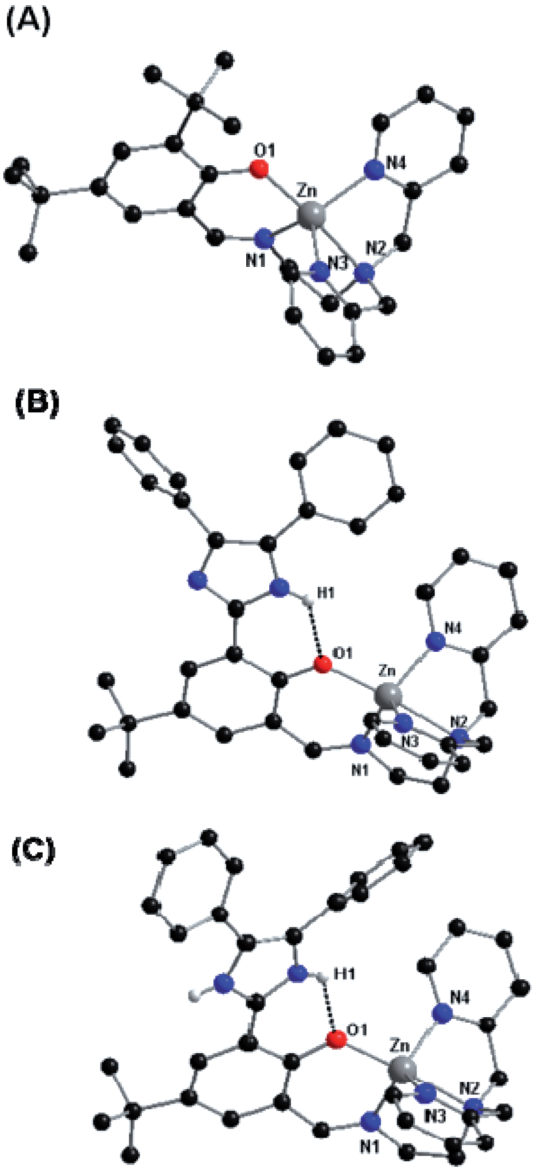


Figure 1. Crystal structure of (a) $[Zn(tBuL)]^+$, (b) $[Zn(ImH\text{-}L)]^+$, and (c) $[Zn(Im^+H_2\text{-}L)]^{2+}$. Hydrogen atoms [except for the imidazole proton(s)], the counteranions, and the solvent molecules are omitted for clarity.

curve of $[Zn(tBuL)]^+$ (Figure 2) shows a quasireversible anodic process centered at $E_{1/2}$ = 0.98 V versus the saturated calomel electrode (SCE), which can be assigned to the reversible one-electron oxidation of the coordinated phenolate, which leads to the formation of a phenoxyl radical. This value is comparable to that reported for a similar complex.[12]

To confirm the radical nature of the oxidized species, we performed exhaustive bulk electrolysis of a 2 mM solution of $[Zn(tBuL)](BF_4)$ in acetonitrile at –30 °C at 1.3 V versus SCE. Controlled potential coulometric measurements evidenced a one-electron oxidation process. Spectroelectrochemical studies in a thin optical cell at –30 °C in acetonitrile (0.2 M TBAP) showed significant changes in the electronic absorption spectrum. The oxidized species (Figure 3, a) exhibited an intense absorption at λ = 427 nm (5492 $M^{-1}cm^{-1}$) and a lower intensity band at λ = 868 nm (286 $M^{-1}cm^{-1}$) typical for a π→π* transition of a metal-bound phenoxyl

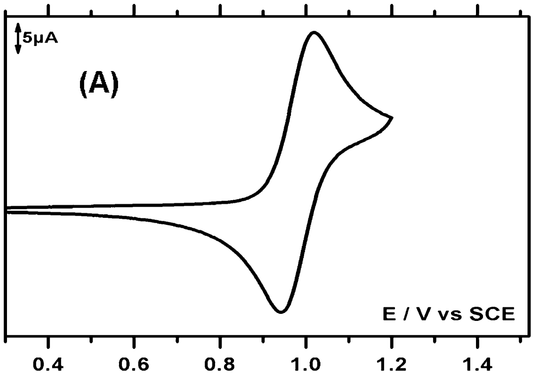


Figure 2. Cyclic voltammograms of a 1 mM solution of $[Zn(tBuL)](BF_4)$ in acetonitrile [0.1 M tetrabutylammonium perchlorate (TBAP)]. Scan rate: 100 mV s^{-1}; T = 20 °C; glassy carbon.

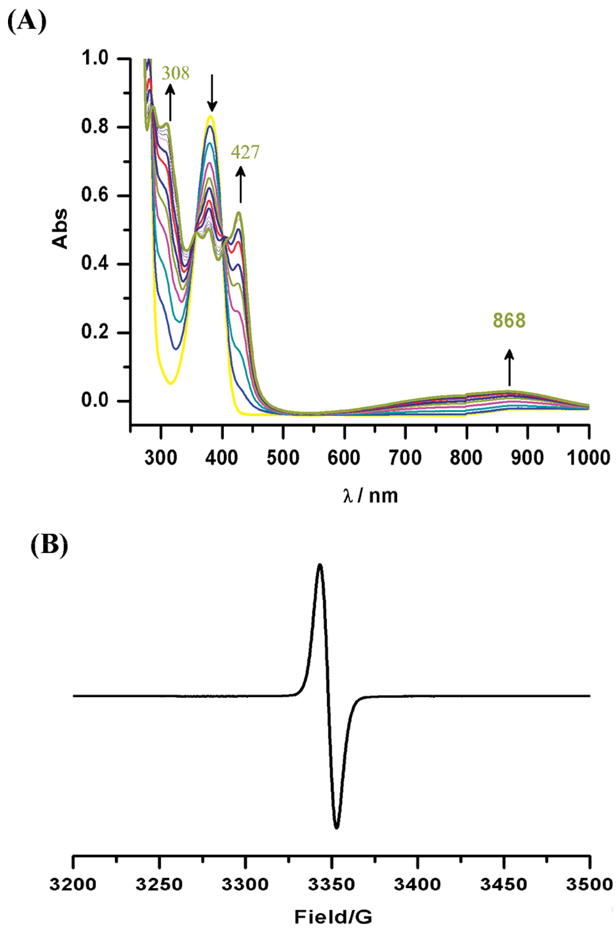


Figure 3. (a) UV/Vis absorption spectra recorded over the course of the electrochemical oxidation of a 2 mM solution of $[Zn(tBuL)](BF_4)$ at 1.3 V vs. SCE; conditions: 0.2 M TBAP in acetonitrile, T = –30 °C, optical path: 0.5 mm. (b) X-band EPR spectrum of the electrochemically generated phenoxyl radical $[Zn(tBuL)]^{2+\cdot}$ in acetonitrile (0.2 M TBAP) at 10 K. Microwave frequency: 9.4034 GHz; power: 0.7970 mW; modulation frequency: 100 kHz; amplitude: 16 mT.

radical.[11] Isosbestic points at λ = 290, 355, and 405 nm confirmed that the oxidation of [Zn(*t*BuL)](BF_4) produced a single species. The electrochemical re-reduction of the oxidized species gave a spectrum identical to that initially observed for the starting [Zn(*t*BuL)](BF_4) complex; this demonstrates the chemical reversibility of the one-electron electrochemical process. The oxidized species was stable for several hours under these conditions. The electron paramagnetic resonance (EPR) spectrum of the oxidized solution in frozen acetonitrile (0.2 M TBAP) at 10 K (Figure 3, b) consists of a single isotropic signal with g_{iso} = 2.0047. The signal is typical for a radical species and the *g* value is similar to that reported for a Zn^{II} phenoxyl radical complex.[13]

Electrochemical Studies of the Hydrogen-Bonded Phenolate $[Zn(ImH\text{-}L)]^+$ and $[Zn(Im^+H_2\text{-}L)]^{2+}$ Complexes

The cyclic voltammograms of 1 mM solutions of $[Zn(ImH\text{-}L)]^+$ and $[Zn(Im^+H_2\text{-}L)]^{2+}$ in acetonitrile are shown in Figure 4 (a,b).

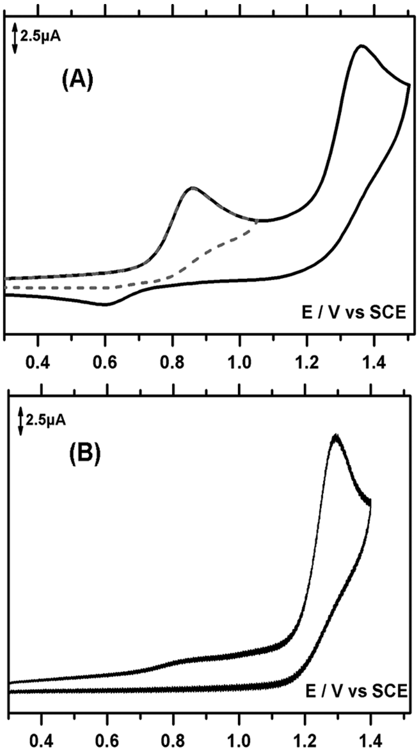


Figure 4. Cyclic voltammograms of a 1 mM solution of (a) [Zn(ImL)](ClO_4) and (b) $[Zn(Im^+H_2\text{-}L)](ClO_4)_2$ in acetonitrile (0.1 M TBAP). Scan rate: 100 mV s^{-1}; *T* = 20 °C; glassy carbon.

The CV trace of $[Zn(ImH\text{-}L)]^+$ exhibits two irreversible oxidation processes at $E_{pa}(1)$ = 0.86 V and $E_{pa}(2)$ = 1.36 V vs. SCE. Cycling after the first oxidation wave did not alter the electrochemical response of the system [Figure 4, a (dashed line)]. Interestingly, the CV curve of $[Zn(Im^+H_2\text{-}L)]^{2+}$ displays only one irreversible anodic wave peaking at 1.36 V vs. SCE. The lack of the first oxidation wave leads us to assign the wave peaking at 0.86 V to the imidazole ring for $[Zn(ImH\text{-}L)]^+$. Indeed, running the CV experiment of $[Zn(ImH\text{-}L)]^+$ in the presence of $HClO_4$ (1 equiv.) shows the loss of the first oxidation process (Figure 5).

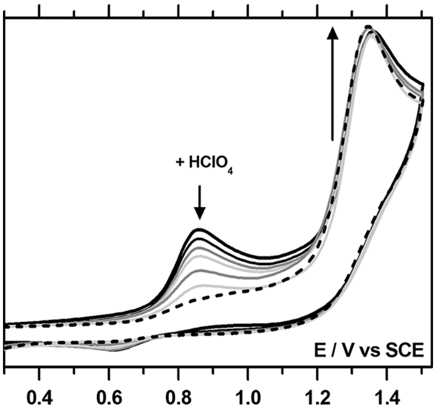


Figure 5. Evolution of the cyclic voltammograms of a 1 mM solution of $[Zn(ImH\text{-}L)](ClO_4)$ in acetonitrile (0.1 M TBAP) with the addition of $HClO_4$. Scan rate: 100 mV s^{-1}; *T* = 20 °C.

Importantly, we notice a shift of 380 mV to a more positive potential for the hydrogen-bonded phenolate group for compounds $[Zn(ImH\text{-}L)]^+$ and $[Zn(Im^+H_2\text{-}L)]^{2+}$ relative to that recorded for the $[Zn(t\text{BuL})]^+$ compound. We suggest that this shift can be attributed to the hydrogen-bonded phenolate that leads to a decrease in the electron density on the phenolate ring. Moreover, our results point to the fact that protonation of the imidazole imino nitrogen atom does not lead to a further inductive effect on the phenolate ring. This is confirmed by the same oxidation potential observed for the phenolate ring for both the $[Zn(ImH\text{-}L)]^+$ and $[Zn(Im^+H_2\text{-}L)]^{2+}$ complexes. All attempts to characterize the electrogenerated radical species spectroscopically by electrolysis were unfruitful because of the chemical instability of the radical species formed.

With the target to investigate the influence of hydrogen bonding from the amine function of the imidazole ring further, we prepared a methylated benzimidazole ligand derivative, and the corresponding zinc complex was isolated (see the Supporting Information). The cyclic voltammogram of $[Zn(BenziMe\text{-}L)]^+$ in acetonitrile is given in Figure 6 (blue line). Similarly, we noticed a first irreversible wave peaking at 1.2 V vs. SCE that could be attributed to the oxidation of the methylated benzimidazole unit. The higher potential relative to that for the $[Zn(ImH\text{-}L)]^+$ (0.86 V) complex is attributed to the more electron-withdrawing nature of the benzimidazole group. Another quasireversible wave at around 1.51 V vs. SCE was observed that we assigned to the oxidation of the bound phenolate. Again, the anodic shift of the phenolate bound group is directly related to the presence of the benzimidazole group in the *ortho* position of the phenolate fragment.

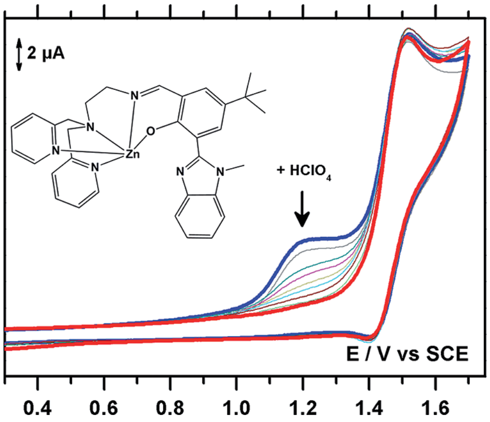


Figure 6. Evolution of the cyclic voltammograms of a 1 mM solution of [Zn(BenziMe-L)](ClO$_4$) in acetonitrile (0.1 M TBAP) with the addition of HClO$_4$. Scan rate: 100 mV s^{-1}; T = 20 °C.

The addition of increasing amounts of acid to the solution led to fading of the first oxidation wave, which confirms its attribution to the benzimidzole motif. However, no concomitant shift in the oxidation potential of the ligated phenolate ring was observed, and this supports the statement that the protonic state of the benzimidazole cycle does not influence the oxidation potential of the phenolate ring. All attempts to isolate and characterize any singly oxidized species were not successful.

Conclusions

We reported herein the synthesis of a pentadentate N$_4$O ligand possessing an imidazole group and developing a hydrogen-bonding interaction with the oxygen atom of the phenol group. The electrochemical properties of the zinc(II) derivatives were compared with those of the corresponding analogue without the additional imidazole group. We found that the hydrogen-bonded oxidized phenolate group was more unstable than the non-hydrogen-bonded compounds and more unstable than compounds in which the imidazole group is bound to the metal center. Our findings point to the considerable task that lies ahead for chemists designing ligands with a second coordination sphere to tune the chemical reactivity of metal complexes.

Supporting Information (see footnote on the first page of this article): Experimental details.

Acknowledgments

The authors thank the CNRS and the Labex CHARMMMAT for funding.

---

[1] a) C. K. Jørgensen, *Coord. Chem. Rev.* **1966**, *1*, 164; b) W. Kaim, *Coord. Chem. Rev.* **1987**, *76*, 187–235; c) W. Kaim, B. Schwederski, *Coord. Chem. Rev.* **2010**, *254*, 1580; d) P. Chaudhuri, C. N. Verdani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, *123*, 2213–2223; e) C. G. Pierpont, *Coord. Chem. Rev.* **2001**, 216–217; f) W. Kaim, *Inorg. Chem.* **2011**, *50*, 9752–9765; g) J. M. Darmon, S. C. E. Stieber, K. T. Sylvester, I. Fernández, E. Lobkovsky, S. P. Semproni, E. Bill, K. Wieghardt, S. DeBeer, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 17125–17137; h) J. L. Boyer, J. Rochford, M.-K. Tsai, J. T. Muckerman, E. Fujita, *Coord. Chem. Rev.* **2010**, *254*, 309–330.

[2] a) P. J. Chirik, *Inorg. Chem.* **2011**, *50*, 9737–9740; b) S. Blanchard, E. Derat, M. Desage-El Murr, L. Fensterbank, M. Malacria, V. Mouriès-Mansuy, *Eur. J. Inorg. Chem.* **2012**, 376–389; c) L. Benisvy, E. Bill, A. J. Blake, D. Collison, E. S. Davies, C. D. Garner, C. I. Guindy, E. J. L. McInnes, G. McArdle, J. McMaster, C. Wilsona, J. Wolowskac, *Dalton Trans.* **2004**, 3647–3653; d) V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270–279; e) M. Orio, O. Jarjayes, H. Kanso, C. Philouze, F. Neese, F. Thomas, *Angew. Chem. Int. Ed.* **2010**, *49*, 4989–4992; *Angew. Chem.* **2010**, *122*, 5109–5112.

[3] a) V. Bachler, G. Olbrich, F. Neese, K. E. Wieghardt, *Inorg. Chem.* **2002**, *41*, 4179–4193; b) D. Herebian, K. E. Wieghardt, F. Neese, *J. Am. Chem. Soc.* **2003**, *125*, 10997–11005; c) D. Herebian, E. Bothe, F. Neese, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2003**, *125*, 9116–9128; d) F. Michel, S. Torelli, F. Thomas, C. Duboc, C. Philouze, C. Belle, S. Hamman, E. Saint-Aman, J.-L. Pierre, *Angew. Chem. Int. Ed.* **2005**, *44*, 438–441; *Angew. Chem.* **2005**, *117*, 442–445; e) K. Chłopek, E. Bothe, F. Neese, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2006**, *45*, 6298–6307.

[4] a) J. Stubbe, W. A. van der Donk, *Chem. Rev.* **1998**, *98*, 705–762; J. A. Cotruvo Jr., T. A. Stich, R. D. Britt, J. Stubbe, *J. Am. Chem. Soc.* **2013**, *135*, 4027–4039; b) J. A. Cotruvo Jr., J. Stubbe, *Biochemistry* **2010**, *49*, 1297–1309; c) J. D. Megiatto Jr., D. D. Méndez-Hernández, M. E. Tejeda-Ferrari, A.-L. Teillout, M. J. Llansola-Portolés, G. Kodis, O. G. Poluektov, T. Rajh, V. Mujica, T. L. Groy, D. Gust, T. A. Moore, A. L. Moore, *Nature Chem.* **2014**, *6*, 423–428.

[5] a) A. Sokolowski, J. Müller, T. Weyhermüller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **1997**, *119*, 8889–8900; b) A. Kunishita, H. Ishimaru, S. Nakashima, T. Ogura, S. Itoh, *J. Am. Chem. Soc.* **2008**, *130*, 4244–4245; c) T. Osako, S. Nagatomo, Y. Tachi, T. Kitagawa, S. Itoh, *Angew. Chem. Int. Ed.* **2002**, *41*, 4325–4328; *Angew. Chem.* **2002**, *114*, 4501–4504; d) T. Storr, P. Verma, R. C. Pratt, E. C. Wasinger, Y. Shimazaki, T. D. P. Stack, *J. Am. Chem. Soc.* **2008**, *130*, 15448–15459.

[6] a) O. Jarjayes, B. Baptiste, C. Philouze, C. Duboc, J.-L. Mathias, F. Thomas, M. Eckshtain-Levi, M. Orio, R. Lavia, L. Benisvy, *Dalton Trans.* **2013**, *42*, 13323–13326; b) L. Benisvy, R. Bittl, E. Bothe, C. D. Garner, J. McMaster, S. Ross, C. Teutloff, F. Neese, *Angew. Chem. Int. Ed.* **2005**, *44*, 5314–5317; *Angew. Chem.* **2005**, *117*, 5448–5451; c) M. Lucarini, V. Mugnaini, G. Pedulli, M. Guerra, *J. Am. Chem. Soc.* **2003**, *125*, 8318–8329; d) T. Maki, Y. Araki, Y. Ishida, O. Onomura, Y. Matsumura, *J. Am. Chem. Soc.* **2001**, *123*, 3371–3372; e) J. A. Halfen, B. A. Jazdzewski, S. Mahapatra, L. M. Berreau, E. C. Wilkinson, L. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1997**, *119*, 8217–8227; f) E. Bill, J. Müller, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **1999**, *38*, 5795–5802.

[7] O. R. Luca, R. H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440–1459.

[8] a) L. Benisvy, A. J. Blake, D. Collison, E. S. Davies, C. D. Garner, E. J. L. McInnes, J. McMaster, G. Whittaker, C. Wilson, *Dalton Trans.* **2003**, *10*, 1975–1985; b) L. Benisvy, A. J. Blake, D. Collison, E. S. Davies, C. D. Garner, E. J. L. McInnes, J. McMaster, G. Whittaker, C. Wilson, *Chem. Commun.* **2001**, *18*, 1824–1825.

[9] F. Michel, F. Thomas, S. Hamman, C. Philouze, E. Saint-Aman, J. L. Pierre, *Eur. J. Inorg. Chem.* **2006**, *18*, 3684–3696.

[10] a) S. El Ghachtouli, B. Lassalle-Kaiser, P. Dorlet, R. Guillot, E. Anxolabéhère-Mallart, C. Costentin, A. Aukauloo, *Energy*

Environ. Sci. **2011**, *4*, 2041–2044; b) S. El Ghachtouli, R. Guillot, A. Aukauloo, P. Dorlet, E. Anxolabéhère-Mallart, C. Costentin, *Inorg. Chem.* **2012**, *51*, 3603–3612; c) S. El Ghachtouli, R. Guillot, P. Dorlet, E. Anxolabéhère-Mallart, A. Aukauloo, *Dalton Trans.* **2012**, *41*, 1675–1677.

[11] F. L. Lindoy, V. G. Meehan, N. Svenstrup, *Synthesis* **1998**, 1029–000.

[12] S. Itoh, M. Taki, H. Kumei, S. Takayama, S. Nagatomo, T. Kitagawa, N. Sakurada, R. Arakawa, S. Fukuzumi, *Inorg. Chem.* **2000**, *39*, 3708–3711.

[13] A. Sokolowski, J. Müller, T. Weyhermüller, R. Schnepf, P. Hildebrandt, K. Hildenbrand, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **1997**, *119*, 8889–8900.

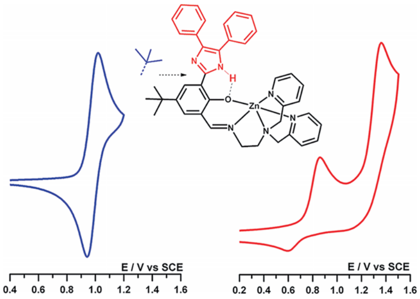
Received: July 4, 2014

Redox-Active Ligands

S. El Ghachtouli, B. Lassalle-Kaiser, R. Guillot, A. Aukauloo* 1–7

Electrochemical Implication of a Hydrogen-Bonded Imidazole on a Redox-Active-Bound Phenolate Group

Keywords: Redox chemistry / Electrochemistry / Zinc / N,O ligands / Radicals



We report the synthesis and crystallographic structures of zinc complexes with a pentadentate N_4O ligand with an imidazole group placed in the *ortho* position of the phenol group. Furthermore, we describe the influence of the outer-sphere imidazole fragment on the electrochemical behavior of the redox-active-bound phenolate ligand.