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Structure and properties of an Fe(III) complex containing a novel amide functionalized polyimidazole ligand†

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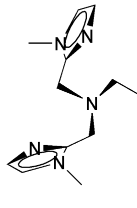
A novel amide functionalized polyimidazole tripod ligand has been synthesized and used to prepare a mononuclear Fe(III) complex that has been characterized by X-ray crystallography and other physical methods.

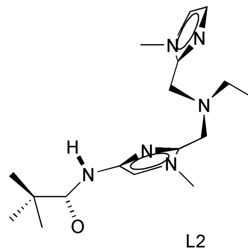
The design and synthesis of metal chelates capable of stabilizing both primary and secondary coordination environments is important to the development of more accurate metalloprotein active site models. Protein crystallographic studies have revealed that amino acid residues oriented in close proximity to active site metal centers play a crucial role in the biological function of metalloproteins.[1] For example, in hydrolase proteins intramolecular hydrogen bonding is particularly important in stabilizing metal–hydroxo or oxo intermediates and controlling the orientation of substrate molecules during reaction.[1,2] Efforts to mimic these interactions have resulted in the development of several model compounds that replicate important second coordination sphere interactions. Most notable are studies by Masuda[3] and Berreau *et al.*[4] who have used amide and amine functionalized pyridine tripod ligands to stabilize M–OH complexes by proper orientation of hydrogen bonding groups. Similarly, Borovik *et al.* have used urea containing tripod ligands to stabilize both M–OH (M = Co, Zn and Fe)[5] and M=O (M = Mn)[6] complexes. However, to date, there have been no studies reported using biologically relevant imidazole ligands containing properly oriented hydrogen bonding groups.

Towards this aim, we have prepared a tripodal polyimidazole ligand functionalized with an amide group in the 4 position of one of the imidazole pendants. Upon coordination, the imidazole ligand should be capable of forming intramolecular hydrogen bonds with ligands oriented *cis* to the amide functionalized imidazole pendant. To illustrate this point, we have prepared and characterized Fe(III) complexes of both the amide functionalized polyimidazole chelate and an unfunctionalized imidazole analog (tmima).[7] A comparison of the crystal structures, electronic and electrochemical properties of the Fe(III) complexes are described below.†

The two tripod ligands used in this study are represented as **L1**(tmima) and **L2**(^{Am}tmima) and were prepared using strategies reported previously.[7] Both **L1**[8] and **L2**[9] were prepared in good overall yields, and a detailed description of the synthesis and characterization of **L2** will be reported elsewhere. The iron(III) compounds, [Fe(**L1**)Cl$_2$]ClO$_4$ (**1**), [Fe(**L2**)Cl$_2$]$_2$[Fe$_2$OCl$_6$] (**2**), were synthesized by mixing equimolar quantities of anhydrous FeCl$_3$ and **L1** or **L2** in ethanol. Compound **1** was isolated as a yellow powder after addition of one equivalent of NaClO$_4$ to the reaction mixture‡ and was crystallized§ from EtOH–Et$_2$O (65% yield). Compound **2** was prepared in a similar manner using **L2**, however, the reaction mixture was layered with ether and after several days, flat plate and block-shaped orange crystals were isolated. The plate shaped crystals (~40% yield) rapidly lose solvent molecules of crystallization at room temperature and were found to be unsuitable for X-ray crystallographic analysis. However, electrospray ionization mass spectrometric analysis (ESI†) of the crystals show an *m/z* 524.1 [M$^+$] ion supporting the formation of the [Fe(**L2**)Cl$_2$]$^+$ cation. The block shaped crystals (~20% isolated yield) on the other hand, were found to be very stable at room temperature and of high quality for X-ray diffraction analysis.§ The counter ion of **2** is the well known Fe$_2$OCl$_6$$^{2-}$ ion[10] formed from the hydrolysis of residual FeCl$_3$ present in the reaction solution.

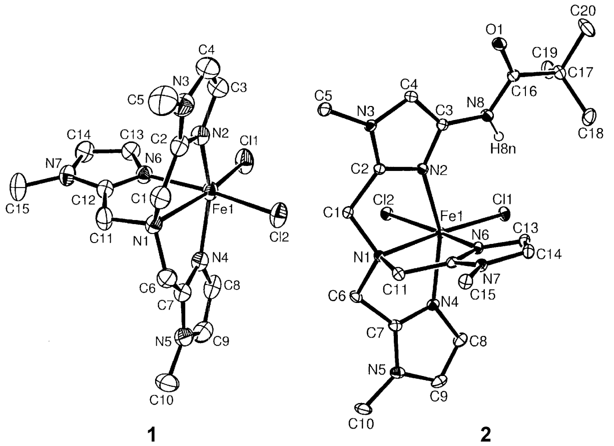


L1



L2

The coordination environments of the [Fe(**L1**)Cl$_2$]$^+$ and [Fe(**L2**)Cl$_2$]$^+$ ions are shown in Fig. 1. The crystal structure of **1** reveals the iron atom has a distorted octahedral geometry and is coordinated to the four nitrogen atoms of **L1** and two chlorine atoms. The Fe–Cl (Fe–Cl(1) 2.233(1), Fe–Cl(2) 2.331(1) Å)



1 **2**

Fig. 1 ORTEP diagrams illustrating the cations in **1** and **2** with H atoms (except for H8n) omitted for clarity. Ellipsoids are drawn at 50% probability level. Selected bond distances (Å) and angles (°). Compound **1**: Fe–Cl(1) 2.233(1), Fe–Cl(2) 2.331(1), Fe–N(1) 2.380(3), Fe–N(2) 2.074(4), Fe–N(4) 2.076(4), Fe–N(6) 2.104(3), Cl(1)–Fe–Cl(2) 99.55(5), Cl(1)–Fe–N(1) 166.40(9), Cl(1)–Fe–N(2) 108.68(12), Cl(1)–Fe–N(4) 102.86(11), Cl(1)–Fe–N(6) 90.92(10), Cl(2)–Fe–N(1) 93.66(9), Cl(2)–Fe–N(2) 87.35(11), Cl(2)–Fe–N(4) 89.21(10), Cl(2)–Fe–N(6) 169.50(10), N(1)–Fe–N(2) 74.97(14), N(1)–Fe–N(4) 73.93(13), N(1)–Fe–N(6) 75.93(12), N(2)–Fe–N(4) 148.41(15), N(2)–Fe–N(6) 88.57(14), N(4)–Fe–N(6) 89.20(14). Compound **2**: Fe–Cl(1) 2.2511(7), Fe–Cl(2) 2.3114(7), Fe–N(1) 2.323(2), Fe–N(2) 2.114(2), Fe–N(4) 2.075(2), Fe–N(6) 2.107(2), Cl(1)–Fe–Cl(2) 100.01(3), Cl(1)–Fe–N(1) 169.79(5), Cl(1)–Fe–N(2) 103.88(6), Cl(1)–Fe–N(4) 104.08(6), Cl(1)–Fe–N(6) 92.85(6), Cl(2)–Fe–N(1) 90.19(5), Cl(2)–Fe–N(2) 89.18(5), Cl(2)–Fe–N(4) 93.10(6), Cl(2)–Fe–N(6) 165.90(6), N(1)–Fe–N(2) 75.58(7), N(1)–Fe–N(4) 75.60(7), N(1)–Fe–N(6) 76.96(7), N(2)–Fe–N(4) 151.09(8), N(2)–Fe–N(6) 82.10(7), N(4)–Fe–N(6) 89.32(8).

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† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C NMR, UV-vis and FTIR spectra, ESI-mass spectra and cyclic voltammetry. See http://www.rsc.org/suppdata/cc/b2/b204799c/

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distances are similar to other Fe(III)–imidazole complexes.[11] The longest Fe–N distance (Fe–N(1) 2.380(3) Å) is associated with the tertiary amine nitrogen atom, and the remaining Fe–N_{Im} distances average 2.085 Å. The constrained nature of the **L1** chelate has been noted in other structures of the ligand,[7a,11] and is reflected in the N–Fe–N angles which are less than 90°.

Close inspection of the distances and angles of the two cations reveals that they are remarkably similar despite the presence of the bulky *tert*-butylamide group on **L2**. The Fe–Cl(1) and Fe–Cl(2) distances in **2** are 2.2511(2) and 2.3114(7) Å, respectively, and the Fe–N(1) distance is 2.323(2) Å; comparable to the distance in **1**. The remaining Fe–N distances in **2** average 2.082 Å, and there are only minor differences in the N–Fe–N angles between the two iron complexes.

The complex anion of **2** is $[Fe_2OCl_6]^{2-}$ which has been reported to crystallize with a variety of cation complexes.[10] $[Fe_2OCl_6]^{2-}$ contains a linear Fe–O–Fe bridge (Fe–O 1.7643(4) Å) which has crystallographically imposed inversion symmetry. A packing diagram of **2** showing the spatial orientation of cations and anions in the unit cell are included in supplementary information.†

As noted above, compound **2** contains a *tert*-butylamide group attached to the 4-position of one of the **L2** imidazole pendants. As a result, **L2** should have the ability to form intramolecular hydrogen bonds to ligands coordinated *cis* to the amide pendant. In **2**, the N(8)—Cl(1) separation is 3.395(2) Å (H8n–Cl(1) 2.55(3) Å) and the N(8)–H8n–Cl(1) angle is 155(3)°, suggesting that there is a weak hydrogen bonding interaction between H8n and Cl(1) similar to those reported for amide functionalized pyridine complexes.[3d] The resulting 6-membered ring formed by the Fe(1), Cl(1), H8n, N(8), C(3) and N(2) atoms is nearly planar.[12]

Compounds **1** and **2** have been further characterized by UV-vis spectroscopy and by cyclic voltammetry.† The UV-vis spectra of **1** and **2** in CH_3CN are very similar and display intense $Cl^- \rightarrow Fe(III)$ charge transfer transitions at 367 nm (ε = 4300 M^{-1} cm^{-1}) and 313 nm (ε = 4200 M^{-1} cm^{-1}), respectively.[11] The spectrum of **1** is slightly blue shifted relative to the pyridine containing $[Fe(tpa)Cl_2]^+$ complex which displays a CT transition at 382 nm (ε = 3170 M^{-1} cm^{-1}).[13] Similar hypsochromic shifts have been observed in the spectra of Fe–pyridine compounds compared to related imidazole compounds.[11]

Cyclic voltammetry on **1** and **2** in CH_3CN/0.1 M TBAP shows quasireversible redox behaviour. The $E_{1/2}$ values are +0.16 V ([Fe(**L1**)Cl_2]$^+$) and +0.05 V ($[Fe_2OCl_6]^{2-}$)[14] and +0.25 V ([Fe(**L2**)Cl_2]$^+$) *vs.* Ag/AgCl (Fc/Fc^+ = +0.44 V). The $E_{1/2}$ value for $[Fe(tpa)Cl_2]^+$ in CH_3CN is −0.095 V (*vs.* Ag/AgCl).[13] The approximate 90 mV shift in the redox potential of [Fe(**L2**)Cl_2]$^+$ compared to [Fe(**L1**)Cl_2]$^+$ is attributed to the electron withdrawing nature of the amide group.

In summary, we have prepared and characterized the first biologically relevant amide functionalized polyimidazole ligand that forms thermodynamically stable six-membered hydrogen bonded rings with *cis*-coordinated ligands. Finally, the synthesis of **L2** represents a new paradigm in the preparation of biomimetic imidazole ligands capable of regulating both the primary and secondary coordination environments of metal complexes through intramolecular hydrogen bonding. The structure and properties of complexes of **L2** and its derivatives will be the subject of future studies.

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Notes and references

‡ **CAUTION**: Perchlorate salts of metal complexes are potentially explosive and should always be handled in small quantities.

§ *Crystal data*: for [Fe(**L1**)Cl_2]ClO_4·0.5CH_3CN: orange block, monoclinic, space group *C*2/*c*, *a* = 23.026(5), *b* = 9.800(2), *c* = 22.563(4) Å, β = 113.94(2)°, *V* = 4653(1) $Å^3$, *Z* = 8, μ = 1.028 mm^{-1}. Data were collected on an Enraf Nonius CAD4 diffractometer at 293 K using Mo-Kα radiation (λ = 0.7173 Å) and refined using SHELXTL-Plus programs.[15] For all 4351 unique reflections (R_{int} = 0.007) the final anisotropic full matrix least-squares refinement on F^2 for 281 variables converged at *R*1 = 0.057 and *wR*2 = 0.170 with a GOF of 1.06.

For [Fe(**L2**)Cl_2]$_2$[Fe_2OCl_6]: small orange block, monoclinic, space group $P2_1/c$, *a* = 11.2811(12), *b* = 17.7490(2), *c* = 14.7148(16) Å, β = 114.619(2)°, *V* = 2850.9(5) $Å^3$, *Z* = 4, μ = 1.519 mm^{-1}. Data were collected on a Bruker Smart Apex CCD diffractometer at 100 K using Mo-Kα radiation. For all 6672 unique reflections (R_{int} = 0.043) the final anisotropic full matrix least-squares refinement on F^2 for 344 variables converged at *R*1 = 0.053 and *wR*2 = 0.084 with a GOF of 1.04.

CCDC 186290 and 186291. See http://www.rsc.org/suppdata/cc/b2/b204799c/ for crystallographic data in CIF or other electronic format.

1 (*a*) D. E. Wilcox, *Chem. Rev.*, 1996, **96**, 2435; (*b*) W. N. Lipscomb and N. Sträter, *Chem. Rev.*, 1996, **96**, 2375; (*c*) D. W. Christianson and J. D. Cox, *Annu. Rev. Biochem.*, 1999, **68**, 33.

2 (*a*) R. H. Holm, P. Kennepohl and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239; (*b*) J. B. Vincent, G. L. Oliver-Lilley and B. A. Averill, *Chem. Rev.*, 1990, **90**, 1447; (*c*) L. Que, Jr. and A. E. True, *Prog. Inorg. Chem.*, 1990, **38**, 97.

3 (*a*) S. Ogo, S. Wada, Y. Watanabe, M. Iwase, A. Wada, M. Harata, K. Jitsukawa, H. Masuda and H. Einaga, *Angew. Chem., Int. Ed.*, 1998, **37**, 2102; (*b*) M. Harata, K. Jitsukawa, H. Masuda and H. Einaga, *Chem. Lett.*, 1995, 61; (*c*) A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa and H. Einaga, *Angew. Chem., Int. Ed.*, 1998, **37**, 798; (*d*) M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda and H. Einaga, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1031.

4 L. M. Berreau, R. A. Allred, M. M. Makowska-Grzyska and A. M. Arif, *Chem. Commun.*, 2000, 1423.

5 (*a*) B. S. Hammes, V. G. Young, Jr. and A. S. Borovik, *Angew. Chem., Int. Ed.*, 1999, **38**, 666; (*b*) Z. Shirin, B. S. Hammes, V. G. Young, Jr. and A. S. Borovik, *J. Am. Chem. Soc.*, 2000, **122**, 1836; (*c*) C. E. Macbeth, A. P. Golombeck, V. G. Young, Jr., C. Yang, K. Kuczera, M. P. Hendrich and A. S. Borovik, *Science*, 2000, **289**, 938; (*d*) C. E. Macbeth, B. S. Hammes, V. G. Young, Jr. and A. S. Borovik, *Inorg. Chem.*, 2001, **40**, 4733.

6 R. Gupta, C. E. Macbeth, V. G. Young, Jr. and A. S. Borovik, *J. Am. Chem. Soc.*, 2002, **124**, 1136.

7 (*a*) K. J. Oberhausen, R. J. O′Brien, J. F. Richardson and R. M. Buchanan, *Inorg. Chim. Acta*, 1990, **159**, 219; (*b*) S. Chen, J. F. Richardson and R. M. Buchanan, *Inorg. Chem.*, 1994, **33**, 2376; (*c*) K. J. Oberhausen, J. F. Richardson, R. M. Buchanan and W. Pierce, *Polyhedron*, 1989, **5**, 659.

8 Compound **L1** was purified by column chromatography (silica gel) using $CHCl_3$–CH_3OH (yield 65%). Calc. for $C_{15}H_{21}N_7 \cdot H_2O$: C, 56.8; H, 7.3; N, 30.9. Found: C, 56.4; H, 7.3; N, 30.6%. ESI-MS: *m*/*z* 299.5 (M + H 299.3, calc. for $C_{15}H_{23}N_7O$). ^1H NMR ($CDCl_3$): δ 6.88 (s, 3H, Im(C5H)), 6.74 (s, 3H, Im(C4H)), 3.78 (s, 6H, Im(CH_2)), 3.03 (s, 9H, Im(NCH_3)).

9 Compound **L2** was isolated as a pale yellow oil (yield 60%). Calc. for $C_{20}H_{30}N_8O \cdot H_2O$: C, 57.7; H, 7.7; N, 27.0. Found: C, 58.0; H, 7.9; N, 27.0%. ESI-MS: *m*/*z* 399.3 (M + H 399.3, calc. for $C_{20}H_{30}N_8O$). ^1H NMR ($CDCl_3$): δ 7.75 (s, 1H, ^{Am}Im(NH)), 7.21 (s, 1H, ^{Am}Im(C5H)), 6.95 (d, 2H, Im(C5H), 6.80 (d, 2H, Im(C4H)), 3.78 (s, 4H, Im(CH_2)), 3.77 (s, 2H, ^{Am}Im(CH_2)), 3.11 (s, 6H, Im(NCH_3)), 3.08 (s, 3H, ^{Am}Im(NCH_3)), 1.30 (s, 9H, ^{t}Bu-CH_3); ^{13}C NMR ($CDCl_3$): δ 175.7 (s, ^{Am}Im(C=O)); FTIR: ν_{NH} 3152, $\nu_{C=O}$ 1638 cm^{-1}.

10 (*a*) W. H. Armstrong and S. J. Lippard, *Inorg. Chem.*, 1985, **24**, 981; (*b*) G. Haselhorst, K. Wieghart, S. Keller and B. Schrader, *Inorg. Chem.*, 1993, **32**, 520 and references therein.

11 (*a*) R. M. Buchanan, S. Chen, J. F. Richardson, M. Bressan, L. Forti, A. Morvillo and R. H. Fish, *Inorg. Chem.*, 1994, **33**, 3208; (*b*) R. M. Buchanan, R. J. O'Brien, J. F. Richardson and J.-M. Latour, *Inorg. Chim. Acta*, 1993, **214**, 33.

12 Rms deviation of the atoms in the six-membered ring is 0.0577 Å.

13 T. Kojima, R. A. Leising, S. Yan and L. Que, Jr., *J. Am. Chem. Soc.*, 1993, **115**, 11328.

14 In CH_3CN/0.1 M TBAP $[NH_4]_2[Fe_2OCl_6{}^{2-}]$ displays a reversible redox couple at +0.05 V *vs.* Ag/AgCl.

15 (*a*) G. M. Sheldrick, SHELXS-90, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997; (*c*) SHELXTL 6.12, Program Library for Structure Solution and Molecular Graphics; Bruker Advanced X-ray Solutions: Madison, WI, 2001; (*d*) L. J. Farrugia, ORTEP-3 for Windows, *J. Appl. Crystallogr.*, 1997, **30**, 565.