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# Synthesis and Characterization of First Row Metal Complexes Derived from a Pyridinophane Ligand Functionalized by Fluoroalcohol

Dr. Pascal Guillo,<sup>[a,b]\*</sup> Dr. Jean-Claude Daran,<sup>[b]</sup> Dr. Eric Manoury<sup>[b]</sup> and Pr. Rinaldo Poli<sup>[b,c]</sup>

**Abstract:** A new tetradentate N-donor ligand (**L**) based on 2,11-diaza[3.3](2,6)pyridinophane with N-bonded (CF<sub>3</sub>)<sub>2</sub>(OH)CCH<sub>2</sub> groups is presented, along with the coordination compounds [(**L**)FeCl<sub>2</sub>][FeCl<sub>4</sub>], [(**L**)MnCl<sub>2</sub>], [(**L**)Cu(OAc)<sub>2</sub>] and [(**L**)Zn(OTf)(H<sub>2</sub>O)](OTf) (OAc = acetate; OTf = trifluoromethylsulfonate). All metal complexes possess a distorted octahedral geometry around the metal center.

## Introduction

Access to new molecular complexes inspired by the active sites of metalloenzymes that involve metal-oxo intermediates during their catalytic action is of great interest for the inorganic community.<sup>[1]</sup> Indeed, these complexes allow better understanding of processes and mechanisms taking place in these metalloenzymes<sup>[2]</sup> and some of them have also proven very efficient catalysts in numerous catalytic reactions.<sup>[1b, 3]</sup> Most of these molecular models are inspired by the first coordination sphere of the active sites of metalloenzymes. Only few take into account the influence of the second coordination sphere.<sup>[4]</sup> This aspect is however crucial. Indeed, the local environment engendered by the second coordination sphere is responsible for establishing non-covalent interactions, mainly by the presence of a hydrogen-bond network.<sup>[5]</sup> In the realm of metalloenzyme reactions involving highly unstable species such as metal-oxo intermediates, H-bond networks have been proven essential to control dioxygen binding and activation and the stabilization of intermediates.<sup>[6]</sup>

In order to better understand the role of the second coordination sphere, synthetic systems with a second coordination sphere able to create an H-bond network have been synthesized. Initial works have focused on the functionalization of porphyrin-based systems, which indeed allowed the stabilization of highly reactive intermediates.<sup>[7]</sup> However, the synthesis and the selective functionalization of this ligand family is often multi-step and low yielding. A breakthrough has been achieved by the Borovik's group<sup>[8]</sup> with the development of systems based on a

tripodal urea-based ligand. These systems provide an appropriate H-bond network able to stabilize highly reactive species and thus to characterize them.<sup>[9]</sup> Thanks to this approach, Fe<sup>IV</sup>-oxo<sup>[10]</sup> and Mn<sup>V</sup>-oxo<sup>[11]</sup> complexes have notably been isolated and even characterized by X-ray crystallography for the Fe<sup>IV</sup>-oxo compound.<sup>[10a]</sup>

More recently, Fout's group also used C<sub>3</sub>-symmetric ligands, based on a pyrrolide platform and modified by an imine fragment acting as an H-bond acceptor.<sup>[12]</sup> With this approach, Mn<sup>III</sup>-oxo<sup>[12d]</sup> and Fe<sup>III</sup>-oxo<sup>[12b, 12e]</sup> complexes have notably been synthesized. Interestingly, the Fe<sup>III</sup>-oxo complex is able to catalytically reduce nitrate and perchlorate anions.<sup>[12e]</sup> Goldberg's group has focused on the development of amide group-functionalized polypyridyl ligands,<sup>[13]</sup> leading to an accelerated oxygen-atom transfer in comparison to the non-modified systems.

Given that the utilization of H-bonds in the design and preparation of biomimetic metal complexes is still in the early stages of development, we have focused on a new strategy that consists of introducing fluoroalcohol groups. This is motivated by the fact that fluoroalcohols are strong H-bond donors.<sup>[14]</sup> Notably, fluorinated alcohol solvents are able to activate hydrogen peroxide toward electrophilic oxidation by hydrogen bonding.<sup>[14-15]</sup> In the context of reactions involving oxygen atom transfer, this feature is particularly interesting.

In the present contribution, we report the synthesis and characterization of a new tetradentate N-donor ligand **L** possessing two fluoroalcohol group-functionalized nitrogen atoms and a few first row metal complexes (metal = manganese, iron, copper and zinc) obtained from this ligand.

## Results and Discussion

The 2,11-diaza[3.3](2,6)pyridinophane molecule was targeted as an interesting precursor for our studies. Indeed, this tetradentate ligand possesses two secondary amine groups that can be functionalized. Moreover, the amine functionalization by alkyl groups has already been reported for this system and the syntheses of octahedral metal complexes possessing two *cis* labile sites have also been reported.<sup>[16]</sup> The ligand **L** was obtained as a white powder in 79 % yield by reaction between 2,11-diaza[3.3](2,6)pyridinophane and 2 equiv of 3,3,3-trifluoro-2-(trifluoromethyl)-1,2-propenoxide *via* a regioselective epoxide ring opening in absolute ethanol (scheme 1) at the expected 1-position.<sup>[17]</sup> The X-ray structure of **L** (Figure 1) shows significant differences relative to that containing *tert*-butyl groups instead of the fluoroalcohol groups.<sup>[18]</sup> Indeed, the 12 atoms of the macrocyclic ring constitute a *syn* chair-chair conformation for the ligand with *tert*-butyl groups whereas **L** adopts a *syn* boat-boat conformation, which is already properly disposed to complex

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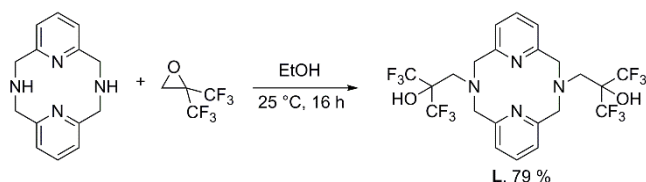
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metal salts. The two pyridyl rings are nearly parallel to each other (dihedral angle of  $27.79(3)^\circ$ ). The formation of a symmetrical species is also confirmed by the solution  $^1\text{H}$  NMR spectrum in  $\text{THF-d}_8$  with only one doublet and one triplet for the pyridine ring *m*-H and *p*-H nuclei, respectively, in a 2:1 ratio.



Scheme 1. Ligand L synthesis.

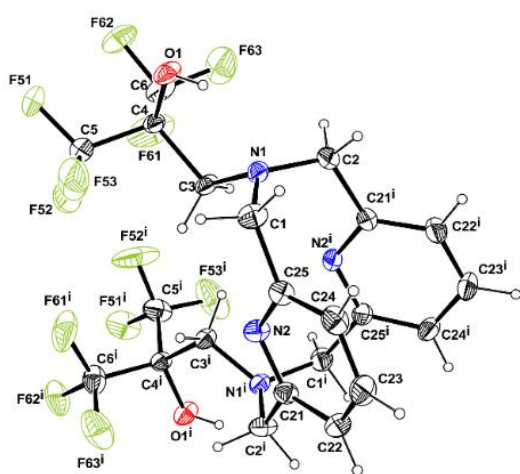
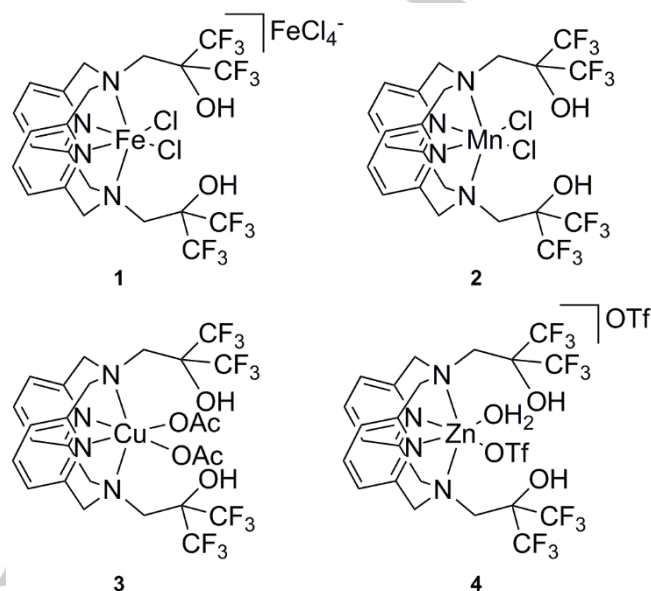


Figure 1. Molecular structure of L displaying thermal ellipsoids at the 50 % probability level.

The reaction of L with various first row metal salts led to the formation of the complexes listed in Scheme 2. Reaction with 2.5 equiv of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  at  $25^\circ\text{C}$  resulted in the formation of  $[(\text{L})\text{FeCl}_2](\text{FeCl}_4)$  (**1**) as a yellow solid in 90 % yield. The presence of  $\text{FeCl}_4^-$  as counteranion instead of  $\text{Cl}^-$  was not anticipated, but this behavior has already been reported for similar systems in the literature.<sup>[19]</sup> Starting from only one equiv of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  led to the formation of the same metal-complex **1** in 40 % yield. Reaction with 1 equiv of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  at  $25^\circ\text{C}$  resulted in the quantitative formation of  $(\text{L})\text{MnCl}_2$  (**2**) as a pale yellow powder.  $(\text{L})\text{Cu}(\text{OAc})_2$  (**3**) was obtained in 77 % yield as a blue powder by reaction between L and 1 equiv of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  in a  $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$  (1:1) mixture at  $25^\circ\text{C}$ . The reaction between  $\text{Zn}(\text{OTf})_2$  and L in  $\text{CH}_3\text{CN}$  resulted into the quantitative formation of a product that was identified as a monoaquo monotriflate complex  $[(\text{L})\text{Zn}(\text{OH}_2)(\text{OTf})](\text{OTf})$  (**4**) in the solid state, according to the X-ray analysis. The  $^1\text{H}$  NMR spectrum of **4** in acetone- $d_6$  reveals a symmetrical species in solution that exhibits only one doublet and one triplet respectively for the pyridine ring *m*-H and *p*-H nuclei. Due to the presence of water in the solvent, this likely results from an equilibrium and rapid exchange between the three possible complexes  $[(\text{L})\text{Zn}(\text{OH}_2)_n](\text{OTf})_2$  ( $n = 0, 1, 2$ ) in solution.

A broad signal at 4.39 ppm, attributed to the  $\text{H}_2\text{O}$  protons and integrating for 4H per complex molecule, confirms the presence of rapid exchange reactions involving water.



Scheme 2.  $[(\text{L})\text{FeCl}_2](\text{FeCl}_4)$  (**1**),  $(\text{L})\text{MnCl}_2$  (**2**),  $(\text{L})\text{Cu}(\text{OAc})_2$  (**3**) and  $[(\text{L})\text{Zn}(\text{OH}_2)(\text{OTf})](\text{OTf})$  (**4**) synthesized.

Crystals suitable for X-ray diffraction analysis were obtained, in all cases, by slow diffusion of diethyl ether into concentrated solutions in  $\text{CH}_3\text{CN}$ . The ORTEP plots for compounds **1**, **3** and **4** are given in Figure 2 and selected parameters are shown in Table 1. For complex **2** (Supporting Information, figure S1), the analysis was of sufficient quality to establish the atom connectivity, but the obtained structural parameters should be interpreted with caution because of the large R values.

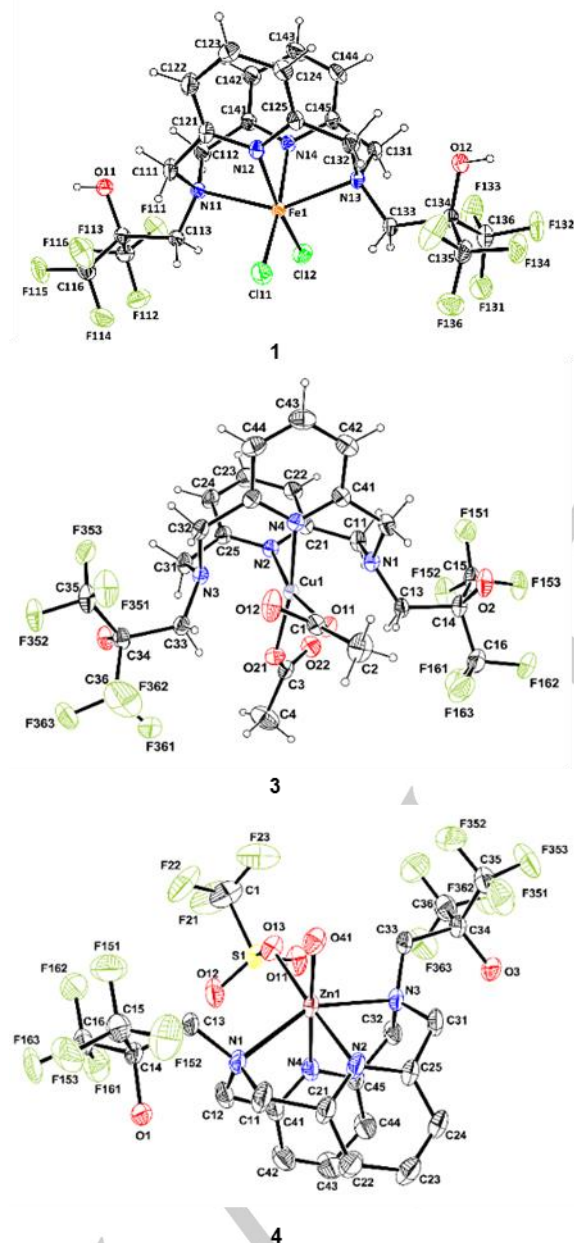
Table 1. Selected bond distances ( $\text{\AA}$ ) and angles (deg.) for complexes **1**, **3** and **4**.

	1	3	4
M-N1 (N11)	2.263(3)	2.4230(19)	2.315(2)
M-N2 (N12)	2.124(3)	2.0266(19)	2.080(2)
M-N3 (N13)	2.274(2)	2.420(2)	2.309(2)
M-N4 (N14)	2.104(2)	2.0009(19)	2.098(2)
N1(N11)-M-N2(N12)	76.81(9)	78.40(7)	79.08(9)
N3(N13)-M-N4(N14)	76.79(9)	78.75(7)	78.32(8)
N2(N12)-M-N4(N14)	77.30(9)	82.00(8)	82.13(10)
N1(N11)-M-N3(N13)	146.94(9)	149.54(6)	149.51(8)

All complexes display the same *syn* boat-boat conformation as described for free L. However, while the two pyridyl rings are roughly parallel for L (*vide supra*), this is no longer the case for

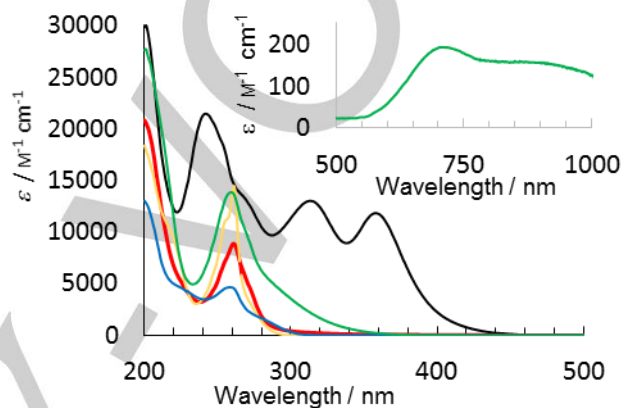
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the metal complexes, especially for **1** and **3** (dihedral angles of 51.5(1)°, 65.70(7)° and 34.81(11)° for **1**, **3** and **4**, respectively). All metal complexes possess a distorted octahedral geometry around the metal center with an  $N_{am}$ -M- $N_{am}$  angle between 147° and 150° and an  $N_{py}$ -M- $N_{py}$  angle between 77° and 82°. The M- $N_{am}$  distances are longer than the M- $N_{py}$  distances in all complexes (2.263 to 2.4230 Å vs. 2.0009 to 2.124 Å). Similar trends have been previously observed for similar complexes obtained from pyridinophane based ligands.<sup>[16a, 16c]</sup> Concerning the Cu<sup>II</sup>-metal complex **3**, elongated M- $N_{am}$  bond lengths are observed due to a Jahn-Teller effect as usually observed for d<sup>9</sup> ions.



**Figure 2.** Molecular structures of **1**, **3** and **4** displaying thermal ellipsoids at the 50 % probability level. H-atoms have been omitted for clarity for **4**.

The UV-Visible spectra of **L** and **1-4** were recorded in CH<sub>3</sub>CN solution. The free ligand **L** exhibits an intense transition at 259 nm attributed to a  $\pi \rightarrow \pi^*$  transition with an extinction coefficient of 4 600 M<sup>-1</sup> cm<sup>-1</sup>. The metal-complexes **1-4** exhibit similar transitions with extinction coefficients in the 4600 – 21 200 M<sup>-1</sup> cm<sup>-1</sup> range. In addition, the spectrum of **1** also displays two bands at 315 nm ( $\epsilon = 12\,900\text{ M}^{-1}\text{ cm}^{-1}$ ) and 361 nm ( $\epsilon = 11\,600\text{ M}^{-1}\text{ cm}^{-1}$ ) originating from the FeCl<sub>4</sub><sup>-</sup> counteranion, as previously reported.<sup>[20]</sup> Concerning (L)Cu(OAc)<sub>2</sub> (**3**), a weak d-d transition observed at 710 nm ( $\epsilon = 700\text{ M}^{-1}\text{ cm}^{-1}$ , see insert of Figure 3) is responsible for the blue color of the complex.



**Figure 3.** UV-Visible spectra of CH<sub>3</sub>CN solutions of **L** (blue), **1** (black), **2** (red), **3** (green) and **4** (orange). Insert: Zoom on the UV-Visible spectrum of **3**.

## Conclusions

In conclusion, in this study we have disclosed the synthesis of a new ligand **L** possessing a nitrogen based environment for the first coordination sphere and a second coordination sphere constituted of fluoroalcohol groups. **L** is able to coordinate first row metal centers, as shown by the synthesis of four metal-complexes **1-4** (metal = iron, manganese, copper and zinc), all of them characterized by X-ray crystallography. The ability of the fluoroalcohol groups to act as H-bond donor for the activation of substrates such as H<sub>2</sub>O<sub>2</sub> and the stabilization of reactive intermediates such as oxo complexes are now being evaluated and the results will be reported in due course.

## Supporting Information Summary

Synthetic and spectroscopic details corresponding to **L**, **1**, **2**, **3** and **4** are available in the Supporting Information. Crystal data and refinement parameters are shown in Table S1. CCDC 1527381 (for **L**), 1527382 (for **1**), 1527383 (for **3**) and 1527384 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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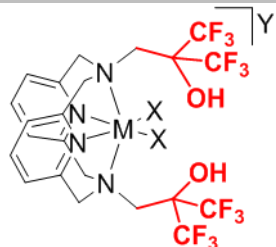
**Keywords:** fluoroalcohol • metal complexes • molecular models • pyridinophane

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Fluoroalcohol groups have been introduced on a tetradentate N-donor ligand. Four metal complexes containing this ligand are described.



M = Fe, X = Cl, Y = FeCl<sub>4</sub><sup>-</sup>  
M = Mn, X = Cl  
M = Cu, X = OAc  
M = Zn, X = OTf

**Metal complexes**

*Dr. Pascal Guillo, Dr. Jean-Claude Daran, Dr. Eric Manoury and Pr. Rinaldo Poli*

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**Synthesis and Characterization of First Row Metal Complexes Derived From a Pyridinophane Ligand Functionalized by Fluoroalcohol**