

ELUCIDATING THE ROLE OF THE O-METHOXY GROUP AT THE LOWER RIM APPENDED SALICYLIDENEAMINE SUBSTITUENTS OF CALIX[4]ARENE LIGAND ON THE MOLECULAR AND ELECTRONIC STRUCTURE OF DINUCLEAR Fe(III) BASED "DIAMOND CORE" COMPLEXES



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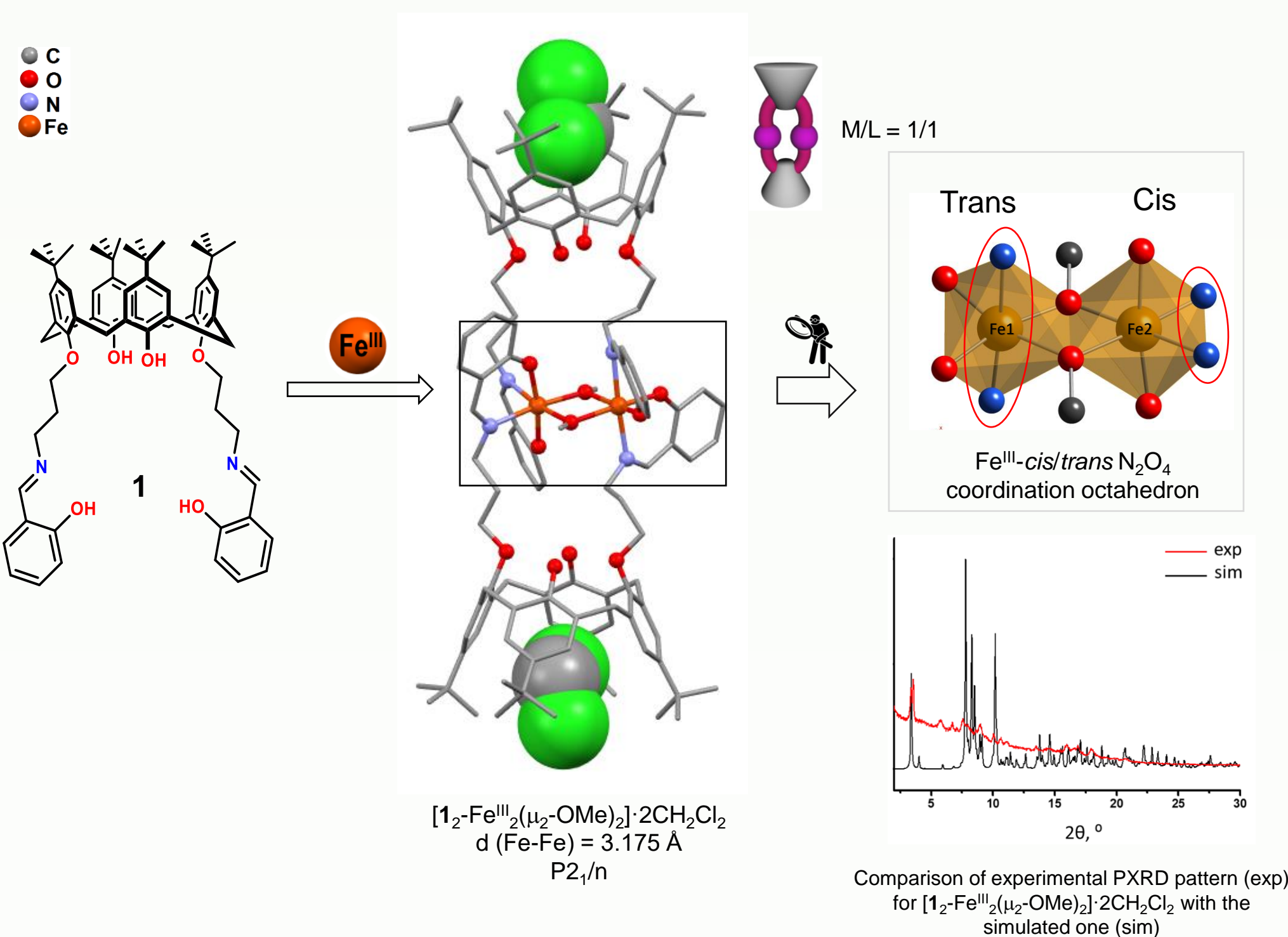
Introduction

New materials capable of storing and processing information at the level of a single molecule (atom) will contribute to the development of digital technologies. This type of molecules has to possess the property of bistability – the ability of molecules to exist in two stable spin states, for example, spin-crossover. In recent decades, there has been a growing interest in control over spin states of coordinative compounds based on Fe(III) cations because of their potential application in fields like molecular spintronics, memory and electronic devices, switches, sensors, etc [1].

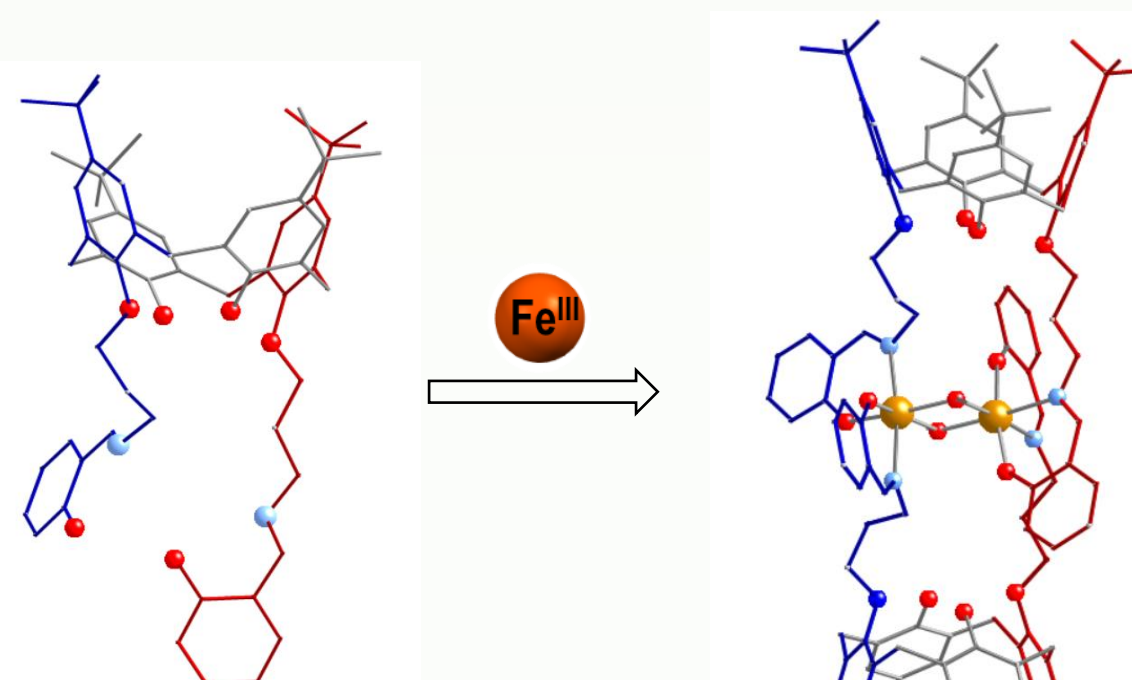
The rational design of molecular building blocks allows to manage over the coordination sphere of metal, hence magnetic properties can be controlled [2]. Due to the possibility of wide functionalization, calix[4]arenes are extremely attractive for the design of pre-organized ligands. Moreover, modification of calix[4]arene makes it possible to tune the structure of the complexes as well as to control their size and geometry. Disubstituted derivatives of calix[4]arenes allow fine-tuning of the metal environment by varying the length of the alkyl spacer and the nature of the substituent in the coordinating fragment. It is particularly attractive to obtain salen-type ligands possessing *N,O*-coordinating chelate fragments.

In this work we report on the synthesis of new Fe(III)-complexes based on polydentate lower rim disubstituted calix[4]arenes ligands, displaying salen-type coordination pocket. The structures of prepared coordination compounds were studied by X-ray diffraction analysis, IR and Mössbauer spectroscopy, HR-ESI mass spectrometry.

● C
● O
● N
● Fe

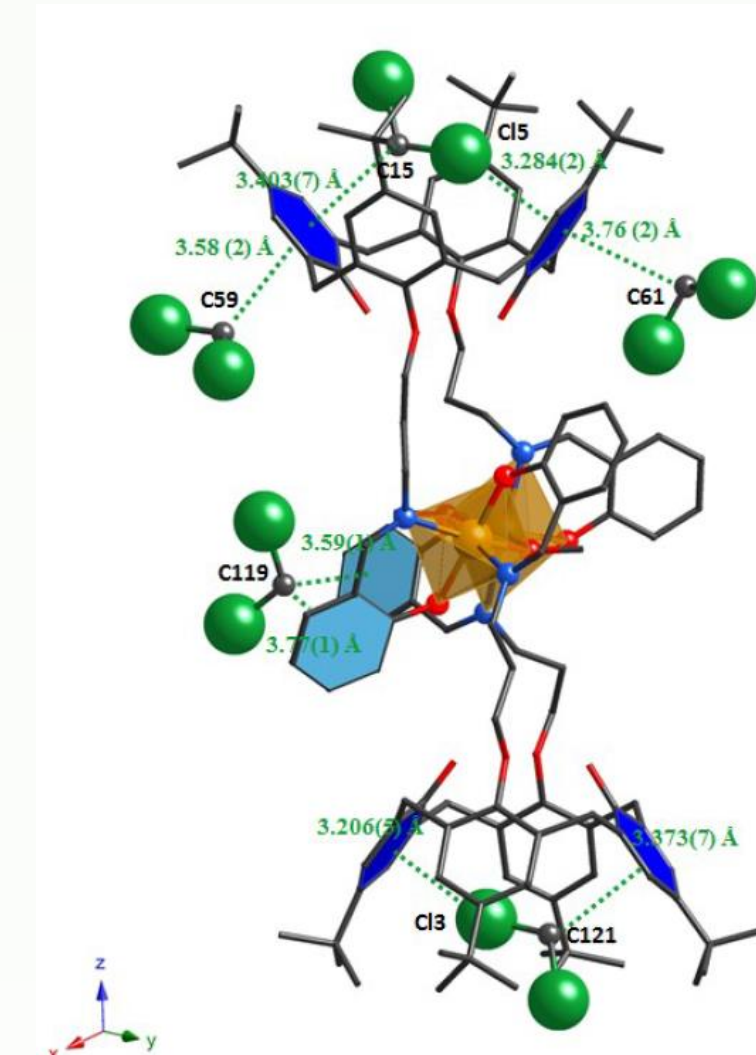


The structure of calix[4]arene 1 and the [1₂-Fe^{III}₂(μ₂-OMe)₂] complex optimized by DFT/B3LYP calculations

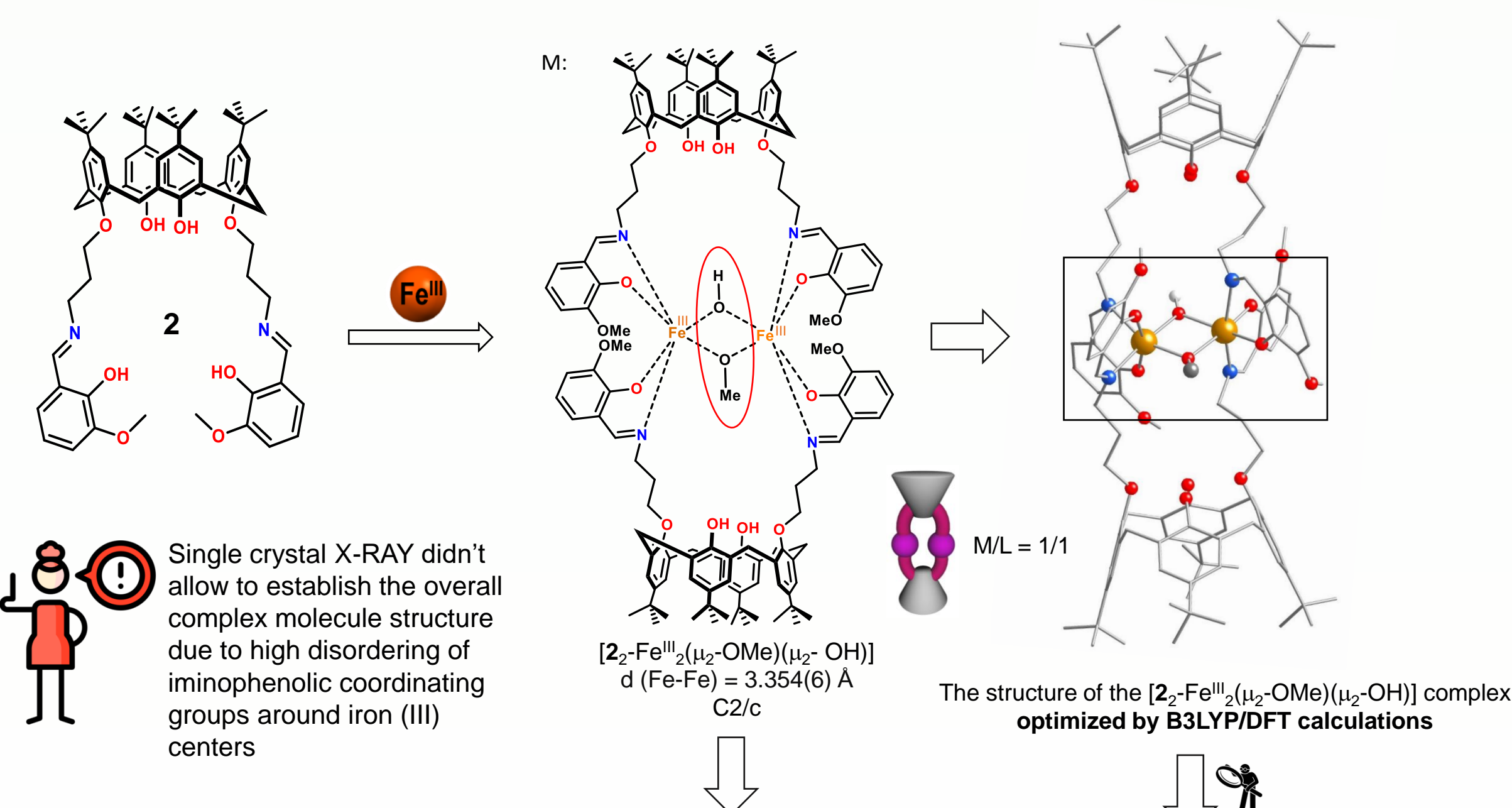


The substituent oriented along the axis of the macrocyclic platform → binds the Fe^{III} atom to the *cis*-position of nitrogen atoms

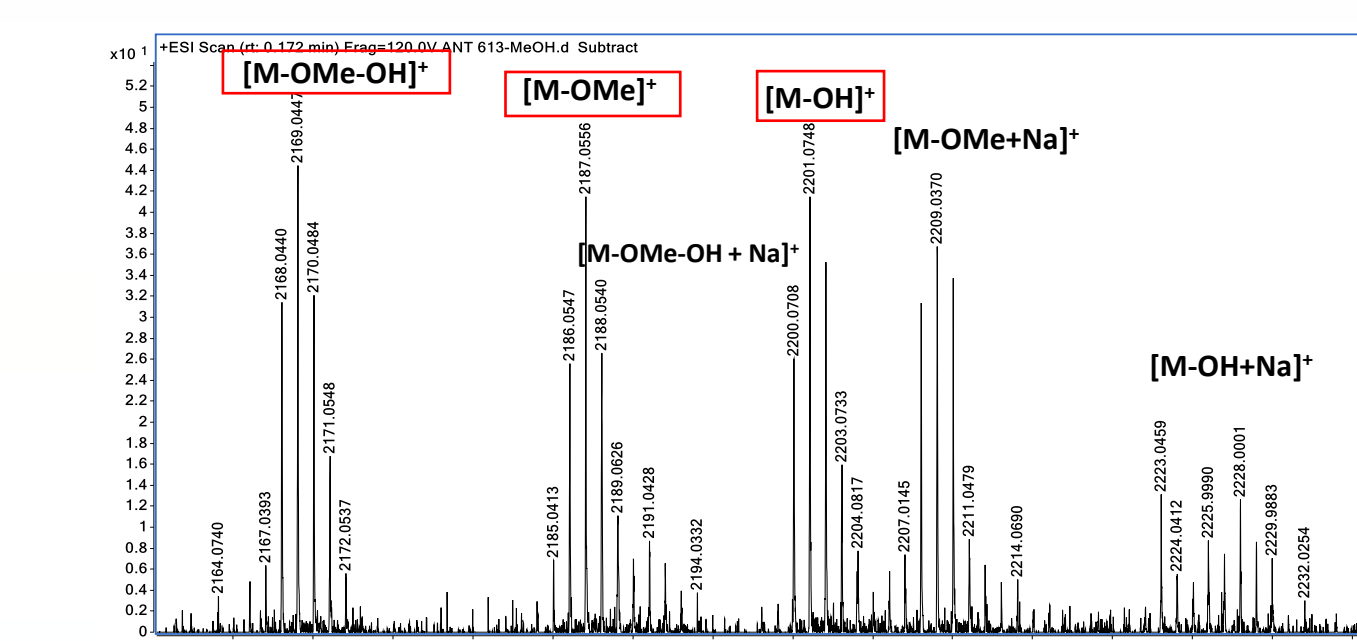
The substituent twisted towards the macrocyclic platform → binds the Fe^{III} atom to the *trans*-position of nitrogen atoms



For [1₂-Fe^{III}₂(μ₂-OMe)₂], non-covalent interactions within the crystal packing: CH/π bonding involving solvent CH₂Cl₂ molecules and aromatic units of calix[4]arene ligand.



Single crystal X-RAY didn't allow to establish the overall complex molecule structure due to high disordering of iminophenolic coordinating groups around iron (III) centers



HR-ESI-MS spectrum of the [2₂-Fe^{III}₂(μ₂-OMe)(μ₂-OH)] complex

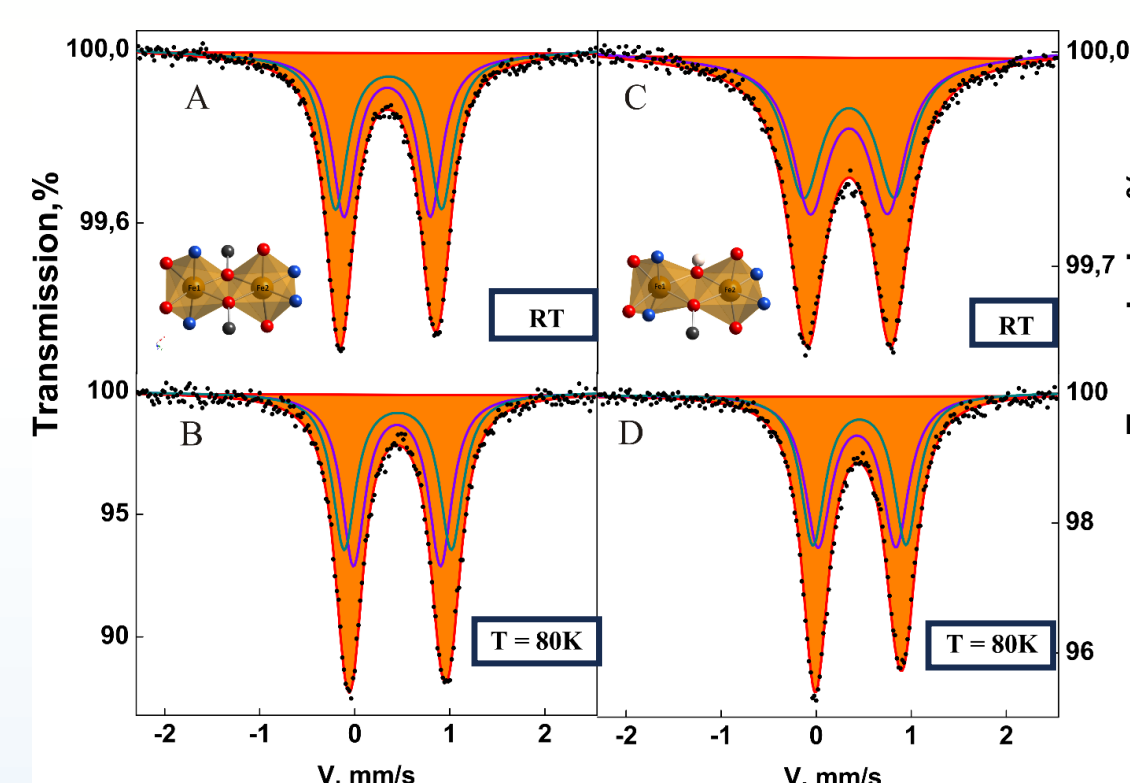
Presence of two different bridging moieties in complex [2₂-Fe^{III}₂(μ₂-OMe)(μ₂-OH)] was established by HR-ESI-MS analysis

Complex	[1 ₂ -Fe ^{III} ₂ (μ ₂ -OMe) ₂] _{exp}		[2 ₂ -Fe ^{III} ₂ (μ ₂ -OMe)(μ ₂ -OH)] _{exp}		[1 ₂ -Fe ^{III} ₂ (μ ₂ -OMe) ₂] _{sim}		[2 ₂ -Fe ^{III} ₂ (μ ₂ -OMe)(μ ₂ -OH)] _{sim}	
	<i>Cis</i> -N ₂ O ₄	<i>Trans</i> -N ₂ O ₄	<i>Cis</i> -N ₂ O ₄	<i>Trans</i> -N ₂ O ₄	<i>Cis</i> -N ₂ O ₄	<i>Trans</i> -N ₂ O ₄	<i>Cis</i> -N ₂ O ₄	<i>Trans</i> -N ₂ O ₄
∠ N-Fe-N, °	92.1(7)	176.0(8)	-	-	89.41	171.61	99.40	163.32
d(Fe-N), Å	2.183(7)	2.150(6)	-	-	2.2840	2.2321	2.1556	2.0570
d(Fe-O _{eq}), Å	2.175(7)	2.181(7)	-	-	2.2784	2.2190	2.2200	2.3150
d(Fe-O _{ax}), Å	1.946(6)	1.957(6)	-	-	1.9572	1.9616	1.9595	1.9719
d(Fe-O _{in}), Å	1.952(5)	1.929(5)	-	-	1.9586	1.9596	1.9698	1.9620
d(Fe-O _{out}), Å	2.010(5)	2.001(5)	-	-	2.0229	2.0745	2.0359	2.0914
d(Fe-Fe), Å	1.995(5)	2.021(5)	-	-	2.0281	2.0710	2.0398	2.0810
d(Fe-Fe), Å	3.175(2)		3.354(6)		3.215		3.272	
Angle distortion Σ, °	59.0981	64.7778	-	-	57.8832	57.8211	91.1959	92.6889
Torsional distortion Θ, °	189.4862	199.4586	-	-	186.9892	202.6332	319.7771	318.9536
Difference between the dihedral angles of the opposing aryl rings of the macrocyclic platform Δφ, °	24.31		37.84		44.25		47.27	
LUMO-HOMO, eV	1.97		2.05		2.39		2.29	

Bond lengths and distortion parameters of octahedral coordination spheres for Fe^{III} atoms in obtained complexes

Introduction of -OMe groups into *ortho*-position of iminophenolic moiety of ligand leads to:

- Increase of distances between iron (III) cations;
- Increase of distortion of coordinating sphere;
- Increase of symmetry of iron (III) coordinating spheres;
- Increase of distortion of macrocycle conformation.



⁵⁷Fe Mössbauer spectra [1₂-Fe^{III}₂(μ₂-OMe)₂] (A,B) and [2₂-Fe^{III}₂(μ₂-OMe)(μ₂-OH)] (C,D) at T=300 K and 80 K

Superposition of two doublets corresponding to the high-spin state (HS) of Fe^{III}-*cis/trans* in N₂O₄ environment independent of temperature

Conclusions

- The structure of new complexes with Fe(III) cations based on diimine derivatives of (thia)calix[4]arenes on the lower rim in *cone* configuration with different length of alkyl spacer has been established by single crystal X-ray diffraction analysis;
- The obtained complexes were characterized by physicochemical methods of analysis (¹H NMR, MALDI-TOF, XRD);
- DFT/B3LYP calculations demonstrated that the formation of two non-equivalent Fe^{III}-*cis/trans* N₂O₄ cations in complex [1₂-Fe^{III}₂(μ₂-OMe)₂] is caused by the most stable conformation of the ligand 1 and 2.
- The effect of the substituent in the iminophenolic moiety on the coordination sphere of metal ions in the formed complexes with Fe^{III} cations has been demonstrated;
- Complexes [1₂-Fe^{III}₂(μ₂-OMe)₂] and [2₂-Fe^{III}₂(μ₂-OMe)(μ₂-OH)] shows stable high spin state in ⁵⁷Fe Mössbauer spectra.

References

1. K. Kaushik, S. Mehta, M. Das, S. Ghosh, S. Kamilya, A. Mondal. *Chem. Com.* **2023**, 59(88), 13107-13124.
2. D. J. Harding, P. Harding, W. Phonsri. *Coord. Chem. Rev.* **2016**, 313, 38-61.

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