Synthesis, Structures and Properties of iron^{III} complexes with (*o*-carboranyl)bis-(2-hydroxymethyl)pyridine: racemic *versus* meso

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Abstract

The reaction of iron(II) chloride with *anti*- or *syn*-1,2-bis{(pyridin-2'-yl)methanol}-1,2-dicarba-*closo*-dodecaborane (*anti*- or *syn*-**oCB-L1**) afforded two new complexes, [Fe₂Cl₂(*anti*-**oCB-L1**²⁻)₂] (**1**) or Fe₂Cl₃(*syn*-**oCB-L1**²⁻)(EtO)(H₂O) (**2**), respectively. Both complexes were unambiguously characterized by means of X-ray structure analysis. Their solid state structures give evidence for the different coordination modes of the ligands. Both compounds are dinuclear Fe^{III} complexes, however, whereas in complex **1** there are two *anti*-**oCB-L1**²⁻ ligands per molecular unit, in complex **2** only one *syn*-**oCB-L1**²⁻ is found. In complex **1**, *anti*-**oCB-L1**²⁻ acts as a tetradentate N₂O₂-ligand affording a homochiral complex as a partial racemic mixture of Δ,Δ -[Fe₂Cl₂(^{RR}*anti*-**oCB-L1**²⁻)₂] and Λ,Λ -[Fe₂Cl₂(^{SS}*anti*-**oCB-L1**²⁻)₂]. In complex **2**, *syn*-**oCB-L1**²⁻ behaves as a bis-bidentate NO ligand. Only complex **1** could be synthesized in good yield and as a pure phase and it has been therefore fully characterized by spectroscopic methods and the magnetic properties studied.

Graphical abstract

Diastereoisomers of 1,2-bis{(pyridin-2'-yl)methanol}-1,2-dicarba-*closo*-dodecaborane have been separated and they show a distinct coordination modes toward iron.

1. Introduction

In recent decades, the design of hybrid functional materials has been a matter of special interest due to their potential applications in various areas.¹ A common approach for the preparation of such systems is the synthesis of organic-inorganic frameworks where transition metal ions and nitrogen containing heterocyclic ligands have proved useful for the construction of solid-state architectures.² In particular, pyridyl based ligands have been successfully used for building a wide array of architectures with applications ranging from gas storage in porous frameworks to novel luminescence or magnetic materials.³ The increasing need for evolved systems and demanding assemblies has led to the emergence of hetero-donating functions,^{3a,f} among which *N,O* ligands are candidates. During the last years we have synthesized and studied the supramolecular structures of a family of mono- and disubstituted chiral *o*-carboranylalcohols (Scheme 1), which are isolated as racemic mixtures.⁴ These molecules, that are prepared in very good yields from one pot reactions and from readily available starting materials, are centered on an *o*-carborane core with one or two arms radiating out of one of the cluster carbons, containing a chiral carbon that bears an alcohol and an aromatic moiety. The high thermal and chemical stability, hydrophobicity, acceptor character, ease of functionalization and three-dimensional nature of the icosahedral carborane clusters⁵ make these new molecules valuable ligands in coordination chemistry. Thus, soon after we obtained our first *o*-carboranylalcohols we initiated a systematic study of the

coordination chemistry of all these *N,O* monosubstituted *o*-carboranylalcohol ligands with cobalt and iron,⁶ and more recently on our disubstituted ligands (**oCB-L1**), with palladium and cobalt.⁷ The disubstituted ligand **oCB-L1** contains two chiral centers that can adopt either *R* or *S* configuration and therefore could lead to the formation of two diastereoisomers, a meso compound (*RS*; OH groups in a *syn* orientation) and a racemic compound (mixture of *SS* and *RR*; OH groups in an *anti* orientation). In the following we will name *anti* or *syn*-isomers as the racemate or meso compounds, respectively, as shown in Scheme 2. Since we were not able to fully separate the *syn*- from the *anti*-forms of **oCB-L1**, we performed the reactions with the *syn/anti* mixture as obtained from the synthesis. Using this mixture we have obtained a first family of *o*-carboranyl NBN (N: Nitrogen; B: Boron) based pincer palladium complexes, where the OH moieties remained uncoordinated.^{7b} Therefore the relative orientation of the hydroxyl moieties did not affect the complex formation in this case and both *syn* and *anti*-ligands reacted in the same way. However, the reactivity was more complex when we reacted the same mixture with a more oxophilic metal such as cobalt.^{7a} Only the *anti*-isomer provided an isolable mononuclear Co(II) complex $[\text{CoCl}_2(\text{anti-}\mathbf{oCB-L1}^{2-})]$, with the ligand acting as a tetradentate N_2O_2 -ligand. The fate of the corresponding *syn*-**oCB-L1** ligand could not be determined at that time. We are now able to separate the *anti* and *syn*-isomers of the **oCB-L1** compound by column chromatography and we report the reactivity of the separated diastereoisomers toward the also oxophilic metal iron. Structural data for all complexes and cyclic voltammetry and magnetic properties for one of the complexes is reported and discussed.

Scheme 1. Previously synthesized carboranylalcohols

Scheme 2. Stereoisomers for compound **oCB-L1**

2. Experimental

2.1. Materials and methods

All manipulations were carried out in air unless noted. The reactions were carried out in a glass vials equipped with a magnetic stirring bar and capped with a septum. The following chemicals were used: anhydrous FeCl_2 (98% Sigma Aldrich; used as received). 1,2-bis{(pyridin-2'-yl)methanol}-1,2-dicarba-*closo*-dodecaborane (**oCB-L1**) was synthesized as previously reported.^{4d} IR ATR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer. ^1H and ^{11}B spectra were recorded respectively at 300 and 96 MHz with a Bruker Advance-300 spectrometer in deuterated acetone or dimethyl sulfoxide, and referenced to the residual solvent peak for ^1H or to $\text{BF}_3\cdot\text{OEt}_2$ as an external standard for ^{11}B NMR. Chemical shifts are reported in ppm and coupling constants in Hertz. Multiplets nomenclature is as follows: s, singlet; d, doublet; t, triplet; br, broad; m, multiplet. Cyclic voltammetry measurements were made in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) electrolyte solutions in acetonitrile. A two-compartment cell equipped with a glassy carbon working electrode, a platinum gauze as counterelectrode and an Ag wire as pseudoreference electrode, properly checked against a ferrocene/ferrocenium couple (Fc/Fc^+) before test, was used.

Measurements were made on a BASi C-3 Cell Stand. Data were obtained at a scan rate of 100 mVs⁻¹. UV-visible measurements were carried out on a Hewlett Packard 8453 diode array spectrometer equipped with a Lauda RE 207 thermostat using a screw capped quartz cuvette.

2.2. Diastereomer separation of 1,2-bis{(pyridin-2'-yl)methanol}-1,2-dicarba-closo-dodecaborane (**oCB-L1**).

A synthesized mixture of *syn*- and *anti*-diastereoisomers of **oCB-L1** as previously obtained^{4d} was subjected to column chromatography on silica gel. Pure *anti*-**oCB-L1** was first obtained (eluent: hexane/ethanol 9:1), followed by *syn*-**oCB-L1** (eluent: dichloromethane).

NMR for *anti*-**oCB-L1** in deuterated acetone and dimethyl sulfoxide:

(**Acetone-D6**): ¹H NMR: 8.61 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 2H, C₅H₄N), 7.92 (td, *J* = 7.8, 1.8, 2H, C₅H₄N), 7.65 (d, *J* = 7.9, 2H, C₅H₄N), 7.44 (ddd, *J* = 7.5, 5.6, 1.0, 2H, C₅H₄N), 6.35 (d, *J* = 6.5, 2H, OH), 5.75 (d, *J* = 6.4, 2H, CHOH). ¹¹B NMR: -2.29 (br s, 2B), -9.63 (br s, 8B).

(**DMSO-D6**): ¹H NMR: 8.57 (d, *J* = 5.2 Hz, 2H, C₅H₄N), 7.89 (td, *J* = 7.7, 1.8, 2H, C₅H₄N), 7.70 (d, *J* = 7.8, 2H, C₅H₄N), 7.39 (dd, *J* = 7.4, 4.8, 2H, C₅H₄N), 7.06 (d, *J* = 5.8, 2H, OH), 5.55 (d, *J* = 5.8, 2H, CHOH). ¹H{¹¹B} NMR: Only signals due to B-H protons are given: 2.83 (br s, 2H), 2.27 (br s, 2H), 1.95 (br s, 2H), 1.82 (br s, 2H), 0.96 (br s, 2H). ¹¹B NMR: -2.98 (br s, 2B), -10.19 (br s, 8B).

NMR for *syn*-**oCB-L1** in deuterated acetone and dimethyl sulfoxide:

(**Acetone-D6**): ¹H NMR: 8.61 (ddd, *J* = 4.8, 1.7, 1.0, 2H, C₅H₄N), 7.91 (td, *J* = 7.8, 1.8, 2H, C₅H₄N), 7.66 (d, *J* = 7.9, 2H, C₅H₄N), 7.43 (ddd, *J* = 7.5, 4.8, 1.1, 2H, C₅H₄N), 6.19 (d, *J* = 6.5, 2H, OH), 5.98 (d, *J* = 6.3, 2H, CHOH). ¹¹B NMR: -2.40 (s, 2B), -9.08 and -10.02 (b s, 8B).

(**DMSO-D6**): ¹H NMR: 8.56 (d, *J* = 4.8 Hz, 2H, C₅H₄N), 7.88 (td, *J* = 7.6, 1.8, 2H, C₅H₄N), 7.58 (d, *J* = 7.9, 2H, C₅H₄N), 7.39 (dd, *J* = 7.4, 4.7, 2H, C₅H₄N), 6.98 (d, *J* = 5.7, 2H, OH), 5.80 (d, *J* = 5.9, 2H, CHOH). ¹H{¹¹B} NMR: Only signals due to B-H protons are given: 2.92 (br s, 1H), 2.33 (br s, 2H), 1.99 (br s, 4H), 1.65 (br s, 1H), 1.33 (br s, 2H). ¹¹B NMR: -2.96 (br s, 2B), -9.62 (br s, 8B).

2.3. $[Fe_2Cl_2(anti-oCB-LI^{2-})_2]$ (**1**)

A solution of *anti-oCB-L1* (50 mg, 0.14 mmol) in acetone (1 mL) was added to a stirred solution of $FeCl_2$ (17.78 mg, 0.14 mmol) in acetone (1 mL) in a small capped vial. The vial was closed and the orange-brown mixture was then gently warmed at about 50°C and shaken until formation of a clear yellowish solution. Once the solution was at room temperature, it was filtered through a Celite leach and left with the cap slightly open. Evaporation of the acetone gave yellow crystalline solid that were dried under vacuum to give **1** (41.7 mg, 63.8 %; phase purity established by powder X-ray Diffraction (PXRD) and FTIR-ATR. Elemental analysis calcd (%) for $C_{28}H_{40}B_{20}Cl_2Fe_2N_4O_4$, C, 37.56; H, 4.50; N, 6.26; found C, 37.50; H, 4.45; N, 6.33.

2.4. $[Fe_2Cl_3(syn-oCB-LI^{2-})_2]$ (**2**)

In a typical experiment, *syn-oCB-L1* (10 mg, 0.028 mmol) and $FeCl_2$ (3.54 mg, 0.028 mmol) were added to a small capped vial and the corresponding solvent was added (0.5 ~ 1.0 mL) and stirred until a clear solution was obtained. The solution was left undisturbed with the cap slightly open and monitored over the time for crystals growth. When acetone was used as the solvent, a yellow solution was initially formed that became darker over the time. No crystals were obtained and NMR analysis of the oily residue obtained after complete evaporations showed paramagnetic species. Further recrystallization from acetone only provided isolated white crystals for deboronated carborane species and paramagnetic species as the major species. The same results were obtained repeatedly with other solvents such as acetonitrile, dimethyl formamide, methanol or ethanol. Only in one of the experiments in ethanol, a few yellow crystals for **2** were grown on the vial walls that were used for crystallographic studies. As in all other experiments, the major species after work up of the reaction mixtures were non crystalline and paramagnetic. Not enough crystals were obtained for full characterization.

2.5. X-ray diffraction

Data were collected on a Bruker D8 Venture diffractometer. Data collection and processing were performed using the programs APEX2⁸ and SAINT⁹ and a multi-scan absorption correction was applied using SADABS.¹⁰ Structure solution and refinement were performed the crystallographic suite Olex2.¹¹ The structures were solved by direct methods,¹² which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.¹³ All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 (C–H, B–H, P–H) or 1.5 (O–H) times those of the respective atom. In **1**,

the refinement of the Flack parameter¹⁴ resulted in a value of 0.49 (2), indicating partial racemic twinning of the crystal.

Table 1. Crystallographic parameters for crystalline structures for complexes **1** and **2**.

	1	2
Empirical formula	C ₂₈ H ₄₀ B ₂₀ Cl ₂ Fe ₂ N ₄ O ₄	C ₁₈ H ₃₃ B ₁₀ Cl ₃ Fe ₂ N ₂ O ₅
Formula weight	895.44	683.61
Temperature [K]	150	100
Wavelength [Å]	0.71073	1.54178
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ /n
Unit cell dimensions [Å] and [°]	<i>a</i> = 9.5804(9) <i>b</i> = 14.3373(12) <i>c</i> = 30.150(2) α = 90 β = 90 γ = 90	<i>a</i> = 11.2915(4) <i>b</i> = 10.3670(4) <i>c</i> = 26.9294(9) α = 90 β = 93.199(2) γ = 90
Volume [Å ³]	4141.4(6)	3147.4(2)
<i>Z</i>	4	4
ρ_{calcd} [g cm ⁻³]	1.436	1.443
Absorption coefficient [mm ⁻¹]	0.872	9.994
<i>F</i> (000)	1816	1392
Crystal	Prism, red	Block, red
Crystal size [mm]	0.22 x 0.13 x 0.11	0.12 x 0.10 x 0.08
θ range for data	2.23 – 25.00	3.287 – 66.590
Collection [°]		
Reflections collected	38845	17584
Independent reflections	7321 [<i>R</i> _{int} = 0.0686]	5498 [<i>R</i> _{int} = 0.0923]
Completeness to	25.03, 99.8	66.59, 98.7
θ = [°], [%]		
Max. and min. Transmission	0.7454 and 0.6225	0.7528 and 0.3960
Largest difference peak and hole [e Å ⁻³]	1.379 and -0.379	1.041 and -1.153
Data / restraints / Parameters	7321 / 0 / 542	5498 / 0 / 365
Goodness-of-fit on <i>F</i> ²	1.076	1.047
Final <i>R</i> indices [<i>F</i> ² > 2 σ (<i>F</i> ²)]	<i>R</i> ₁ = 0.0501, w <i>R</i> ₂ = 0.1069	<i>R</i> ₁ = 0.0817, w <i>R</i> ₂ = 0.2086
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0635, w <i>R</i> ₂ = 0.1121	<i>R</i> ₁ = 0.1261, w <i>R</i> ₂ = 0.2461

CCDC 1446856 (**1**) and 1446810 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

2.6. Magnetic Measurements

Magnetic measurements were carried out on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2-300 K range. The magnetic fields used in the measurements were 0.03 T (from 2-30 K) and 0.5 T (from 2-300 K). Diamagnetic corrections were evaluated from Pascal's constants.

3. Results and discussion

3.1. Synthesis and characterization of $[Fe_2Cl_2(anti-oCB-L1^{2-})_2]$ (**1**)

The reaction of *anti*-**oCB-L1** with $FeCl_2$ in a 1:1 ratio in acetone at room temperature under air afforded a clear yellowish golden solution from which the dinuclear Fe^{III} complex **1** was subsequently isolated in nearly quantitative yield (Scheme 3). We have confirmed the structure of **1** by single crystal X-ray Diffraction (XRD) studies (Fig. 1) and the phase purity of the final product by powder X-ray Diffraction (PXRD). Complex **1** was also characterized by IR, cyclic voltammetry and UV-vis spectrometry. The magnetic properties of **1** have also been measured in the solid state.

The formation of this complex is summarized in eq. 1, assuming atmospheric O_2 is the oxidizing agent.

Note that no base is added to abstract the alcohol protons in this ligand. However, in the final complex **1** the ligands are both fully deprotonated. An increasing tendency to deprotonation of alcohols upon coordination is expected with increasing hardness of the metal ion, as was also observed in the corresponding monosubstituted ligands.^{6a}

Complex **1** crystallizes in the noncentrosymmetric space group $P2_12_12_1$ with a Flack parameter of 0.48. Therefore the solid structure is formed by domains of Δ,Δ -[Fe₂Cl₂(^{RR}*anti*-oCB-L1²⁻)₂] (Δ,Δ -**1**) (Fig. 1) and Λ,Λ -[Fe₂Cl₂(^{SS}*anti*-oCB-L1²⁻)₂] (Λ,Λ -**1**) where only homochiral Fe^{III} dimers are present. The molecular structure shows that six coordinated Fe^{III} atoms are linked by μ -alkoxo bridges from one of the oxygen atoms of each ^{RR}*anti*-oCB-L1²⁻ ligand to the opposite metal center. The environment around each iron atom can be described as a distorted octahedral geometry. The octahedral coordination of each Fe^{III} ion is completed by tetradentate ^{RR}*anti*-oCB-L1²⁻ ligand and a terminal Cl⁻ ion. As in the related mononuclear Co(II) complex,^{7a} the pyridine nitrogens are *trans*-positioned and the oxygen atoms of the chelating ligands are in a *cis*-position. Thus, our *anti*-oCB-L1²⁻ ligand behaves as a distinct tetradentate N₂O₂ ligand, as already observed in the previous Co complex,^{7a} and confirms this ligand as a new type of C₂-symmetric chiral building block. Unlike the common Schiff base backbone N₂O₂ ligands, our ligand preferentially adopts a *cis*- α configuration around the metal atoms (Fig. 1) and it is therefore able to produce chiral-at-metal complexes.

Fig. 1. Molecular structure of Δ,Δ -[Fe₂Cl₂(^{RR}*anti*-oCB-L1²⁻)₂] (Δ,Δ -**1**); hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Fe1–O14 1.897(4), Fe1–O22

2.073(4), Fe1–O44 2.083(4), Fe1–N20 2.129(5), Fe1–N28 2.173(5), Fe1–Cl1 2.283(2), Fe2–O22 2.053(4), Fe2–O44 2.083(4), Fe2–O52 1.902(4), Fe2–N50 2.131(6), Fe2–N58 2.128(6), Fe2–Cl2 2.274(2), O22–Fe1–O44 75.03(17), O22–Fe1–O14 93.94(18), O14–Fe1–N20 79.03(19), O22–Fe1–N28 75.97(19), O22–Fe1–Cl1 163.78(13), O44–Fe2–O52 92.84(18), O22–Fe2–O44 75.47(17), O44–Fe2–N50 75.91(19), O52–Fe2–N58 78.6(2), O44–Fe2–Cl2 166.65(14).

The presence of homochiral dimers in the crystal measured suggests that the enantiomeric forms of racemic *anti*-**oCB-L1** ((^{SS}*anti*-**oCB-L1**) and (^{RR}*anti*-**oCB-L1**)) self-recognize to form exclusively stereospecific, homochiral dinuclear complexes. We observed that the corresponding mononuclear Co^{II} complex [CoCl₂(*anti*-**oCB-L1**)],^{7a} whose OH group remained intact on coordination, formed homochiral ribbons (*RR* or *SS* enantiomeric complexes) along the *b* axis via O–H⋯Cl hydrogen bonding as represented in Scheme 4. A comparison between these homochiral ribbons in the Co complex and the crystal structure of complex **1** (Figure 1) is very instructive and may shed some light on the stereospecific formation of the homochiral dinuclear Fe(III) complex **1**. If we assume that a related supramolecular network is formed in the early stage of the reaction of *anti*-**oCB-L1** (*RR* and *SS*) with Fe^{II}, oxidation of the latter to Fe^{III} with release of HCl within each homochiral ribbon would lead to homochiral dimers as represented in Scheme 4. This could explain the stereospecific formation of Δ,Δ -[Fe₂Cl₂(^{RR}*anti*-**oCB-L1**²⁻)₂] (Δ,Δ -**1**) (Fig. 1) and Λ,Λ -[Fe₂Cl₂(^{SS}*anti*-**oCB-L1**²⁻)₂] (Λ,Λ -**1**).

Scheme 4

X-ray powder diffraction of the bulk crystalline material for **1** shows that all solid is isomorphous with $[\text{Fe}_2\text{Cl}_2(\textit{anti}\text{-oCB-L1}^{2-})_2]$ (**1**) (Figure 2) and therefore it is obtained as a pure phase. The infrared spectrum for complex **1** exhibits a typical intense and broad band for the carborane moiety at 2571 cm^{-1} . The electronic spectrum of complex **1** was measured in acetonitrile solution, and the corresponding spectral data is shown in Figure 3. The complex shows an intense band near 250 nm that is attributed to the $\pi-\pi^*$ transition of the ligand. Two other broad bands are observed at lower energy (300 and 360 nm), that can be assigned to alkoxo-to-iron charge transfer bands.¹⁵

Fig. 2. Comparison of experimental (top) and calculated (bottom) PXRD of complex **1**.

Fig. 3. UV/visible absorption spectrum of complex **1** in acetonitrile

The cyclic voltammogram (CV) of **1** was measured in acetonitrile (Fig. 4). One quasi-reversible redox process (I) was observed at $E_{1/2} = -0.08$ V which is attributed to the successive one-electron couples $\text{Fe}^{\text{III}} + 1e^- \rightarrow \text{Fe}^{\text{II}}$. In addition, an irreversible wave (II) was observed at +0.56 V. Such redox properties of **1** in solution are comparable to other related iron compounds in the literature.^{9a,16}

Fig. 4: Cyclic voltammetry (CV) of complex **1** at 100 mV^{-1} in dry acetonitrile. Plots versus Ag wire; the Fc/Fc^+ couple was measured at +0.220 V versus this reference under the same conditions.

Solid-state, variable-temperature (2-300 K) magnetic susceptibility data using 0.03 and 0.5 T fields were collected on polycrystalline samples of compound **1**. The resulting plot is shown in Figure 5 as $\chi_{\text{M}}T$ vs T (and M vs H inset). The data for compound **1** shows strong antiferromagnetic behavior, whereas $\chi_{\text{M}}T$ values drop from a value of $6.56 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K (lower than the expected for two independent high spin Fe^{III} centers of $8.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ having $g = 2.00$) to a value of $0.19 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K, providing clear evidence of a significant antiferromagnetic interaction between the two Fe^{III} centers. Experimental $M/N\mu_{\text{B}}$ vs H data at 2 K corroborate such facts by exhibiting low values at the maximum field (5 T), indicating strong antiferromagnetic exchange and/or low-lying excited states. Magnetic susceptibility data were analyzed using the highest field and program PHI,¹⁷ that incorporates the spin exchange Hamiltonian $H = -2JS_1S_2$, where here $S_1 = S_2 = 5/2$. The best fit matches well with

experimental data and provided the following values: $g = 1.98$, $2J = -8.06$ ($J = -16.12$ cm^{-1}) cm^{-1} and $\rho = 5$ %. Overall, the analysis of the data agrees with the shape and numbers observed in the experimental measure, where the exchange coupling for both Fe^{III} compounds is strongly antiferromagnetic.¹⁸

Fig. 5. Fitting of the $\chi_M T$ vs T of compound **1** between 2 and 300 K. The experimental data is shown as black squares and the red line corresponds to the fitting values. Onset: experimental data of $M/N\mu_B$ vs H at 2 K is shown as dots and with a line.

3.2. Reactivity of *syn*-oCB-L1 toward FeCl_2 .

One of the questions that we asked ourselves was whether the less flexible *syn*-oCB-L1 ligand, due to the close proximity of both alcohol groups, could coordinate and in that case its coordination mode. As in all iron chemistry in this work, the paramagnetic nature of the Fe^{III} complexes, formed when mixed with the ligand under aerobic conditions, prevented the analysis with NMR spectroscopy. Thus, reactions of *syn*-oCB-L1 with FeCl_2 were set up under different solvent conditions (acetone, acetonitrile, dimethyl formamide, methanol and ethanol), giving in all cases clear solutions that were left evaporating under ambient conditions. Unfortunately, crystals for uncoordinated *nido* species were obtained in most cases after 3-4 days that account for the weakness of this ligand under prolonged contact with relatively polar and/or basic solvents.¹⁹ The major species after work up of the reaction mixtures were non crystalline and paramagnetic so that full characterization was not possible (see experimental section). Only in one case a few crystals for an Fe^{III} complex could be obtained from ethanol and

that corresponded to a dinuclear Fe^{III} complex $[\text{Fe}_2\text{Cl}_3(\text{syn-}\mathbf{oCB-L1}^{2-})(\text{EtO})(\text{H}_2\text{O})]$ (**2**). Molecular structure for complex **2** is shown in Figure 6 and crystallographic data is summarized in Table 1 and experimental section. As it can be seen in Figure 6, the coordination of the $\text{syn-}\mathbf{oCB-L1}^{2-}$ is different to that of the corresponding $\text{anti-}\mathbf{oCB-L1}^{2-}$ ligand. Whereas the latter behave as a tetradentate N_2O_2 ligand, the syn- isomer behaves as a bis-bidentate NO ligand. The crystal structure of **2** reveals a dinuclear Fe^{III} unit, linked by two μ -alkoxo bridges from the oxygen atoms of the $\text{syn-}\mathbf{oCB-L1}^{2-}$ ligand and another from an alkoxide EtO^- group. The complex is however asymmetric as the environment around each iron atom is different. Whereas one Fe^{III} center is six-coordinate and has a distorted octahedral geometry, the other Fe^{III} center is now five-coordinate with a distorted square pyramidal geometry (as ascertained by the factor $\tau = 0.05$; $\tau = 0$ for a square pyramid and $\tau = 1$ for trigonal bipyramid).²⁰ One chloride ion, the bridging alkoxo oxygens and the nitrogen atom of the pyridine ring constitute the basal plane of the square pyramid, and the other chloride ion occupies the apical position of the pyramid. The other Fe^{III} center shows a conventional octahedral geometry, which is completed by the two μ -alkoxo bridges from the $\text{syn-}\mathbf{oCB-L1}^{2-}$ ligand and EtO^- , one alkoxo oxygen $\text{syn-}\mathbf{oCB-L1}^{2-}$, a nitrogen from the pyridine ring, a chloride ion and a water molecule. The Fe-O distances and Fe $\cdots$ Fe separation (3.162(2)Å) are within the range of values found for other bis(μ -alkoxo) bridged Fe^{III} complexes.²¹ Formation of related bis(μ -alkoxo) bridged Fe^{III} complexes in methanol solutions has been reported.²²

Fig. 6. Molecular structure of **2**; hydrogen atoms are omitted for clarity). Selected interatomic distances (Å) and angles (°): Fe1–O1 2.019(5), Fe1–O14 1.949(5), Fe1–O22 2.059(5), Fe1–O29 1.982(5), Fe1–N20 2.133(6), Fe1–Cl1 2.267(2), Fe2–O22 1.936(5), Fe2–O29 1.971(6), Fe2–N28 2.153(9), Fe2–Cl2 2.175(3), Fe2–Cl3 2.268(3), O14–Fe1–N20 79.0(2), O1–Fe1–N20 171.5(2), O22–Fe1–Cl1 176.48(16), O22–Fe2–N28 75.1(3), Cl2–Fe2–Cl3 109.51(12), Fe1–O29–Fe2 106.2(2), Fe1–O22–Fe2 104.6(2).

According to the Cambridge Database (CSD, version 5.36 updated in May 2015),²³ **2** appears to be the first dinuclear Fe^{III} complex with such mixed octahedral and square pyramidal geometry. This certainly reflects the difficulties of the *syn*-**oCB-L1** ligand to coordinate as confirmed by the molecular structure of **2**, that shows an ethoxide and a water molecule to complete the coordination of the dinuclear Fe^{III} complex.

Conclusions

anti-**oCB-L1**²⁻ acts as a tetradentate N₂O₂-ligand affording a dinuclear Fe^{III} complex as a partial racemic mixture of homochiral complex Δ, Δ -[Fe₂Cl₂(^{RR}*anti*-**oCB-L1**²⁻)₂] and Λ, Λ -[Fe₂Cl₂(^{SS}*anti*-**oCB-L1**²⁻)₂]. This and our previous results, consolidate this *anti*-**oCB-L1**²⁻ as a C₂-symmetric tetradentate N₂O₂-ligand chiral building block which is able to produce chiral-at-metal complexes. On the contrary, the *syn*-**oCB-L1**²⁻ ligand finds difficult to coordinate and mostly degradate under the crystallization conditions. A dinuclear Fe^{III} complex has been however obtained where the *syn*-isomer behaves as a bis-bidentate NO ligand. The present work also corroborates that the coordination chemistry of the *syn/anti* diastereoisomers of **oCB-L1** ligand is clearly different when the metals employed are oxophilic. Complex **1** is obtained as a single phase in the solid state and shows a strong antiferromagnetic behavior. The redox properties in solution are comparable to other related iron compounds in the literature.

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