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Communication

A New Dinucleating N,O Donor Ligand (H_2BPClNOL) and the Structural and Magnetic Properties of two Diiron Complexes with the di-μ-Alkoxo Motif

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Dois complexos binucleares de Fe^{III}, obtidos a partir de um novo ligante polidentado (H_2BPClNOL = N-(2-hidroxibenzil)-N-(2-piridilmetil)[(3-cloro)(2-hidroxi)]propilamina e contendo a unidade estrutural Fe^{III}(μ-alcoxo)$_2$$Fe^{III}$, foram caracterizados estruturalmente através de estudos cristalográficos e magneto-químicos. Os complexos $[Fe_2(BPClNOL)_2(OAc)]ClO_4$ **(1)** e $[Fe_2(BPClNOL)_2(H_2O)_2](ClO_4)_2.4H_2O$ **(2)** diferem entre si pela presença de um grupo acetato em ponte entre os sítios de Fe^{III} no complexo **(1)**. O complexo contendo a ponte acetato apresenta constante de acoplamento antiferromagnético aproximadamente 20 % menor quando comparado ao complexo sem ponte acetato.

A new polidentade ligand, N-(2-hydroxybenzyl)-N-(2-pyridylmethyl)[(3-chloro)(2-hydroxy)]propylamine (H_2BPClNOL), was synthesized and two Fe_2^{III} complexes containing the Fe^{III}(μ-alcoxo)$_2$$Fe^{III}$ core were structurally and magnetically characterized. Complex $[Fe_2(BPClNOL)_2(OAc)]ClO_4$ **(1)** differs from complex $[Fe_2(BPClNOL)_2(H_2O)_2](ClO_4)_2.4H_2O$ **(2)** by the presence of an acetate-bridge between the two iron centers. The complex with the acetate bridge is about 20 % less antiferromagnetically coupled than the complex without the acetate bridge.

Keywords: binuclear Fe^{III} complexes, X-ray analysis, magnetochemistry.

Introduction

In the last decades, the search of magnetic information on dinuclear iron complexes has received special attention.[1] Studies of iron synthetic complexes have shown that the oxo bridge is responsible for the strong antiferromagnetic coupling (usually $-50 > J > -200$ cm^{-1})[2-5] and that complexes with alkoxo, phenoxo, or hydroxo bridges are weakly coupled (usually $0 > J > -30$ cm^{-1})[4].

The exchange coupling between the high-spin Fe^{III} ions in dinuclear iron model complexes has been a powerful tool to infer about bridging groups that are present in iron enzymes[2,6-8]. In this way, it was suggested that in the deoxy form, hemerythrin has a hydroxo bridge ($J \cong -13$ cm^{-1})[6,9] while in the *met* form, an oxo bridge ($J \cong -134$ cm^{-1})[9] mediates the strong antiferromagnetic coupling between the Fe^{III} centers. In addition, on the basis of magnetic susceptibility studies of the oxidized form of purple acid phosphatases, a dinuclear Fe_2^{III} center bridged by a carboxylate and two hydroxo groups ($J \cong -15$ cm^{-1}) has been proposed[10].

Accordingly to Gorun and Lippard[4], the magnitude of exchange interaction in dinuclear iron (III)-complexes is strongly dependent on the shortest exchange pathway between the two metal centers. They have shown that the magnitude of the exchange coupling constant J is tied up with the structural parameter P through the following correlation: $-J$ (cm^{-1}) = A*exp (B*P [Å]), with A = 8.763*10^{11} and B = -12.663. The parameter P corresponds to half the length of the shortest bridge in the complex. This relationship has been applied with some success for iron (III) oxo-bridged complexes[4]. Moreover, in a recent study, based on a semi-empirical angular overlap model, Weihe and Güdel[5] have shown that the bridging angle Fe-O-Fe also influences the magnitude of the exchange coupling. They concluded that J and the Fe-O-Fe angle are correlated with a total spread, which is about half of the Fe-O dependence for a wide

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Dedicated to Prof. Eduardo Stadler *in memoriam;*

range of μ-oxo diiron complexes. However, no such correlations have been described for di-μ-alkoxo, -phenoxo and –hydroxo complexes. In an attempt to accumulate more data for further discussion of magneto-structural correlations for this type of complexes, we present here the synthesis of a new polidentade ligand (H_2BPClNOL), which was skilfully used to synthesize complexes that allowed to study the influence of the Fe-O-Fe angle on the exchange coupling.

Experimental

*Syntheses of complexes [Fe_2(BPClNOL)$_2$(OAc)]ClO_4 (**1**) and [Fe_2(BPClNOL)$_2$(H_2O)$_2$](ClO_4)$_2$.4H_2O (**2**)*

Complex [Fe_2(BPClNOL)$_2$(OAc)]ClO_4 (**1**) (Figure 1a) was obtained by addition of 1.03 g (2 mmol) of $Fe(ClO_4)_3.9H_2O$ to a solution of 0.61 g (2 mmol) of H_2BPClNOL[11] in 20 cm^3 of methanol, resulting in a dark blue color. After addition of 0.54 g (4 mmol) NaOAc.3H_2O, the color changed to purple. Immediately, a solid was formed, which was collected by filtration, washed with cold 2-propanol and ether. Yield = 1.19 g, 68 %. Anal. Calc. for $C_{34}H_{37}N_4O_6Cl_2Fe_2.ClO_4$: C, 46.42; H, 4.24; N, 6.37. Found: C, 46.48; H, 4.27; N, 6,49%. Crystals[13] of the complex were obtained by recrystallization in MeOH/CH_3CN (1:1). The complex [Fe_2(BPClNOL)$_2$(H_2O)$_2$] (ClO_4)$_2$.4H_2O **2** (Figure 1b) was synthesized similarly to complex **1**. However, only 1 mmol of NaOAc.3H_2O was added. Suitable crystals[13] for a single crystal X-ray structure analysis of **2**, were obtained on prolonged standing of the solution at room temperature. Yield = 1,48 g, 72%. Anal. Calc. for $C_{32}H_{38}N_4O_6Cl_2Fe_2.(ClO_4)_2(H_2O)_4$: C, 37.38; H, 4.50; N, 5.45. Found: C, 37.77; H, 4.57; N, 5.50%.

Results and Discussion

The dinuclear complex cation [Fe_2(BPClNOL)$_2$(OAc)]$^+$ consists of two six-coordinated iron centers, which are bridged by two alkoxo oxygen atoms (O_3 and O_4) from the ligand H_2BPClNOL and one acetate group. The two iron atoms exhibit a distorted octahedral structure with an N_2O_4 donor set where the nitrogen atoms from the tertiary amine and from the pyridine groups and the oxygen from the phenolate are in a facial arrangement. The bridging oxygen atoms from the alkoxo groups are bond asymmetrically to the two iron centers [Fe1-O_3 = 2.071(3), Fe_2-O_3 = 1.959(3) Å and Fe1-O_4 = 1.925(3), Fe_2-O_4 = 2.079(3) Å]. The Fe···Fe distance is 3.041(1) Å and lies in the range of Fe···Fe distances observed in other di-μ-alkoxo-Fe_2^{III} and di-μ-hidroxo-Fe_2^{III} complexes[4,7].

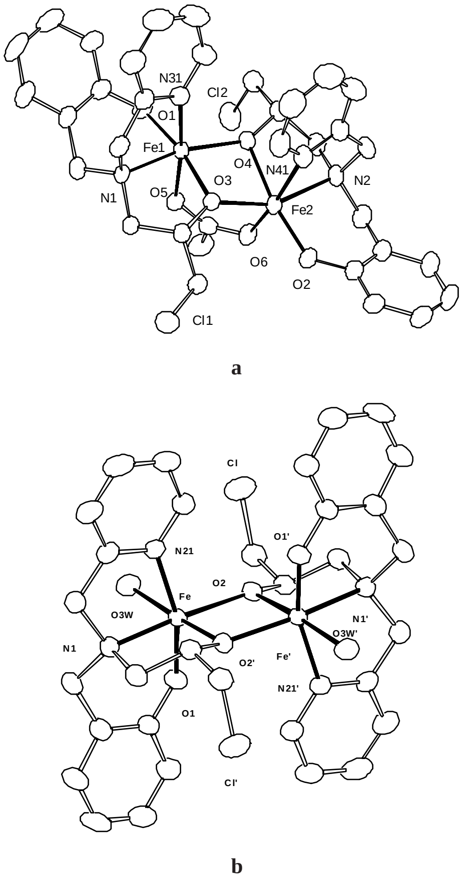
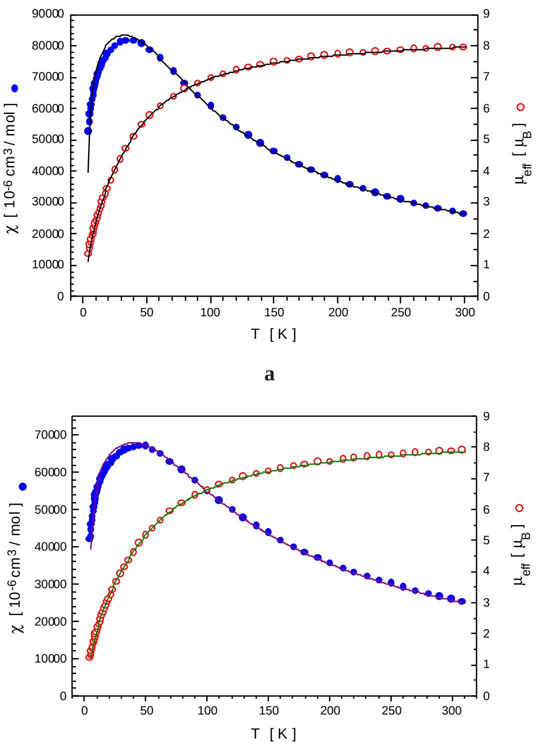


Figure 1. Molecular structure, selected bond lengths (Å) and angles (°) of complex **1** (a): Fe1-O1 1.885(3), Fe1-O4 1.925(3), Fe1-O5 2.017(3), Fe1-O3 2.071(3), Fe1-N31 2.155(4), Fe1-N1 2.171(3), Fe2-O2 1.859(3), Fe2-O3 1.959(3), Fe2-O6 2.034(3), Fe2-O4 2.079(3), Fe2-N2 2.178(3), Fe2-N41 2.178(4), Fe1**..**Fe2 3.041(1), Fe1-O3-Fe2 97.9(1), Fe1-O4-Fe2 98.7(1) and complex **2** (b): Fe-O1 1.886(2), Fe-O2 1.961(2), Fe-O(3W) 2.029(2), Fe-O(2)' 2.057(2), Fe-N21 2.162(2), Fe-N1 2.189(2), Fe**..**Fe' 3.122(1), Fe-O2-Fe' 101.95(8).

The iron atoms in the centrosymmetric, binuclear structure of [Fe_2(BPClNOL)$_2$(H_2O)$_2$]$^{2+}$ are bridged by two alkoxo oxygen atoms of the two H_2BPClNOL ligands. Each of these ligands also binds one Fe atom through two nitrogen atoms (the tertiary N atom and one from the pyridyl group) and one oxygen from the phenolate in a meridional fashion, differently from complex **1**, in which the same group of atoms of H_2BPClNOL are coordinated facially. Two water molecules in *anti*-configuration complete the distorted octahedral coordination around the Fe atoms. In complex **1** the Fe-O_{alkoxo} bond distances (av. 2.008 Å) are very similar to those observed in complex **2** (av. 2.009 Å) whereas the Fe···Fe distance of 3.122 Å in **2** is somewhat longer than that detected in **1** (3.041 Å). Consequently the Fe-O_{alkoxo}-Fe angles in **2** are larger (av. 101.95°) compared to those in **1** (98.8°). This feature represents the major difference between the bridging units in these complexes.

Variable temperature magnetic studies of powder samples of **1** and **2** between 4.5 and 300 K show that the two Fe^{III} centers are weakly antiferromagnetically coupled in both complexes (Figure 2). Very good agreement between theory and experimental data was obtained by using the following parameters: g = 2.0, J = -3.9 (2) cm^{-1}, % imp = 0.0 and TIP = 400 x 10^{6} cm^3/mol for **1** and g = 2.0, J = - 4.8 (2) cm^{-1}, % imp = 0.07 and TIP = 400 x 10^{6} cm^3/mol for **2**. These values of J lie in the range but at the lower end, of di-μ-alkoxo bridged Fe_2^{III} complexes[14-16]. Moreover, a comparison between **1** and **2** reveals a small but significant increase (~ 20 %) in the J value with larger Fe-O_{alkoxo}-Fe bridging angle. Since the shortest superexchange pathway [Fe-O_{alkoxo}= 2.008 Å in the Fe_2- (μ-alkoxo)$_2$ unit] and the coordination environment around the Fe^{III} centers are very similar in **1** and **2**, the increase in the Fe-O_{alkoxo}-Fe bridging angle should be the main factor responsible for the increase of the coupling constant in **2**. A direct interaction between the Fe^{III} centers can be excluded for this type of complexes, due to the large metal-metal distance (over 3 Å).[17] On the other hand, all attempts to correlate our data with Güdel's model[5] were unsuccessful.



a

b

Figure 2. Magnetic susceptibility and effective magnetic moment as a function of the temperature for complex **1** (a) and **2** (b).

In summary, we have synthesized and characterized two Fe_2^{III} complexes of the new polydentate ligand H_2BPClNOL. This ligand is able to keep the dinuclear Fe^{III}(μ-alkoxo)$_2$$Fe^{III}$ unit fixed. The presence of an additional acetate bridge in **1** has been shown to influence exclusively the Fe-O_{alkoxo}-Fe angle and consequently the magnitude of the exchange coupling between the Fe^{III} centers. The terminally ligated phenolate and the (μ-alkoxo)$_2$(μ-carboxylate) bridging unit in **1** also provide an interesting model for the oxidized form of purple acid phosphatases, which contains a dinuclear Fe_2^{III} unit, probably bridged by a carboxylate and two hydroxo groups[10]. The synthesis and structural characterization of further dinuclear Fe^{III} complexes with H_2BPClNOL and their magnetic properties are under way and will be the subject of future reports.

Acknowledgements

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Supplementary Material

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers, 128891-128892.

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(5g, 23.3 mmol) dissolved in methanol (50 cm^3) and an equimolar amount of epychloridine. After stirring overnight at room temperature, the solution was concentrated and purified by chromatography employing chloroform as the eluent. An orange oil was obtained. Yield = 92%. ^{1}H NMR ($CDCl_3$); d: 2.7 (dd, 2H, CH_2N), 3.4 (dd, 2H, CH_2Cl), 3.6-3.9 (m, 5H, CH, NCH_2py, NCH_2ph), 6.6-7.1 (m, 6H, CH aromatic), 7.5 (td, 1H, CH aromatic), 8.5 (d, 1H, CH py).

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13. X–ray data: Complex (**1**): $Fe_2C_{34}H_{37}N_4O_{10}Cl_3$, FW = 879.73 g.mol^{-1}. Space group: $P2_1/n$ [nr. 14], a = 12.284(3), b = 13.642(3), c = 23.040(5) Å, b = 99.90(3)^{o}, V = 3803.5(2) Å^3, Z = 4, d = 1.536 Mg.m^{-3}, R = 0.0438 for 6683 unique reflections and 479 parameters. Complex (**2**): $Fe_2C_{32}H_{46}N_4O_{18}Cl_4$, FW = 1028.23 g.mol^{-1}. Space group: $P2_1/c$ [nr. 14], a = 9.573(2), b = 10.989(2), c = 20.462(4) Å, b = 101.62(3)^{o}, V = 2108.4(7) Å^3, Z = 2, d = 1.620 Mg.m^{-3}, R = 0.0340 for 3704 unique reflections and 325 parameters.
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