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Synthesis and characterization of Fe(III)(3-CH$_3$O-qsal)$_2$PF$_6$ · nH$_2$O (n = 0, 2)

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Abstract

Compounds Fe^{III}(3-CH$_3$O-qsal)$_2$PF$_6$·nH$_2$O (n = 0, 2) (**1**, **1**·2H$_2$O) were synthesized and characterized: the structure of **1** and the magnetic properties of both compounds were determined. **1**·2H$_2$O presents properties characteristic of high-spin Fe(III), while **1** presents properties of low-spin Fe(III) with an onset of a gradual spin crossover at ca. 300 K.

Keywords: Spin crossover; crystal structures; magnetic properties; ligands; iron (III)

1. Introduction

Some transition metal complexes, e.g. some of iron (III), present a spin crossover (SCO) phenomenon induced by the application of an external stimulus such as temperature, pressure or light. This transition is indicated by a magnetic and structural change, and depends strongly on the cooperativity between building blocks [1]: the phenomenon may be tuned through changes in, e.g., ligand, counter-ion or even the presence of solvates. The coordination environment FeN$_4$O$_2$ is able to produce several complexes with SCO properties [1]. An example is [Fe^{III}(qsal)$_2$]$^+$ (Hqsal = N-(8-quinolyl)salicylaldimine) (see e.g. refs. [2] and [3]). Several other Fe(III) complexes with a N$_2$O-donor set are also able to exhibit SCO properties, however, as far as we

know, regarding the qsal, only the unsubstituted one and the derivated qnal (Hqnal = N-(8-quinolyl)-2-hydroxy-1-naphthaldimine) were reported [1,4]. Recently we have started to use ligands derived from qsal in order to obtain new SCO Fe(III) complexes. The chosen substituents are expected to lead to an increase of the interaction between the Fe(III) complexes and, in this way, to the enhancement of the cooperativity of the SCO transitions. This is included in a much broader effort that is taking place: the search of multifunctionality, either through the introduction of the appropriate counter-ion or through the modification of the ligands. In the present paper we report the introduction of a CH_3O- group in the qsal ligand (see Scheme 1), where this electron donor group is expected to favour the stabilization of the high-spin (HS) configuration relative to the complex with the unsubstituted ligand. This group is also expected to lead to the increase of the interactions between the Fe(III) complexes through H-bonding.

<Scheme 1>

2. Experimental

2.1 General procedures

Commercial solvents were used without further purification unless otherwise specified. Although the synthesis of $Fe^{III}(3-CH_3O-qsal)_2Cl \cdot H_2O$ and the 3-CH_3O-qsal ligand were not previously described they were prepared according to an adapted literature procedure [2]. The purity of the complexes was verified determining the carbon, hydrogen and nitrogen content by the ITN Elemental Analysis Service. X-ray diffraction experiments were performed with a Bruker AXS APEX CCD detector diffractometer using graphite monochromated Mo-Kα radiation source ($\lambda = 0.71073$ Å), in the ψ and ω scans mode. A semi-empirical absorption correction was carried out using SADABS [5]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [6]. The structures were solved by direct methods using SIR97 [7] and refined by full-matrix least-squares methods using the program SHELXL97 [8] using a WINGX software package [9]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were

prepared using PLATON [10]. The crystallographic data and structure refinement results are presented in Table 1 and selected bond distances and angles in Table 2.

Table 1 – Crystal data and structural refinement of compound **1**.

	$Fe^{III}(3\text{-}CH_3O\text{-}qsal)_2PF_6$ (**1**)
Empirical formula	$C_{34} H_{26} F_6 Fe N_4 O_4 P$
Formula weight	755.41
T (K)	150(2)
Wavelength (Å)	0.71073 (MoKα)
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	10.4220(6)
b (Å)	12.6799(7)
c (Å)	13.6242(8)
α (°)	101.134(4)
β (°)	101.570(3)
γ (°)	107.487(3)
V (Å^3)	1619.31(16)
Z, calculated density (Mg/m^3)	2, 1.549
μ (mm^{-1})	0.596
F(0 0 0)	770
Crystal size (mm^3)	$0.18 \times 0.08 \times 0.02$
θ range (°)	3.59 - 25.03
h, k, l ranges	-12/12, -15/15, -16/16
Reflections collected/unique [R_{int}]	11346 / 5656 [R_{int} = 0.0535]
Completeness to θ	98.8%
Absortion correction	Semi-empirical from equivalents
Transm – max/min	0.9882 / 0.9003
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5656 / 0 / 456
Goodness-of-fit on F^2	0.962
Final R indices [$I > 2 \sigma(I)$]	$R_1 = 0.0730$, $wR_2 = 0.1829$
R indices (all data)	$R_1 = 0.1154$, $wR_2 = 0.2026$
Largest diff. peak/hole (e.Å^{-3})	1.736 / -0.544

Table 2 – Selected bond lengths (Å) and angles (°) for compound **1**.

1
Bond lengths

Fe1-O3	1.859(4)
Fe1-O1	1.870(4)
Fe1-N2	1.934(4)
Fe1-N3	1.940(4)
Fe1-N4	1.971(4)
Fe1-N1	1.973(4)

Bond angles

O3-Fe1-O1	93.33(16)
O3-Fe1-N2	85.86(17)
O1-Fe1-N2	94.89(17)
O3-Fe1-N3	94.95(16)
O1-Fe1-N3	86.95(17)
N2-Fe1-N3	177.94(18)
O3-Fe1-N4	176.29(17)
O1-Fe1-N4	89.90(17)
N2-Fe1-N4	95.68(18)
N3-Fe1-N4	83.40(18)
O3-Fe1-N1	90.33(18)
O1-Fe1-N1	175.78(17)
N2-Fe1-N1	83.26(18)
N3-Fe1-N1	94.83(18)
N4-Fe1-N1	86.51(18)

Magnetic measurements were performed on a *S700X* SQUID magnetometer with a 7 T magnet (Cryogenic Ltd.) using polycrystalline samples. The temperature dependence of the magnetic susceptibility in the temperature range 5-320 K was measured under a magnetic field of 1 T. For measurements with temperatures higher than 320 K a 5.5 T *MPMS* SQUID magnetometer (Quantum Design) was used. The paramagnetic susceptibility was obtained from the experimental magnetization data after a diamagnetism correction was estimated from the tabulated Pascal constants as -504.1×10^{-6} emu/mol for **1** and -519.1×10^{-6} emu/mol for **1**·$2H_2O$.

2.2 $Fe^{III}(3\text{-}CH_3O\text{-}qsal)_2PF_6$ (**1**)

Under inert atmosphere, in a glove box and using dry solvents, a solution of $NaPF_6$ (31.8 mg, 0.2 mmol) in hot methanol was added drop-wise to a filtered solution of $Fe^{III}(3\text{-}CH_3O\text{-}qsal)_2Cl \cdot H_2O$ (66.4 mg, 0.1 mmol) in hot methanol. The mixture was left standing hot for 30 min. and then cooled to 4ºC overnight. The collected solid was crystallized from hot acetone. It was obtained $Fe^{III}(3\text{-}CH_3O\text{-}qsal)_2PF_6$. Yield: 17.0 mg (23%). Elemental Anal. Calc.: C, 54.06; H, 3.47; N, 7.42. Found: C, 54.63; H, 2.72; N, 7.03.

*2.3 Fe^{III}(3-CH$_3$O-qsal)$_2$PF$_6$·2H$_2$O (**1**·2H$_2$O)*

The procedure was similar to the above one with the exception that the solid was not crystallized from acetone. It was collected and dried under vacuum with heating. Yield: 48.2 mg (63%). Elemental Anal. Calc.: C, 53.77; H, 3.98; N, 7.38. Found: C, 53.59; H, 3.85; N, 7.41.

3. Results and discussion

Fig. 1 shows the standard ORTEP [10] with 50% thermal ellipsoids and atom numbering scheme cation residue of compound **1**, the crystallographic parameters are presented in Table 1 and selected bond lengths and angles in Table 2. The compound crystallizes in the triclinic space, space group $P\bar{1}$. The asymmetric unit contains one cationic unit lying on a general position and two halves of anionic units with the P atom lying on centers of symmetry. The coordination bond lengths around the Fe(III) ion (see Table 2) are similar to those reported previously for the Fe^{III}(qsal)$_2$$^+$ [Fe···O: 1.869-1.879 Å, Fe···N: 1.941-1.991 Å] in the low-spin (LS) state [11] and lower than those reported for Fe(pap)$_2$$^+$ (Hpap = 2-hydroxyphenyl-(2-pyridyl)-methaneimine, a Schiff base similar to Hqsal) in the HS state [12] [Fe···O$_{av}$: 1.932 Å; Fe···N$_{av}$: 2.105-2.202 Å] suggesting that **1** is in the LS state.

The Fe(III) octahedral site is distorted due to the shorter Fe-O distances compared to the Fe-N distances (see Table 2). Each 3-CH$_3$O-qsal ligand form a substantially distorted plane: the dihedral angle between the phenyl ring and the quinoline ring of each ligand are 5.72(17)° and 10.69(24)°. More, the dihedral angles between the phenyl ring (C10 to C15) and the Fe1-O1-N2 chelate ring, between the respective quinoline ring and the Fe1-N1-N2 chelate ring, between the other phenyl ring (C27 to C32) and the Fe1-O3-N3 chelate ring and between the respective quinoline ring and the Fe-N3-N4 chelate ring are 6.0(2)°, 2.61(18)°, 6.0(3)° and 4.9(2)°, respectively. In the first ligand the metoxy group is aligned with the aromatic part, however in the second the metoxy group is not, as denoted by the dihedral angle between the phenyl group and the CH$_3$-O-C plane: 4.0(4)° and 61.3(3)°, respectively. The two tridentate ligands are almost orthogonal: the least-squares planes between the aromatic part of the two ligands is 87.31(5)°.

< Fig. 1 – ORTEP diagram with 40% thermal ellipsoids and the atom numbering scheme for Fe complex residue of compound $Fe^{III}(3-CH_3O-qsal)_2PF_6$ (**1**). Hydrogen atoms have been omitted for clarity. >

The packing diagram of the compound **1** at 150(2) K is shown in Fig. 2. The cations form dimers along c through π-π interactions between quinoline rings of neighboring cations, being the distance between the least-squares planes of 3.44(2) Å. These two complexes are also connected through two H-bonds C3-H···O4 (2.60(4) Å). The phenyl ring and imine residue of the orthogonal ligands are connected two-by-two by short contacts (C29···C26, 3.32(8) Å; C28···C26, 3.2(2) Å and C28···C27, 3.39(1) Å). With the H-bonds O4···H-C9 (2.69(4) Å) form a chain of contacts along b axis. The most planar ligands have two H-bonds with a quinoline residue of a least planar ligand: O1···H-C19 (2.61(4) Å), O2···H-C19 (2.40(5) Å) and O2···H-C29 (2.68(4) Å).

The anions PF_6^- are not located in the first coordination sphere, being instead located in the voids inside the network of qsal-based ligands. They are connected with the complexes through several H-bonds (F1···H-C24, 2.670(1) Å; F1···H-C26, 2.5(1) Å; F2···H-C1, 2.4(3) Å; F2···H-C16, 2.6(2) Å; F3···H-C7, 2.6(3) Å; F4···H-C8, 2.5(2) Å; F4···H-C9, 2.5(3) Å; F5···H-C23, 2.6(2) Å; F6···H-C17, 2.2(2) Å) and short contacts (F2···C24, 3.10(6) Å; F3···C26, 3.10(7) Å; F3···C28, 3.13(4) Å; F6···C9, 2.87(6) Å; F6···C17, 3.14(7) Å).

< Fig. 2 – (a) Packing of compound $Fe^{III}(3-CH_3O-qsal)_2PF_6$ (**1**) along the b axis showing the π-π interactions (arrows).(b) Some neighbouring complexes, indicating short contacts (traced line) and H-bonds (dotted lines), showing a chain along b axis. Hydrogen atoms have been omitted for clarity. >

The temperature dependence of $\chi_M T$, where χ_M is the molar magnetic susceptibility, for compounds **1** and **1**·2H$_2$O are plotted in Fig. 3. Compound **1**·2H$_2$O shows a nearly temperature independent $\chi_M T = 4.56$ emu K mol^{-1}, indicating that this compound presents a HS configuration (with $S = 5/2$ and $g = 2.042$). Compound **1** presents also a nearly temperature independent $\chi_M T \sim 0.45$ emu K mol^{-1} up to ca. 260 K, then it starts to increase gradually and $\chi_M T = 0.68$ emu K mol^{-1} at ~400 K. This behaviour indicates that this compound presents a LS configuration for the Fe^{III} ion ($S = 1/2$, $g = 2.156$) until

ca. 260 K, where there the onset of a gradual SCO process is observed. At 390 K the HS fraction is quite small, $\gamma_{HS} \sim 0.06$.

< Fig. 3 - Thermal variation of the $\chi_M T$ product for compounds **1** and **1**·2H$_2$O. >

In conclusion Fe^{III}(3-CH$_3$O-qsal)$_2$PF$_6$ was obtained in two forms: one non-solvated (**1**), and another with two H$_2$O molecules (**1**·2H$_2$O). In the crystal structure of **1**, the bond lengths between the Fe and the coordinating atoms (N and O) are consistent with a LS configuration, which is in good agreement with the magnetic data. As anticipated, π-π interactions between ligands of neighbouring complexes were observed. Also, as expected, it was detected an increase of H-bonds between neighbouring complexes relative to the unsubstituted Fe^{III}(qsal)$_2^+$, due to the four H-bonds based on the CH$_3$O-groups (the O2···H-C19 is quite strong). In compound **1**, the magnetic susceptibility data show a LS configuration up $\sim$ 260 K and then the onset of a gradual SCO transition. While, in case of the solvated compound, **1**·2H$_2$O, the magnetic behaviour is consistent with an HS state. The HS configuration observed in **1**·2H$_2$O can be attributed to the presence of the H$_2$O molecules that could eventually establish strong H-bonds with the 3-CH$_3$O-qsal ligands. These bonds can lead to a significant distortion in the Fe^{III}(3-CH$_3$O-qsal)$_2$ complex and stabilize the HS electronic configuration. However a full understanding of the effect of the presence of the H$_2$O molecules in **1**·2H$_2$O is dependent on the crystal structure determination of this compound. It is worth mentioning previous works on the effect of the solvate on the magnetic properties by Hendrickson and Hernandez-Molina [13] that also observe strong effects related with the solvate molecules. This work will proceed with a strong effort in the preparation of crystals of the hydrated compound and also of crystals with other counter-ions usable for X-ray diffraction. As similar SCO compounds based on the unsubstituted ligand (qsal) were found to exhibit the LIESST (light-induced excited spin state trapping) effect [1], efforts to study this effect in compound **1** are also planned.

4. Supplementary material

CCDC 695885 contains the crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

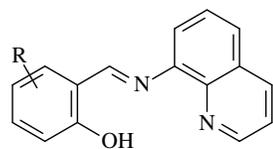**Figures and Schemes**

Scheme 1

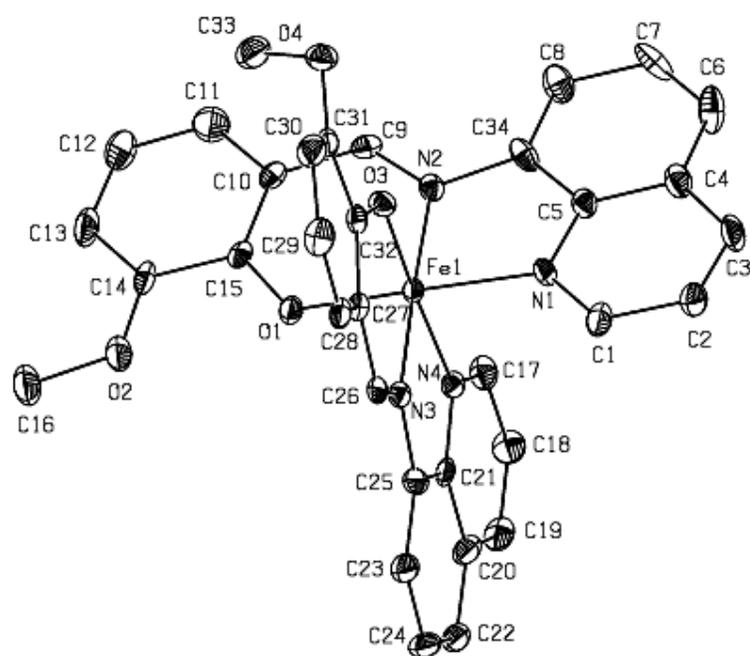H(R-qsal)   H(3-CH$_3$O-qsal)

Fig. 1

Fig. 2

a)

b)
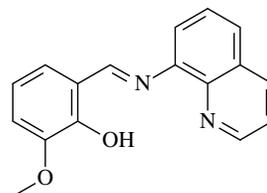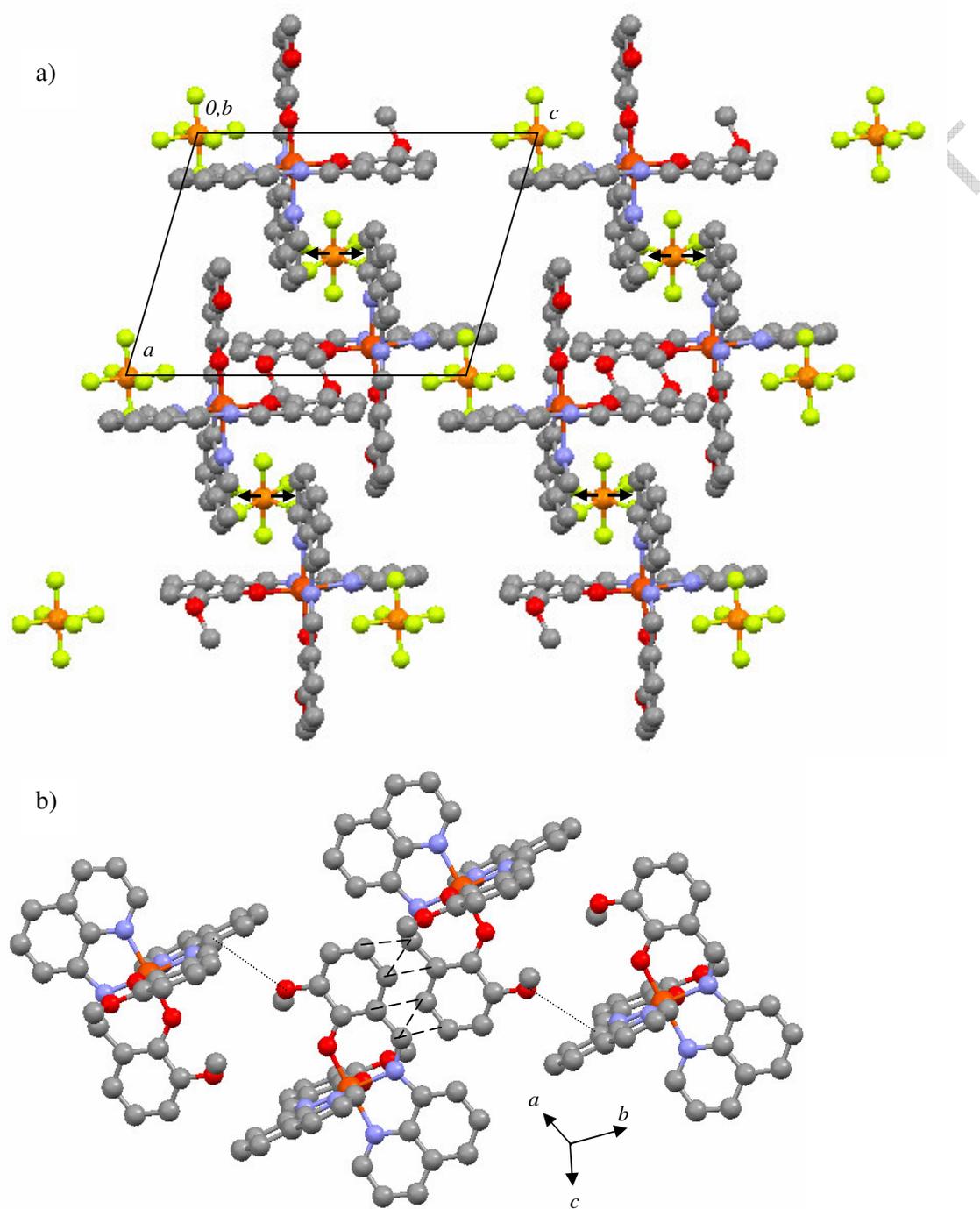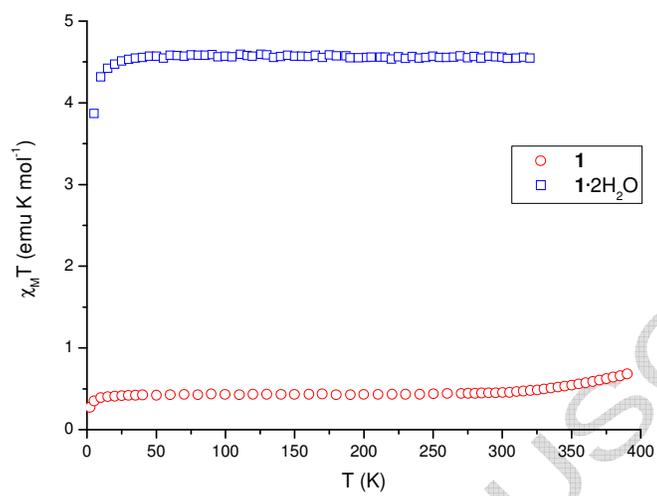
Fig. 3

Figure Captions

Fig. 1 – ORTEP diagram with 40% thermal ellipsoids and the atom numbering scheme for Fe complex residue of compound $Fe^{III}(3\text{-}CH_3O\text{-}qsal)_2PF_6$ (**1**). Hydrogen atoms have been omitted for clarity.

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Graphical abstract

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