



Synthesis and magnetic properties of a hybrid molecular salt $[\text{Fe}(\text{qsal})_2][\text{Fe}(\text{CA})(\text{qsal})\text{Cl}]\cdot\text{MeNO}_2$



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ABSTRACT

A new hybrid molecular salt $[\text{Fe}^{\text{III}}(\text{qsal})_2][\text{Fe}^{\text{III}}(\text{CA})(\text{qsal})\text{Cl}]\cdot\text{MeNO}_2$ (**1**), where $\text{qsal}^- = N$ -(8-quinolyl)salicylaldehyde and $\text{CA}^{2-} = \text{chloranilate}$ was synthesized and structurally characterized by single-crystal X-ray crystallography. Each cationic $[\text{Fe}^{\text{III}}(\text{qsal})_2]^+$ and anionic $[\text{Fe}^{\text{III}}(\text{CA})(\text{qsal})\text{Cl}]^-$ unit is self assembled through intermolecular π - π stacking interactions between qsal^- ligands, which stabilize the supramolecular networks in the crystal lattice. Magnetic measurements for **1** revealed that both Fe^{III} ions were in HS spin states with a small contribution from ZFS over the whole temperature region.

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In the past few decades, considerable efforts in field of solid state chemistry and physics are focused on development of multifunctional molecular materials, which are compounds exhibiting more than one physical property within the same molecule and/or two or more difference molecular hybrid system [1]. A variety of their systems such as magnetism/electroconductivity [2], magnetism/polarization [3], and magnetism/proton conduction [4] have been studied from the multifunctional molecular material point of view. Moreover, the physical property of some of these gave the brilliant cooperative and the synergetic effect. Along this line, one of particular interests is the combination of a spin crossover (SCO) complex as the magnetic part and another complex with the other physical property. SCO complexes can switch magnetic spin states of a molecule between high-spin (HS) and low-spin (LS), which respond to external perturbations such as temperature, light, pressure and magnetic field in both the solid state and in solution [5]. Meanwhile, a chloranilic acid (H_2CA) is one of 2,5-dihydroxy-1,4-benzoquinone derivatives, which possesses both electron-accepting and proton-donating properties and undergoes multistage deprotonation processes because of a strong dibasic acid ($\text{p}K_{\text{a}1} = 0.58$, $\text{p}K_{\text{a}2} = 3.18$) [6].

To explore new multifunctional molecular materials, we now report synthesis and magnetic properties of a new hybrid molecular salt, $[\text{Fe}^{\text{III}}(\text{qsal})_2][\text{Fe}^{\text{III}}(\text{CA})(\text{qsal})\text{Cl}]\cdot\text{MeNO}_2$ (**1**) composed of a cationic SCO complex, $[\text{Fe}^{\text{III}}(\text{qsal})_2]^+$ ($\text{qsal}^- = N$ -(8-

quinolyl)salicylaldehyde) [7] and an anionic complex, $[\text{Fe}^{\text{III}}(\text{CA})(\text{qsal})\text{Cl}]^-$ including the dianionic form CA^{2-} .

The molecular structure of **1** was determined by using single-crystal X-ray diffraction at 123 K. The compound of **1** crystallized in the monoclinic space group $P2_1/c$ (#14) with $Z=4$ [8,9]. X-ray analysis of **1** revealed that there were both a cationic $[\text{Fe}^{\text{III}}(\text{qsal})_2]^+$ and an anionic $[\text{Fe}^{\text{III}}(\text{CA})(\text{qsal})\text{Cl}]^-$ moieties in the asymmetric unit, which are abbreviated as A and B (Fig. 1), where the compound of **1** contains one MeNO_2 (= nitromethane) molecule as a lattice solvent per unit cell.

The geometry around the Fe^{III} ion of A are meridionally occupied by an N_4O_2 donor set from two tridentate qsal^- ligands. The $\text{Fe}-\text{N}$ bond distances are longer than the $\text{Fe}-\text{O}$ distances, which induce a pronounced distortion of the Fe^{III} octahedral site. The respective $\text{Fe}-\text{N}_{\text{quinoline}}$, $\text{Fe}-\text{N}_{\text{imine}}$, and $\text{Fe}-\text{O}_{\text{phenolate}}$ bond distances around the Fe^{III} ion of A (averaged $\text{Fe}-\text{N}_{\text{quinoline}}$: 2.174 Å, $\text{Fe}-\text{N}_{\text{imine}}$: 2.108 Å, and $\text{Fe}-\text{O}_{\text{phenolate}}$: 1.914 Å for **1**, respectively) are longer than those reported previously for LS $[\text{Fe}^{\text{III}}(\text{qsal})]^+$ cations, which fall within the range reported for related HS $[\text{Fe}^{\text{III}}(\text{qsal})]^+$ cations [7]. Moreover, qsal^- ligands form substantially distorted planes. The dihedral angles between the phenyl ring and the $\text{Fe}(1)-\text{O}(1)-\text{N}(2)$ six-membered chelate ring, between the other phenyl ring and the $\text{Fe}(1)-\text{O}(2)-\text{N}(3)$ six-membered chelate ring, between the quinoline ring and the $\text{Fe}(1)-\text{N}(1)-\text{N}(2)$ five-membered chelate ring and between the other quinoline ring and the $\text{Fe}(1)-\text{N}(3)-\text{N}(4)$ five-membered chelate ring were determined to be 3.27°, 4.37°, 2.96°, and 2.95°, respectively. The $\text{trans-N}_{\text{imine}}-\text{Fe}(1)-\text{N}_{\text{imine}}$ angle and the dihedral angle between the least squares planes of the two qsal^- ligands were determined to be 165.54(8)° and 79.7°. The distortion parameters Σ and Θ were estimated to be 64.57(8)° and

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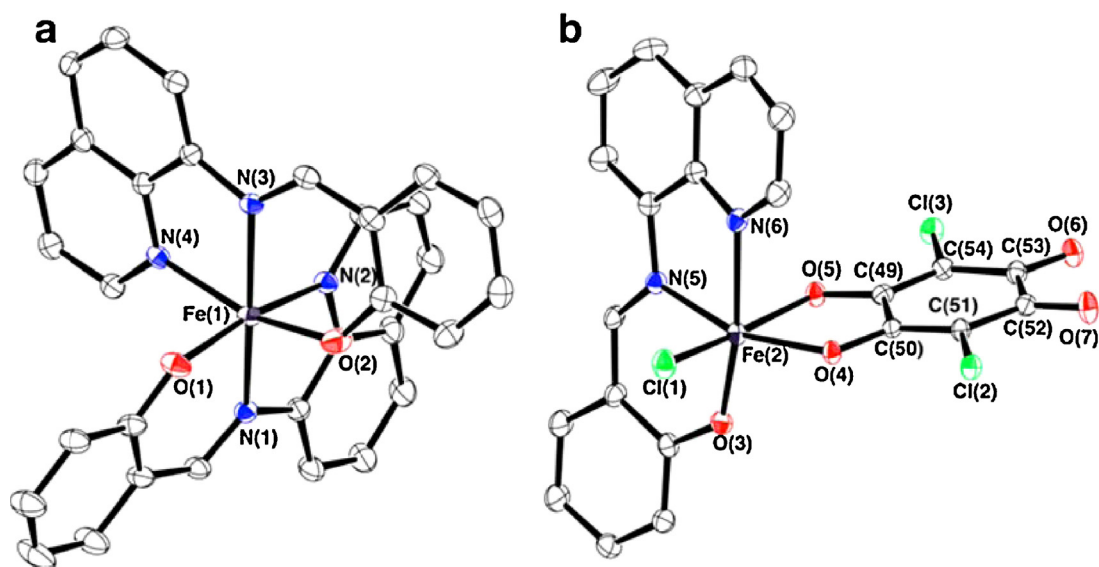


Fig. 1. ORTEP drawing with 50% probability thermal ellipsoids of the single-crystal X-ray crystal structure of (a) A and (b) B for **1**. Hydrogen atoms and the interstitial MeNO₂ solvent molecule are omitted for clarity.

192° [5e,10]. These structural features of A is similar to those of related HS [Fe^{III}(qsal)₂]⁺ cations [11].

On the other hand, the geometry around the Fe^{III} atom of B is a distorted octahedral involving an N₂O donor set from a tridentate qsal⁻ ligand, an O₂ donor set from a bidentate CA²⁻ dianion, and a monodentate Cl atom. The Fe(2)—N bond distances are longer than the Fe(2)—O bond distances. The dihedral angles between the phenyl ring and the Fe(2)—O(3)—N(5) six-membered chelate ring and between the quinoline ring and the Fe(2)—N(5)—N(6) five-membered chelate ring were determined to be 5.37° and 3.94°. The coordination of the CA²⁻ dianion is the approximately symmetrical. The C—C bond distances (C(49)—C(50) = 1.519(3) Å, C(49)—C(54) = 1.372(3) Å, C(50)—C(51) = 1.373(3) Å, C(51)—C(52) = 1.428(3) Å, C(53)—C(54) = 1.428(3) Å, and C(52)—C(53) = 1.564(3) Å) and the difference in the bond distances between coordinated and uncoordinated C—O distances (C(49)—O(4) = 1.289(3) Å, C(50)—O(5) = 1.278(3) Å, C(52)—O(6) = 1.226(3) Å, and C(53)—O(7) = 1.230(3) Å) suggest that CA²⁻ dianion is in the *o*-quinone form. Indeed, the IR spectrum of **1** shows two characteristic bands at 1524 and 1649 cm⁻¹. These bands are assigned to C—O and C=O for chemically distinct sites, confirming the *o*-quinone form of CA²⁻ (Fig. S1). Therefore, CA²⁻ acts as a bidentate ligand and the *o*-quinone site in CA²⁻ is free from coordination. These structural features of B is similar to those of complexes with CA²⁻ dianion as the *o*-quinone form [12].

The intermolecular Fe··Fe separations between A and A, B and B, and A and B are 9.3702(4) Å, 7.2885(4) Å, and 7.2415(4) Å, respectively. Furthermore, each A and B unit is self assembled through rather weak intermolecular π–π stacking interactions between qsal⁻ ligands on each Fe^{III} ion (the shortest C··C distances are 3.713(4) Å for A and 3.609(4) Å for B) (Fig. 2).

The temperature dependence of the dc magnetic susceptibility of a fresh polycrystalline sample of **1** was studied in the temperature range of 1.82–300 K in an applied field of 0.1 T (Fig. 3). The χ_MT value of **1** was determined to be 9.34 cm³ K mol⁻¹ at 300 K, which corresponds to two magnetically non-interacting HS Fe^{III} ions (S = 5/2 × 2) with g_{Fe} > 2.00. The χ_MT value remained constant over the temperature range of 30–300 K, which is consistent with the HS Fe^{III} state. The decrease in χ_MT drops below 30 K was attributed to the single-ion zero-field splitting (ZFS) of the HS Fe^{III} ion of A and B and/or weak intermolecular

antiferromagnetic interactions between Fe^{III} centers through π–π stacking like interactions (vide supra). However, it is difficult to determine whether it is dominantly due to ZFS or intermolecular magnetic interactions. Furthermore, the magnetization curve at 1.82 K for **1** saturated at ca. 10 μ_B at 7.0 T, confirming that **1** is clearly in an HS state even at low temperature (inset of Fig. 3). Therefore, the decrease in χ_MT at lower temperatures is not due to SCO. The absence of SCO is probably due to a rigid crystal lattice.

Most [Fe(qsal)₂]⁺ cations undergo SCO below room temperature, except for four salts including [Fe(qsal)₂]⁺ cation that are in

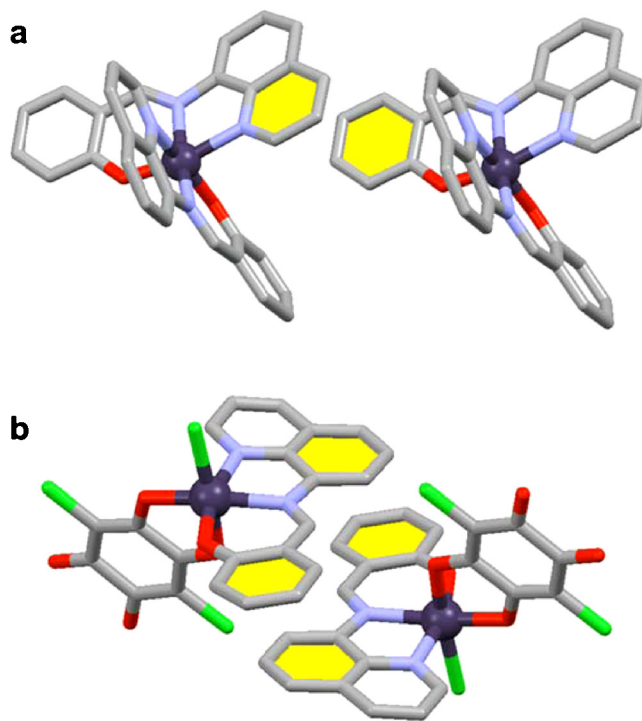


Fig. 2. Emphasizing π–π stacking interaction modes between qsal⁻ ligands of respective consecutive (a) A and (b) B units in **1**. Each mode distances between their centroids are (a) 3.74 Å and (b) 3.94 Å, respectively.

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