

[Fe(sal₂-trien)][Ni(dmit)₂]: towards switchable spin crossover molecular conductors†

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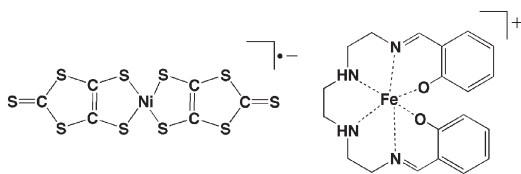
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A cooperative spin transition behaviour with a wide hysteresis loop (30 K) around 240 K has been observed, for the first time, in a salt based on the redox active [Ni(dmit)₂][−] anion and the [Fe(sal₂-trien)]⁺ spin crossover cation.

Supramolecular synthesis of multicomponent materials from spontaneous assembly of molecules into stable and noncovalently joined aggregates is one of the most useful approaches to obtain new functional molecular materials.¹ In this context, spin crossover (SC) building blocks are particularly suitable and represent one of the best examples of molecular bistability. They may be switched between the low-spin (LS) and high-spin (HS) states leading to distinctive changes in magnetism, colour and structure, which may be induced by variation of temperature and/or pressure and by light irradiation.² Strong signal generation and hysteresis is observed in some cases when the molecular structural changes associated to SC are cooperatively transmitted in the lattice.³

Electrical conductivity is a fundamental property of matter currently investigated in the realm of the molecular science.⁴ For instance, electronic conduction derived from dithiolenic complex-based compounds has received much attention.⁵ In particular, compounds of the type (NR₄)_x[M(dmit)₂] (0 < x < 1) with non-integral oxidation state based on 2-thioxo-1,3-dithiole-4,5-dithiolato (dmit) (NR₄⁺ = tetraalkylammonium cation, M = Ni, Pd, Pt) present interesting electric properties. Considering the anionic character of the [Ni(dmit)₂][−] species (Scheme 1, left) and its redox lability as well as the cationic nature and redox stability of most iron(III) SC complexes such as [Fe(sal₂-trien)]⁺ (Scheme 1, right),⁶ we have decided to combine them as building blocks to investigate the possible synergy properties stemming from the coexistence of SC and electronic conduction in the same lattice.⁷ As a first step, here we report the synthesis[‡] and characterisation of the system [Fe(sal₂-trien)][Ni(dmit)₂] (**1**), which represents the first [Ni(dmit)₂][−] based SC compound.



Scheme 1 Schematic view of the [Ni(dmit)₂][−] and [Fe(sal₂-trien)]⁺ units.

† Electronic supplementary information (ESI) available: Chain configuration of the [Ni(dmit)₂][−] anions in **1**; electrical and magnetic variations of **1** after electrocrystallization (three figures). See <http://www.rsc.org/suppdata/cc/b4/b412182a/>

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The structure of **1** has been investigated at 295 and 180 K for the HS and LS states, respectively.§ Compound **1** is made up of slabs of [Fe(sal₂-trien)]⁺ cations and layers of [Ni(dmit)₂][−] anions, which alternate along the *c*-axis and spread out onto the *ab* plane (Fig. 1). In the HS state, the SC sites are constituted of severely distorted octahedral [FeN₄O₂] centres (Fig. 2, left). The average Fe–N and Fe–O bond distances are 2.155(3) and 1.909(2) Å, respectively.

The three diagonals of the octahedron, defined by the bonds N(amine)–Fe–O(phenoxo), {N(amine) = N2, N3} differ strongly from 180° (155.7(1)–159.0(1)°) while the remaining, defined by N(imine)–Fe–N(imine), is 178.3(1)° {N(imine) = N1, N4}. Consequently, the average trigonal distortion $\Phi = 60^\circ - \theta$ (θ is the angle formed by two opposite faces of the octahedron) is 10.9°. These structural features are similar to those already reported for different salts and solvates of the same cationic complex.⁸ In the LS state the coordination octahedron is much more regular (Fig. 2, middle).

The average Fe–N and Fe–O distances are 1.966(4) and 1.874(3) Å, respectively. The average bond changes are $\Delta R(\text{Fe–N}) = 0.188 \text{ \AA}$ and $\Delta R(\text{Fe–O}) = 0.036 \text{ \AA}$ or $\Delta R([\text{FeN}_4\text{O}_2]) = 0.137 \text{ \AA}$ for the whole octahedron, which correspond to what is expected for a complete HS↔LS transition for Fe(III). The diagonals are closer to linearity, the most significant changes, *ca.* 18°, correspond to the N(amine)–Fe–O(phenoxo) = 175.1(2)–174.8(2)° and, consequently, Φ decreases down to 2.32°.

The sal₂-trien ligand wraps the Fe(III) ion in such a way that the two aromatic rings lie approximately in orthogonal planes. Each aromatic ring interacts with an adjacent [Fe(sal₂-trien)]⁺ cation *via* π – π stacking defining infinite chains running parallel to the *a*-axis. In the HS state, there are two distinct types of π – π interactions (Fig. 3, top). Type 1 displays partial superposition of the aromatic rings. These interactions take place mainly along the *bc* direction

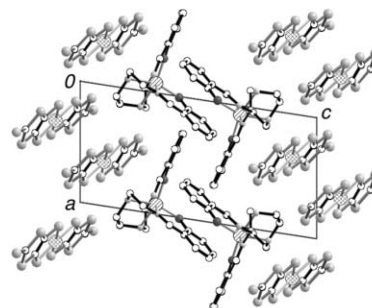


Fig. 1 Projection onto the *ac* plane of the structure of **1** in the HS state.

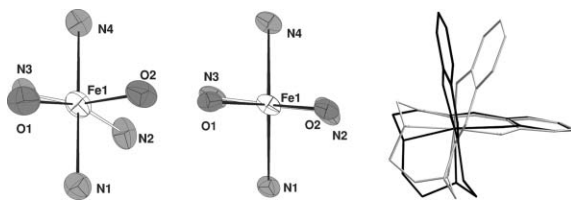


Fig. 2 View of the $[\text{FeO}_2\text{N}_4]$ octahedron in the HS (left) and LS (middle) and overlay (right) of the HS (black) and LS (grey) states of $[\text{Fe}(\text{sal}_2\text{-trien})]^+$ in **1**.

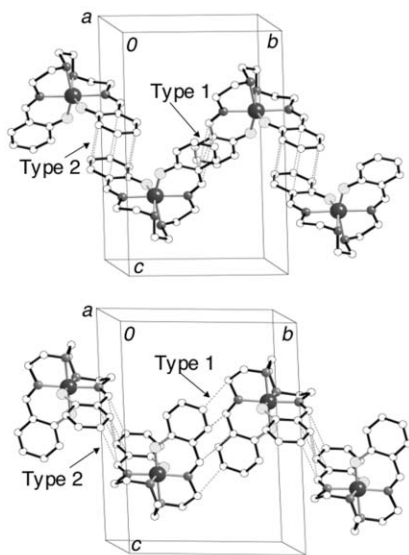


Fig. 3 The two types of π - π interactions of the $[\text{Fe}(\text{sal}_2\text{-trien})]^+$ cations in **1** in the HS state (top) and in the LS state (bottom).

and involve eight $\text{C}\cdots\text{C}$ contacts in the range 3.30–3.59 Å. In type 2, the phenolato rings of two nearest neighbours superpose perfectly. These interactions take place along the ac direction and involve six $\text{C}\cdots\text{C}$ contacts of around 3.53 Å. In the LS state, the complex molecules change markedly their relative orientation inducing stronger π - π contacts (3.14–3.42 Å) and spreading these contacts to the adjacent chains defining layers of $\text{C}\cdots\text{C}$ interactions.

It should be noted that the c -axis shortens by 1.330(2) Å upon spin state change. This remarkable variation affects dramatically the π - π interactions of type 2, and provokes reorientation of the adjacent $[\text{Fe}(\text{sal}_2\text{-trien})]^+$ cations to avoid the increase of repulsive interactions between the aromatic rings. Consequently, the two aromatic rings now display partial interaction (Fig. 3, bottom). These structural modifications occur concomitantly with the remarkable change of the angles N(amine)–Fe–O mentioned above and are responsible for the first-order character of the spin transition (see below).

Whatever the temperature, the layers of $\text{Ni}(\text{dmit})_2$ consist in independent chains of $[\text{Ni}(\text{dmit})_2]$ units, which run along the b axis. Within a chain, the $\text{Ni}(\text{dmit})_2$ units are connected to each other through one (at 295 K) or two (at 180 K) $\text{S}\cdots\text{S}$ short contacts (ESI†).

At room temperature, $\chi_M T$ is ca. $4.84 \text{ cm}^3 \text{ K mol}^{-1}$, close to the expected value of $4.76 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for a system containing two

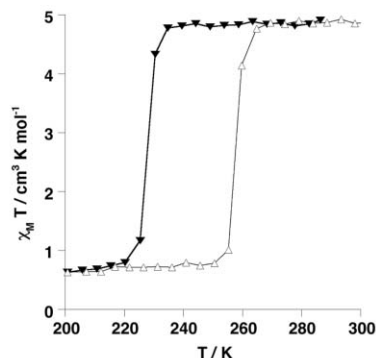


Fig. 4 Magnetic susceptibility measurements for **1** showing the thermal hysteresis loop.

non-interacting spin centres, namely the Fe^{3+} ion in the high-spin state ($S = 5/2$, $g = 2$) and a formally Ni^{3+} ($S = 1/2$, $g = 2$) (Fig. 4). Upon cooling, $\chi_M T$ remains constant down to 234 K, below this temperature the $\chi_M T$ value undergoes a sharp decrease. This behaviour is characteristic of a first order $5/2 \leftrightarrow 1/2$ SC transition. The $\chi_M T$ value drops to $0.66 \text{ cm}^3 \text{ K mol}^{-1}$ at 205 K and remains constant down to 80 K. The warming mode reveals the occurrence of thermal hysteresis. The critical temperature for the cooling (T_c^{down}) and warming (T_c^{up}) modes (228 and 258 K, respectively) indicates the occurrence of a 30 K hysteresis loop.

It is worth noting that **1** represents the first example belonging to the $[\text{Fe}(\text{sal}_2\text{-trien})(\text{X})\cdot n\text{S}]$ family that displays strong cooperativity and wide hysteresis (see ref. 8). By inspection of the crystal structures of the relevant members of this family, it becomes apparent that the particular arrangement of the crystal packing of **1** stems from the geometrical and electronic nature of the anion $[\text{Ni}(\text{dmit})_2]^-$, which favours the occurrence of segregated stacks of anions and cations. The cations are strongly coupled *via* π -stacking.

Consequently, the large intramolecular structural modifications upon SC are transmitted quite efficiently to the whole crystal and represent the coercive force responsible for the observed large hysteresis. The “control” of π -stacking to enhance cooperativity in SC complexes has been demonstrated to be a successful supramolecular synthetic strategy, which has been illustrated in several $\text{Fe}(\text{II})$ (see for instance ref. 3) and $\text{Fe}(\text{III})$ complexes.⁹

The structural findings here reported shed light on the understanding of the microscopic mechanisms involved in the generation of first SC transitions, which are of fundamental importance for practical applications.

Preliminary electrocrystallisation experiments of **1** in acetonitrile solutions have afforded small amounts of crystalline materials $[\text{Fe}(\text{sal}_2\text{-trien})][\text{Ni}(\text{dmit})_2]_x$ whose magnetic and conductivity properties demonstrate that **1** is a suitable precursor for the synthesis of switchable SC molecular conductors (ESI†).

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Notes and references

‡ *Synthesis*: **1** was synthesised by addition of an acetonitrile solution (15 mL) of (*n*-Bu₄N)[Ni(dmit)₂]¹⁰ (59 mg, 0.084 mmol) over an acetonitrile solution (3 mL) of [Fe(sal₂-trien)]PF₆¹¹ (85 mg, 0.153 mmol). The resulting solution was left at 4°C overnight. After filtration, dark green platelet-like crystals (36 mg) were obtained, washed with acetonitrile and dried under vacuum. Yield: 55%. Elemental analysis (%): calc. for C₂₆H₂₂FeN₄NiO₂S₁₀: C 36.41, H 2.59, N 6.53; found C 36.12, H 2.42, N 6.28.

§ *Crystal data* for **1** [Fe(sal₂-trien)][Ni(dmit)₂] (C₂₆H₂₄FeN₄NiO₂S₁₀), *M* = 859.65, *T* = 295 K, triclinic, space group *P* $\bar{1}$, *a* = 9.253(1), *b* = 11.708(1), *c* = 17.241(2) Å, α = 79.49(1), β = 78.11(1), γ = 68.48(1)°, *V* = 1688.6(3) Å³, *Z* = 2, μ = 1.639 mm⁻¹, 16620 reflections, 6108 unique (*R*_{int} = 0.106), *R*(*F*) = 0.0468 (*I* > 2σ(*I*)), *wR*(*F*²) = 0.1227 (all data); *T* = 180 K, triclinic, space group *P* $\bar{1}$, *a* = 8.888(1), *b* = 12.252(1), *c* = 15.911(2) Å, α = 81.61(2), β = 82.19(2), γ = 74.32(1)°, *V* = 1641.8(3) Å³, *Z* = 2, μ = 1.686 mm⁻¹, 16032 reflections measured, 5908 unique, (*R*_{int} = 0.084), *R*(*F*) = 0.0432 (*I* > 2σ(*I*)), *wR*(*F*²) = 0.1011 (all data). CCDC 246500 and 246501. See <http://www.rsc.org/suppdata/cc/b4/b412182a/> for crystallographic data in .cif or other electronic format.

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