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Iron(II) coordination pyrazole complexes with aromatic sulfonate ligands: the role of ether†

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Four novel heteroleptic mononuclear Fe(II) coordination complexes including 3,5-dimethyl-1-(2'-pyridyl)-pyrazole (**DMPP**) and aromatic sulfonate ligands were synthesized and characterized using single crystal-XRD, SQUID magnetometry and ⁵⁷Fe Mössbauer spectroscopy. The crystal structures of the complexes revealed the unusual coordination of sulfonate groups to Fe(II) ions, leading to an Fe–N₄O₂ coordination environment. This specific molecular layout is presumably caused by diethyl ether, which was vapour diffused into the complexation medium to obtain crystalline complexes. Alongside yielding single crystals, diethyl ether also altered the self-assembly process of a usual FeN₆ homoleptic coordination environment. All the complexes remain paramagnetic at all temperatures as suggested by magnetic susceptibility measurements. All are stable in air except [Fe(DMPP)₂(tos)₂] which got partially oxidized to Fe(III) over time as suggested by ⁵⁷Fe Mössbauer spectroscopy.

1. Introduction

Coordination compounds represent a remarkable class of hybrid materials because they can combine the functionalities of both metal cations and organic molecules/anions operating as ligands into a single compound. Besides the intrinsic properties of the involved molecular precursors, they may even exhibit new properties, thanks to the ligand field, which causes a disturbance in the electronic configuration of the metal ions which in turn leads to intriguing phenomena such as spin crossover¹ (SCO), charge transfers² *etc.* Coordination compounds based on azole ligands and transition metals are of particular interest because of their use in various potential applications involving thermochromism,³ photoluminescence,^{3,4} sensors,⁵ vapochromism,^{6,7} gas storage,⁸ molecular magnetism,⁹ metallic Hg storage,¹⁰ catalysis,¹¹ nanomedicine¹² and many others.¹³ Among azole molecules, pyrazoles are particularly useful in coordination chemistry. For instance, our group has recently reported the crystal structures

of the coordination complexes of a pyrazole-dicarboxylate acid ligand and investigated their supramolecular structures.¹⁴ We have also shown the effect of the aliphatic backbone of a bis-pyrazole-bis-carboxylate ligand on the supramolecular structures of their coordination complexes and polymers.¹⁵ The effect of anions and hydrogen bonding on the supramolecular structural diversities of coordination complexes obtained from a novel bis-pyrazole ligand was also reported.¹⁶ Medicinal properties were also investigated for new pyrazole-acetamide ligands and complexes showing remarkable antioxidant activity.¹⁷ More recently we have reported the crystal structure-bioactivity correlation of three mononuclear coordination complexes of a pyrazolyl-benzimidazole ligand.¹⁸

Our interest lies in one such chelating bidentate azole ligand named 3,5-dimethyl-1-(2'-pyridyl)pyrazole (**DMPP**), which has been used in a couple of applications. For instance, Takahira *et al.* synthesized a deep blue colour emitting phosphorescent Ir(III) complex,¹⁹ whereas Das *et al.* not only explored the fluorescence properties of **DMPP** but also of their Cd(II) complexes.²⁰ The **DMPP** molecule also possesses weak cytotoxic properties against cancer cell lines, which gets enhanced by 10–20 fold when complexed to Cu(II) ions.²¹ On the other hand, Baker *et al.* successfully prepared Fe(II) **DMPP** mononuclear complexes and studied their thermally induced spin crossover (SCO) behaviour.²² Fe(II) coordination compounds are indeed particularly attractive primarily because of their SCO behaviour,¹ which may find applications in photomagnetism,²³ data storage,²⁴ charge transport,²⁵ sensors²⁶ *etc.*

These enticing applications motivated us to design Fe(II) coordination complexes with **DMPP** in pursuit of the synthesis

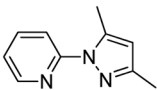
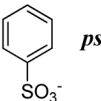
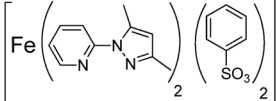
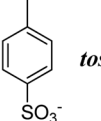
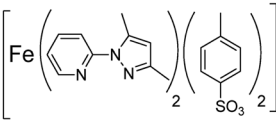
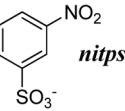
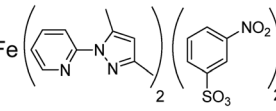
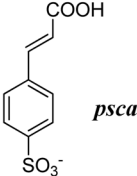
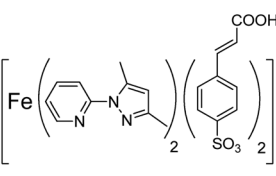
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Neutral ligand	Anionic ligand	Coordination complex
 DMPP	 <i>ps</i>	 1
	 <i>tos</i>	 2
	 <i>nitps</i>	 3
	 <i>psca</i>	 4

Scheme 1 Molecular representation of the ligands and coordination complexes.

of new SCO materials. The novelty in our work lies in employing aromatic phenylsulfonate anions to counterbalance Fe(II) ions, a strategy which has been seldom used in the synthesis of mononuclear SCO complexes.²⁷ The inclusion of sulfonate anions is not only expected to influence the SCO temperature but also to introduce additional functionalities into the coordination compounds.²⁸

In this context, we employed four different aromatic sulfonate anions, *ps* (phenylsulfonate), *tos* (tosylate), *nitps* (3-nitrophenylsulfonate), and *psca* (*p*-sulfocinnamic acid), as shown in Scheme 1. Though all anions possessing oxygen rich functional groups are quite useful in the sense of hydrogen bonding and cooperativity,²⁹ the *psca* anion is especially noteworthy as it is a derivative of a photo-responsive molecule: *trans*-cinnamic acid. *psca* is therefore expected to undergo a [2+2] photodimerization upon irradiation with UV-light following Schmidt's topochemical rules of cycloaddition.^{30,31} In addition, any coordination compound or metal salt including the *psca* anion may also be photo-responsive.³² The present account is devoted to the synthesis and study of four novel Fe(II) complexes, whose formulae are given in Scheme 1. The complexes have been characterized by single crystal X-ray diffraction, elemental analyses, SQUID magnetometry and ⁵⁷Fe Mössbauer spectroscopy.

2. Experimental

2.1 Materials and characterization techniques

All the chemicals were bought from usual chemical companies and used as received without further purification. 3,5-Dimethyl-1-(2'-pyridyl)pyrazole (**DMPP**) was prepared by following a previously reported procedure.³³ Similarly, the Fe(II) salts [Fe(H₂O)₆]₂X₂ with X = *tos*, *nitps* and *tos*, were prepared by following the

reported procedures.^{34–36} C, H, and N elemental analyses were performed at MEDAC Ltd, UK. Infrared spectra were recorded on a Shimadzu FTIR-8400S instrument using KBr pellets. High resolution mass spectral data were recorded on a Q-Exactive mass spectrometer from Thermo Fisher Scientific in the electrospray ionization mode. Powder X-ray Diffraction (PXRD) experiments were carried out on a D8 Advanced diffractometer from Bruker. The diffractogram was recorded using CuK α radiation (λ = 1.5406 Å) and a linkeye XE-T detector (Bruker) in the 5–80° (2 θ) range with an increment of 0.0015° and an integration time of 0.15 s. Single crystal X-ray diffraction data for **1**, **2**, and **3** were collected at 150 K on a Mar345 image plate detector using MoK α radiation (λ = 0.71073 Å) generated by a Rigaku Ultra X18S rotating anode with Xenocs Fox3D mirrors. Single crystal-XRD data for **4** were collected at 100 K on a Rigaku Oxford Diffraction SuperNova, Dual Source, Cu at zero, diffractometer, equipped with an Atlas CCD detector, using ω scans and MoK α radiation (λ = 0.71073 Å). Magnetic susceptibility measurements for all the complexes were carried out on a MPMS3 SQUID magnetometer (Quantum Design Inc.) in the DC mode, under a DC magnetic field of 1000 Oe, with a temperature rate of 2 K min^{−1}. Magnetic data were corrected for both sample holder complex diamagnetic contributions. ⁵⁷Fe Mössbauer spectra were recorded at room temperature in the transmission geometry mode with a constant acceleration mode conventional Wissel Mössbauer spectrometer equipped with a ⁵⁷Co(Rh) radioactive source, a Reuter Stokes proportional counter detector and a CMCA-550 multichannel analyzer. All isomer shifts in Mössbauer spectra are given with respect to α -Fe.

2.2 Synthesis

2.2.1 Synthesis of [Fe(H₂O)₆](*psca*)₂. 5.0 g of finely ground *trans*-cinnamic acid was added in small amounts to fuming

sulfuric acid (8 mL, 20%) kept in an ice-water bath. After complete addition, the reaction mixture was vigorously stirred at room temperature for 30 min. Thereafter, the thick brown reaction mixture was heated in an oil bath set at 60 °C for 2 h. The dark brown solution was then cooled down to room temperature and added to ice water (30 mL). To this solution, an excess of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (~5.0 g) was then added. The resulting reaction mixture was stirred until a nearly white precipitate started to separate from the reaction mixture. The stirring was continued for 20 more min. The precipitate was filtered and recrystallized from distilled water to obtain a pure white product. Yield: 57% (6.25 g). FTIR (KBr, cm^{-1}): 1695 cm^{-1} (C=O), 1631 (C=C), 1314 (asym. S=O), 1126 (sym. S=O), 807 (S-O). Elemental analysis calculated for $\text{FeC}_{18}\text{O}_{18}\text{H}_{30}\text{S}_2$: C, 33.04; H, 4.62; S, 9.80. Found: C, 33.04; H, 4.60; S, 9.79.

2.2.2 Synthesis of Fe(II) complexes (1–4). 3 mmol of **DMPP** was dissolved in hot methanol (5 mL). To this solution was added a 1 mmol methanolic solution of $[\text{Fe}(\text{H}_2\text{O})_6]\text{X}_2$ with $\text{X} = \text{ps}, \text{tos}, \text{nitps}, \text{psca}$. The colour of the reaction mixture turned brownish yellow immediately upon addition. The reaction mixture was stirred at 50 °C for 30 min. Thereafter, diethyl ether was allowed to vapour diffuse into the brownish yellow reaction mixture. Within a period of 3–5 days, yellow crystals of complexes were obtained: blocks for $[\text{Fe}(\text{DMPP})_2(\text{ps})_2]$ (1). Yield 0.34 g (48%). Anal. calc. for $\text{FeC}_{32}\text{H}_{32}\text{N}_6\text{O}_6\text{S}_2$: C, 53.63; H, 4.50; N, 11.73. Found: C, 53.63; H, 4.48; N, 11.70; needles for $[\text{Fe}(\text{DMPP})_2(\text{tos})_2]$ (2). Yield: 0.34 g (46%). Anal. calc. for $\text{FeC}_{34}\text{H}_{36}\text{N}_6\text{O}_6\text{S}_2$: C, 54.84; H, 4.87; N, 11.29. Found: C, 54.71; H, 4.70; N, 11.28; plates for $[\text{Fe}(\text{DMPP})_2(\text{nitps})_2]$ (3). Yield: 0.3 g (38%). Anal. calc. for $\text{FeC}_{32}\text{H}_{30}\text{N}_8\text{O}_{10}\text{S}_2$: C, 47.65; H, 3.75; N, 13.89. Found: C, 47.59; H, 3.80; N, 13.73; rectangular prisms for $[\text{Fe}(\text{DMPP})_2(\text{psca})_2]$ (4). Yield: 0.48 g (56%). Anal. calc. for $\text{FeC}_{38}\text{H}_{36}\text{N}_6\text{O}_{10}\text{S}_2$: C, 53.28; H, 4.24; N, 9.81. Found: C, 53.06; H, 4.57; N, 9.76. Although no solvent was detected in the elemental analysis of **4**, one molecule of Et_2O was observed in the crystal structure. This situation may be due to the high degree of volatility of Et_2O from our complex when sending the crystals for chemical analyses.

2.2.3. Controlled precipitation of 4. The same procedure was followed as above for **4** until the completion of the reaction, *i.e.* after stirring the reaction mixture at 50 °C for 30 min. Subsequently, 10 mL of diethyl ether was added to the reaction mixture, which immediately led to a yellow precipitate. It was stirred for 2 min, and then filtered and dried in air. Yield: 0.69 g (81%). The sample was then recorded by X-ray powder diffraction to compare with single crystal X-ray analysis of **4**.

3. Results and discussion

3.1 Synthesis and crystallization

The Fe(II) salts including sulfonate counteranions were prepared according to a previously reported procedure yielding single crystals,^{34–36} except $[\text{Fe}(\text{H}_2\text{O})_6](\text{psca})_2$ which was synthesized *in situ* by carrying out sulfonation of *trans*-cinnamic acid.³⁷ After the completion of the reaction, instead of separating out *psca* as

described in ref. 37, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added in excess to the diluted sulfonation mixture. The targeted Fe(II) salt starts to precipitate out as a slightly off-white colour powder within five min of stirring. It was filtered out and recrystallized from distilled water. Addition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ not only provided $[\text{Fe}(\text{H}_2\text{O})_6](\text{psca})_2$ but also neutralized sulfuric acid to form FeSO_4 . The advantage of using an excess of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ is that it saturates the aqueous solution by FeSO_4 and unreacted $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ which quickly precipitates out $[\text{Fe}(\text{H}_2\text{O})_6](\text{psca})_2$ because of the relative higher solubility of FeCl_2 and FeSO_4 as compared to the organic Fe salt. The formation of $[\text{Fe}(\text{H}_2\text{O})_6](\text{psca})_2$ was confirmed by Fourier transform infrared spectroscopy and elemental analysis.

For the synthesis of $[\text{Fe}(\text{DMPP})_3]^{2+}$ coordination complexes, the molar ratio of Fe-salts and bidentate **DMPP** was kept at 1:3. Upon mixing both precursors, the colour of the reaction mixture turned brownish yellow immediately and continued to darken with time. The reaction mixture was stirred for 30 min at 50 °C to ensure to completion of the reaction. Thereafter, the solvent was allowed to evaporate slowly to obtain the required product as a powder or preferably as single crystals. However, upon solvent evaporation, a dark brown oily substance was obtained for the four targeted coordination compounds. The reason that the coordination compound could not precipitate as a solid phase may be attributed to the hydrophilic nature of the organic sulfonate anions which are highly polar and are prone to absorb water molecules from the atmosphere. To avoid the absorption of atmospheric moisture into the complexes, Et_2O was vapour diffused into the reaction mixture inside a closed glassware. In a span of 3–5 days, it yielded yellow colour crystals of different shapes. The crystals were not hygroscopic and found to be stable under ambient conditions. The elemental analysis indicated the formation of heteroleptic complexes comprised of two **DMPP** and two sulfonate anion molecules, operating as ligands. Elemental analysis also suggested the absence of any solvent molecules of crystallization in the complexes. Presumably, Et_2O altered the self-assembly process of $[\text{Fe}(\text{DMPP})_3]^{2+}$ coordination complexes and resulted in a more stable $[\text{Fe}(\text{DMPP})_2\text{X}_2]$ ($\text{X} = \text{ps}, \text{tos}, \text{nitps}, \text{psca}$) coordination environment. High resolution mass spectrometry in the reaction mixture containing $[\text{Fe}(\text{H}_2\text{O})_6](\text{psca})_2$ and three molecules of **DMPP** in MeOH revealed a distinct peak at $m/z = 287.61$ which corresponds to $[\text{Fe}(\text{DMPP})_3]^{2+}$ species (Fig. 1). The peak at $m/z = 629.13$ which is assigned to $[\text{Fe}(\text{DMPP})_2(\text{psca})]^+$ is a fragmented species of $[\text{Fe}(\text{DMPP})_3](\text{psca})_2$ and should not be mistaken for the formation of **4**. Such a $[\text{Fe}(\text{Ligand})_2(\text{Anion})]$ peak was earlier observed in the mass spectra of another mononuclear complex, $[\text{Fe}(\text{L}1)_3]\text{Cl}_2$ where L1 = 5-benzylamido-2,2'-bipyridine.³⁸ To further reinforce our finding that the heteroleptic layout is caused by Et_2O , controlled precipitation of the reaction mixture of **4** was carried out using Et_2O . The resulting precipitate was then analysed by powder-XRD. The obtained PXRD pattern was compared with the simulated pattern from the single crystal structure of **4** (see Fig. S2, ESI†). Though the peaks of the powder patterns differ in intensity, their 2θ values match very well with each other, which infers that the precipitate of **4**

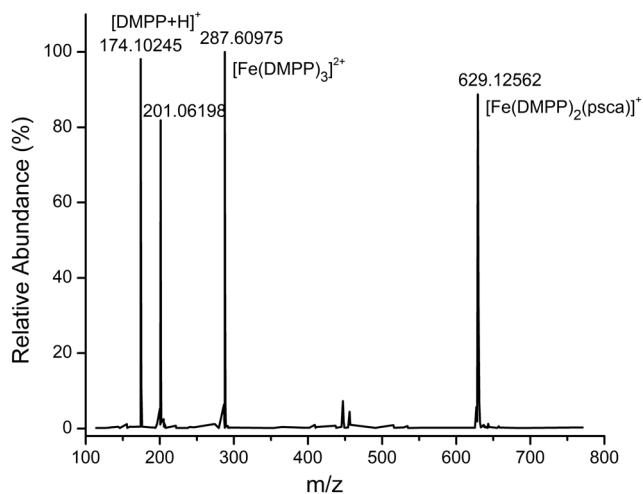


Fig. 1 Mass spectrum of the reaction mixture containing $[\text{Fe}(\text{H}_2\text{O})_6](\text{psca})_2$ and three moles of **DMPP** in MeOH.

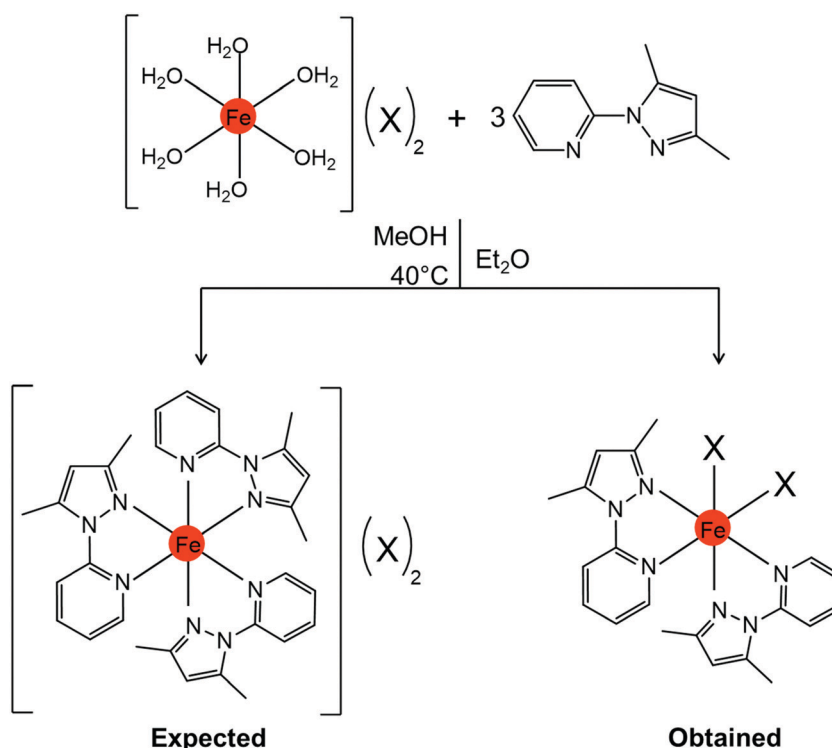
obtained from controlled precipitation has the same chemical formula as crystals of **4** *i.e.*, $[\text{Fe}(\text{DMPP})_2(\text{psca})_2]$. The whole process of expected and obtained products is summed up in Scheme 2. The reproducibility in the formulae of the four complexes thus validates the reproducibility of the employed synthesis procedure.

3.2 Single crystal X-ray diffraction

The data integration and reduction for compounds **1–4** were performed with the CrysAlisPro software from Rigaku Oxford

Diffraction,³⁹ by applying the implemented absorption correction. The structures were solved by Direct Methods, SHELXT⁴⁰ and refined by full-matrix least squares minimization on F^2 using SHELXL2014/7.⁴¹ For complex **4**, the Olex2⁴² software was used as a graphical user interface. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in the calculated positions and refined in the riding mode with isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 times for methyl and hydroxyl groups). A minor disorder was observed for the oxygen atoms of an SO_3^- group in **2**, giving a refined occupancy ratio of approximately 60/40. For the structure of **3**, the selected crystal was found to be twinned, the twin matrix was found by TWINROT/MAT (Platon) and an HKLF 5 type SHELXL file was subsequently written. Refinement cycles were performed against these HKLF 5 reflection data. Additional solvent accessible voids (9% of the unit cell) were treated by the SQUEEZE procedure in Platon,⁴³ accounting for the diffused solvent contribution inside these cavities. The crystallographic and refinement data for all the complexes are summarized in Table S1 (ESI†). CCDC 2000062, 2000063, 2000064 and 2000065 for **1**, **2**, **3** and **4** respectively.†

3.2.1 Crystal structure of 1. **1** crystallizes in the $P2_1$ space group. The asymmetric unit is comprised of one Fe(II) ion as the metal centre, two molecules of **DMPP** and two molecules of the anionic ligand **ps** as shown in Fig. 2(a). **DMPP** is coordinated to Fe(II) through each nitrogen atom of pyridine and pyrazole, whereas **ps** is coordinated through oxygen atoms of sulfonate groups, thus making an FeN_4O_2 coordination environment. The Fe(II) ions exhibit a distorted octahedral geometry as none



Scheme 2 General synthesis scheme of coordination complexes, showing the expected and obtained products. X = **ps**, **tos**, **nitps** and **psca**.

of the bond angles [$\angle \text{O46-Fe1-O16} = 92.3(1)^\circ$, $\angle \text{O16-Fe1-N2} = 94.3(1)^\circ$, $\angle \text{N2-Fe1-N9} = 73.9(1)^\circ$, $\angle \text{N9-Fe1-N32} = 86.1(1)^\circ$, $\angle \text{N32-Fe1-N39} = 72.7(1)^\circ$, $\angle \text{N39-Fe1-O46} = 92.2(1)^\circ$] of the octahedron are right angles. One of the apical positions of the octahedron is occupied by a pyridine ring from **DMPP** and the other is occupied by a sulfonate group from one of the anionic ligands **ps**. The anionic ligands **ps** are found to be coordinated to Fe(II) ions in a *cis* manner with their aromatic rings positioned away from each other. Moreover, the pyridine and pyrazole rings of **DMPP** do not lie in one plane but are slightly twisted. The Fe–N bond lengths which are of the order of 2.1–2.2 Å indicate **1** to be a HS complex.⁴⁴ The crystal packing of **1** is shown in Fig. 2(b). When viewed down the *b*-axis, the molecules seem to arrange themselves in a style as to be forming steps. In the crystal packing, the Fe(II) ions of two differently oriented molecules within the unit cell are 11.001(7) Å apart, while the distance between the Fe(II) ions of the same oriented molecules is 8.702(6) Å, which is also the shortest among all the Fe(II) ions. Non-classical multiple intra-, and intermolecular hydrogen bonds are observed between oxygen atoms of sulfonate groups and neighbouring hydrogen atoms of aromatic rings with C(H)⋯O distances in the range of 2.902(5)–3.427(6) Å. All the D–H⋯A parameters such as distances, angles and types of interactions are summed up in Table S2 (ESI†). Intramolecular π – π interactions are observed between the aromatic rings of **ps** and **DMPP** molecules. A pair of **DMPP** and **ps** molecules on each side of Fe gets involved in π – π interactions. We denote these pairs of **DMPP** and **ps** as pair-1 and pair-2 (see Fig. S1, ESI†). **ps** rings are positioned in the middle of **DMPP** molecules so as to optimize the π – π repulsions and π – σ attractions among the aromatic rings.⁴⁵ In pair-1, the angles between the **ps** ring plane and **DMPP** ring plane are 11.6(2)° (pyridine) and 11.9(2)° (pyrazole), whereas in pair-2, the angles between the planes are 15.9(2)° (pyridine) and 14.0(2)° (pyrazole). The shortest ring centroid to centroid distances are found to be 3.987(2) Å and 3.928(2) Å in pair-1 and pair-2, respectively. Since the planes of the aromatic rings are not parallel, the aromatic interaction is an intermediate of slipped π stacking and edge on C–H⋯ π interaction with slipped π stacking dominating the aromatic interaction. The aromatic interaction parameters in **1** are compiled and given in Table S3 (ESI†).

3.2.2 Crystal structure of 2. **2** crystallizes in the $P2_1/n$ space group. The asymmetric unit is comprised of an Fe(II) ion as the metal centre coordinated to two bidentate **DMPP** ligand molecules and two monodentate **tos** ligand molecules as shown in Fig. 3(a). **DMPP** coordinates to Fe(II) through the nitrogen atoms of pyridine and pyrazole rings whereas **tos** coordinates through the oxygen atoms of sulfonate groups, thus leading to an FeN₄O₂ coordination environment. The mononuclear complex **2** crystallizes in a distorted octahedral geometry with all bond angles [$\angle \text{O16-Fe1-O46} = 96.2(5)^\circ$, $\angle \text{O16-Fe1-N9} = 96.9(5)^\circ$, $\angle \text{N2-Fe1-N9} = 73.0(1)^\circ$, $\angle \text{N39-Fe1-N2} = 91.1(1)^\circ$, $\angle \text{N32-Fe1-N39} = 73.5(1)^\circ$, $\angle \text{N32-Fe1-O46} = 94.7(1)^\circ$] of the octahedron being off right angle. One of the apical positions is occupied by a pyridine ring from **DMPP** and the other one is occupied by a sulfonate group from one of the anionic **tos**

ligands. The anionic **tos** ligands are coordinated to Fe(II) ions in a *cis* manner. The Fe–N bond lengths which are of the order of ~2.2 Å confirm the HS state of **2**.⁴⁴

The crystal packing of **2** is shown in Fig. 3(b) along the *b*-axis. The shortest distance between two Fe(II) ions is 9.058(9) Å as depicted in Fig. 3(b). Intra- and intermolecular (only non-classical) hydrogen bonds are observed between **tos**–SO₃ oxygen atoms and –CH and –CH₃ hydrogen atoms of **tos** and **DMPP** (with C(H)⋯O distances in the range of 2.844(15)–3.404(14) Å). All the D–H⋯A parameters such as distances, angles and types of interactions are summed up in Table S2 (ESI†). Intramolecular π – π interactions are observed between the aromatic rings of **tos** and **DMPP** molecules. Only a pair of **tos** and **DMPP** molecules on one side of Fe gets involved in intramolecular aromatic interaction. The angles between the **tos** ring plane and **DMPP** ring plane are found to be 5.32(17)° (pyridine) and 12.9(19)° (pyrazole). The ring centroid to centroid distances are 3.903(2) Å and 4.286(2) Å. Since the angle between the **tos** ring and pyridine ring plane is very small, they can be considered as nearly parallel. This implies that the aromatic interaction between the **tos** ring and pyridine ring is mostly the slipped π stacking type, whereas between the **tos** ring and pyrazole ring, it is the intermediate of slipped π stacking and edge on C–H⋯ π interaction with slipped π stacking dominating the aromatic interaction.⁴⁵ The aromatic interaction parameters in **2** are given in Table S3 (ESI†).

3.2.3 Crystal structure of 3. **3** crystallizes in the $C2/c$ space group. The asymmetric unit of **3** is shown in Fig. 4(a). It is comprised of an Fe(II) ion as the metal centre coordinated to two **DMPP** and two **nitps** molecules. **DMPP** coordinates to Fe(II) through the nitrogen atoms of pyridine and pyrazole rings whereas **nitps** coordinates through the oxygen atoms of sulfonate groups, thus providing a N₄O₂ coordination environment for the Fe(II) metal centres. The mononuclear complex **3** has a distorted octahedral geometry with all the bond angles [$\angle \text{O46-Fe1-O16} = 84.92(9)^\circ$, $\angle \text{O46-Fe1-N32} = 86.72(9)^\circ$, $\angle \text{N32-Fe1-N39} = 73.02(9)^\circ$, $\angle \text{N9-Fe1-N39} = 93.0(1)^\circ$, $\angle \text{N2-Fe1-N9} = 73.6(1)^\circ$, $\angle \text{N2-Fe1-O16} = 87.96(9)^\circ$] of the octahedron being off right angle. One of the apical positions of the octahedron is occupied by a pyrazole ring from **DMPP** and the other one is occupied by a sulfonate group from one of the anionic **nitps** ligands. The Fe–N bond lengths are in the order of ~2.2 Å, which indicates **3** to be a HS compound.⁴⁴ The anionic ligands **nitps** are found to be coordinating to Fe(II) ions in a *cis* manner with their aromatic rings positioned away from each other. Intra- and intermolecular (only non-classical) hydrogen bonds are observed between **nitps**–SO₃ and –NO₂ oxygen atoms and –CH hydrogen atoms of **nitps** and **DMPP** (with C(H)⋯O distances in the range of 2.852(4)–3.328(5) Å). All the D–H⋯A parameters in **3** such as distances, angles and types of interactions are summed up in Table S2 (ESI†). Aromatic interaction is observed in both the pairs of **DMPP** and **nitps** molecules on each side of Fe(II). We denote these pairs as pair-1 and pair-2. The **nitps** ring is not located in the middle of **DMPP** like **1** and **2** rather it is more shifted towards the pyrazole ring. This shifting of **nitps** is attributed to the –NO₂ group which withdraws the π electron density from the phenyl

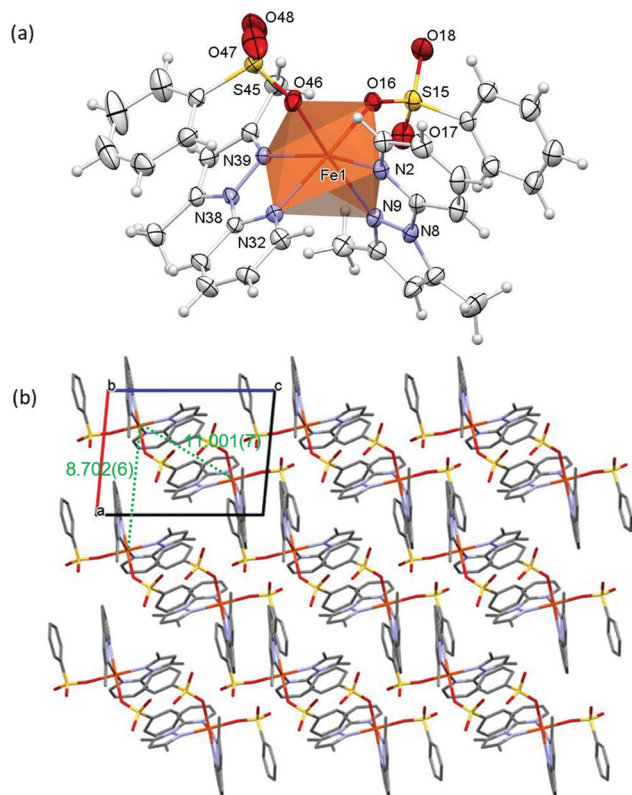


Fig. 2 (a) Asymmetric unit of **1**, showing thermal displacement ellipsoids at the 30% probability level and atom labelling scheme of the non C and H atoms. (b) Crystal packing viewed down the *b*-axis, with Fe...Fe distances (Å) indicated and hydrogen atoms omitted for clarity.

ring and reduces the π - π repulsions⁴⁵ between the pyrazole and phenyl ring, thus allowing the phenyl ring to be positioned over the pyrazole ring. The pyridine centroid and phenyl centroid in pair-1 and pair-2 are 4.497(2) Å and 4.602(2) Å apart, respectively. The closest carbon to carbon distance is however of the order of 3.4 Å, allowing weak slipped π stacking between pyridine and phenyl rings. On the other hand, the pyrazole centroid and phenyl centroid are 3.807(2) Å and 3.767(2) Å apart in both pairs, respectively. In pair-1, the angles between the *nitps* ring plane and **DMPP** rings planes are 1.35(17)° (pyridine) and 7.54(19)° (pyrazole), whereas in pair-2, the angles between the planes are 3.96(17)° (pyridine) and 5.12(18)° (pyrazole). Since the planes containing *nitps* molecules and aromatic rings of **DMPP** molecules are nearly planar, the aromatic interaction can be considered as slipped π stacking interaction. The displacement angle, *i.e.* ring normal (pyrazole) to centroid-centroid vector angle is found to be 18.8° and 21.2° for pair-1 and pair-2 respectively. Besides intramolecular slipped π stacking, an intermolecular aromatic interaction is also observed between the *nitps* molecules as marked in Fig. 4(b). The planes containing the *nitps* molecules are at an angle of 15.59(16)° with the centroids of the ring being 3.871(2) Å apart. These values suggest that the intermolecular aromatic interaction between *nitps* molecules is a combination of slipped π stacking and C-H... π interaction.⁴⁵ All the aromatic interaction parameters in **3** are given in Table S3 (ESI†).

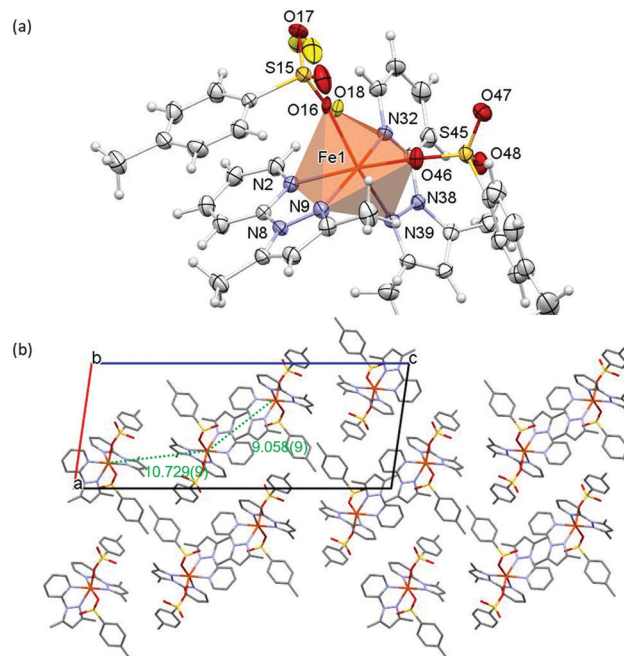


Fig. 3 (a) Asymmetric unit of **2**, showing thermal displacement ellipsoids at the 30% probability level and atom labelling scheme of the non C and H atoms. The disorder of the SO_3^- group is shown in yellow; (b) crystal packing, viewed down the *b*-axis, with Fe...Fe distances (Å) indicated and hydrogen atoms omitted for clarity.

Interestingly, π - π interactions between non coordinated phenylsulfonate units were also found in the crystal structure of $[\text{Cu}(\text{hyprtr})_3](4\text{-chloro-3-nitro-phenylsulfonate})_2 \cdot \text{H}_2\text{O}$ (hyprtr = 4-3'-hydroxypropyl-1,2,4-triazole).⁴⁶ Fig. 4(b) also presents unit cell packing of **3**. The shortest distance between two metal centres is found to be 8.101(7) Å while the longest distance is 13.134(1) Å. Most interestingly, **3** represents the first iron complex incorporating the *nitps* anion for which the crystal structure was determined. This discovery is interesting given the outstanding SCO properties developed by iron complexes including this anion.^{29,34,47}

3.2.4 Crystal structure of 4. **4** crystallizes in the $P2_1/n$ space group. The asymmetric unit of **4** comprises one Fe(II) ion as the metal centre, two molecules of **DMPP**, both as bidentate ligands, two molecules of *psca* as anionic ligands, and one solvent molecule of Et_2O as shown in Fig. 5(a). **DMPP** is coordinated to Fe(II) through both nitrogen atoms of pyridine and pyrazole whereas *psca* is coordinated through the oxygen atoms of sulfonate groups, thus making an FeN_4O_2 coordination environment. The Fe(II) ions exhibit a distorted octahedral geometry as none of the bond angles [$\angle \text{O11-Fe1-O16} = 92.57(9)^\circ$, $\angle \text{O16-Fe1-N1} = 93.0(1)^\circ$, $\angle \text{N1-Fe1-N3} = 74.4(1)^\circ$, $\angle \text{N3-Fe1-N6} = 85.9(1)^\circ$, $\angle \text{N6-Fe1-N4} = 73.8(1)^\circ$, $\angle \text{N4-Fe1-O11} = 91.42(9)^\circ$] of the octahedron are right angles. One of the apical positions of the octahedron is occupied by a pyrazole ring from **DMPP** and the other one is occupied by a sulfonate group from one of the anionic *psca* ligands. The Fe-N bond lengths which are of the order of 2.1–2.2 Å indicate **1** to be a HS complex.⁴⁴ Interestingly, no Et_2O molecules were observed in

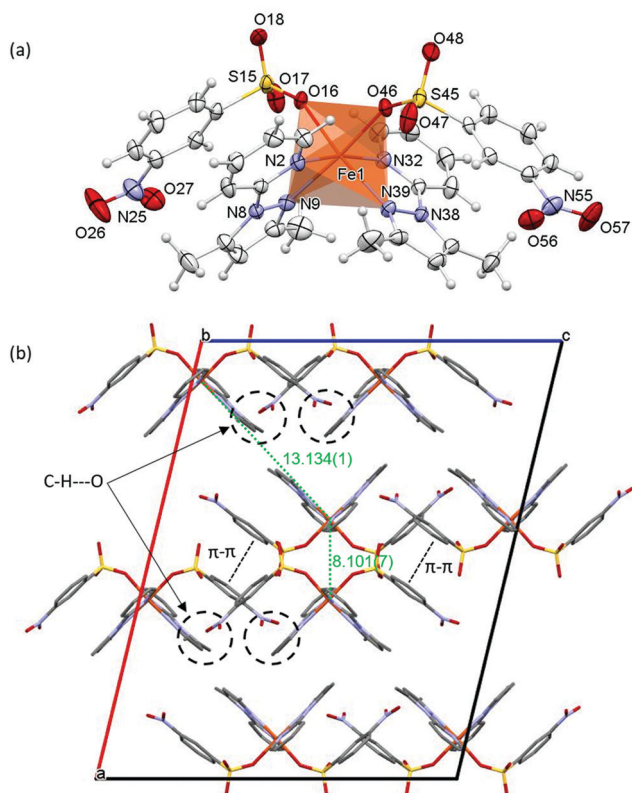


Fig. 4 (a) Asymmetric unit of **3**, showing thermal displacement ellipsoids at the 30% probability level and atom labelling scheme of the non C, H atoms; (b) crystal packing, viewed down the *b*-axis, with Fe...Fe distances (Å), selected C-H...O and π - π stacking interactions and hydrogen atoms omitted for clarity.

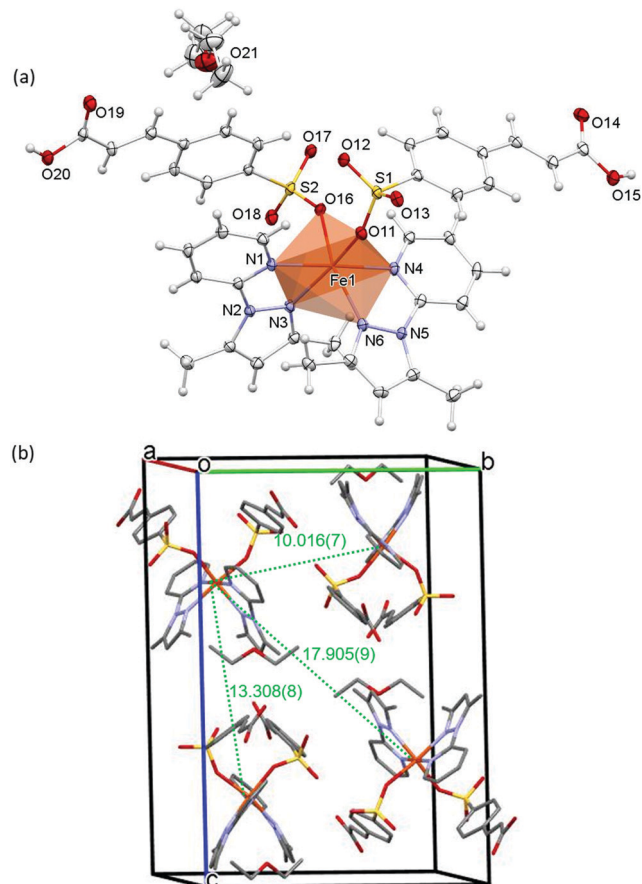


Fig. 5 (a) Asymmetric unit of **4**, showing thermal displacement ellipsoids at the 30% probability level and atom labelling scheme of the non C, H atoms; and (b) crystal packing, viewed down the *a*-axis, with Fe...Fe distances (Å) and hydrogen atoms omitted for clarity.

the elemental analysis of **4**, which could presumably be attributed to the high volatility of Et₂O due to which it might have been evaporated taking into account the time between CHN analysis and the synthesis itself (*ca.* 2–3 months). The anionic *psca* ligands are found to be coordinated to Fe(II) ions in a *cis* manner with their aromatic rings pointing away in opposite directions. The unit cell of **4** is shown in Fig. 5(b). The shortest distance between the two Fe(II) ions is found to be 10.016(7) Å whereas the largest one is 17.905(9) Å. In the crystal packing, classic intermolecular hydrogen bonds are observed between *psca* –SO₃ oxygen atoms and *psca* carboxyl –OH groups (with O(H)···O distances of 2.729(3) and 2.714(3) Å), linking the complexes together in 1D chains along the [100] direction (Fig. 6). An intramolecular aromatic interaction is observed between phenyl and pyridine rings on both sides of Fe. We represent them as pair-1 and pair-2. The phenyl ring of *psca* is more inclined towards the pyridine ring to minimize the π - π repulsions. As a result, the distance between the pyrazole ring of DMPP and the phenyl ring of *psca* is too large to observe any aromatic interaction. On the other hand, the distances between phenyl centroids and pyridine centroids are 3.539(19) Å and 3.791(2) Å, for pair-1 and pair-2, respectively. The planes of pyridine and *psca* rings are at an angle of 6.03(16)° in pair-1. The pyridine and *psca* rings of pair-1 can be treated as nearly

parallel as the angle between their planes is not very large, thus the aromatic interaction in pair-1 can be considered as a slipped π stacking type while the displacement angle (ring normal to centroid-centroid vector) between the rings is 12.7°. In pair-2, the planes of the phenyl ring and pyridine ring are not parallel but lie at an angle of 14.24(16)°. Thus in pair-2 the aromatic interaction is an intermediate type between slipped π stacking and C-H··· π interaction with slipped π stacking dominating the interaction.⁴⁵ The aromatic interaction parameters in **4** are given in Table S3 (ESI†).

The solvent molecule Et₂O in the crystal lattice is not involved in H-bonding, which might be the reason that it evaporated so quickly. Besides non-covalent interactions, the [2+2] potential photodimerization of *psca* molecules was considered too. The vinyl carbons which are supposed to undergo [2+2] photocycloaddition are labelled as C28, C27, C36, and C37 in Fig. 6. The average distance between the two vinyl bonds is 4.6 Å which is beyond the maximum allowed distance (4.2 Å) according to the Schmidt's topochemical postulates.³¹ Also, the angles $\angle$ C27–C28–C36 $\neq$ $\angle$ C36–C37–C27 infer that the two vinyl bonds are not parallel to each other (Fig. 6). Hence, *psca* molecules in **4** unfortunately do not satisfy the criteria to

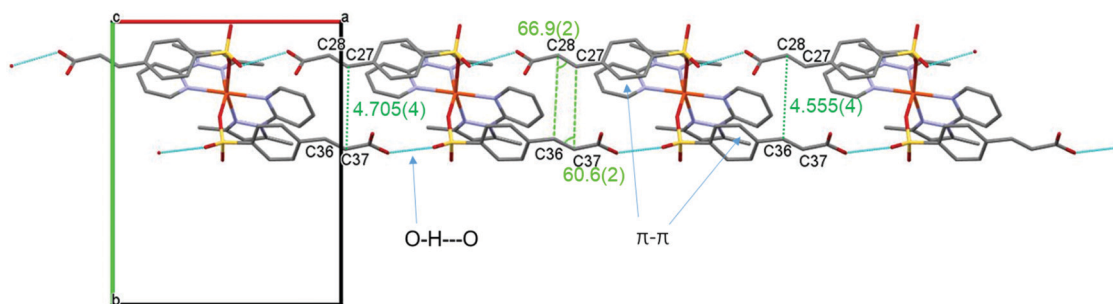


Fig. 6 1-D chains formed by hydrogen bonding along the *c*-axis in the structure of **4**, with π - π interactions indicated.

undergo the [2+2] photodimerization reaction. This situation is associated with the coordination of *pzca* which prevents a suitable photo-responsive arrangement.

3.3 SQUID magnetometry

Magnetic susceptibility measurements of **1–4** were recorded over the temperature range of 300–10 K. Fig. 7 collectively presents the molar magnetic susceptibility, χ , with temperature for all complexes. The room temperature χT values are in the range of 3.0–3.5 $\text{cm}^3 \text{mol}^{-1} \text{K}$ which is typical for HS mononuclear Fe(II) complexes. This situation is maintained on cooling down to 30 K, after which a slight decrease of χT

is observed. This decrease is associated with zero-field splitting effects of HS Fe(II) ions, as a result of octahedral distortions.⁴⁸ As the complexes are paramagnetic, a χ^{-1} vs. T plot was fitted according to the Curie–Weiss law recalled below in eqn (1).⁴⁹

$$\frac{1}{\chi} = \frac{T}{C} - \frac{\theta}{C} \quad (1)$$

where C and θ are the Curie and Weiss constants, respectively. The values presented in Table S4 (ESI†) are within errors and confirm the absence of any magnetic interactions between Fe(II) ions, as expected from the large distances between magnetic centres. The same conclusions were drawn for a magnetic study

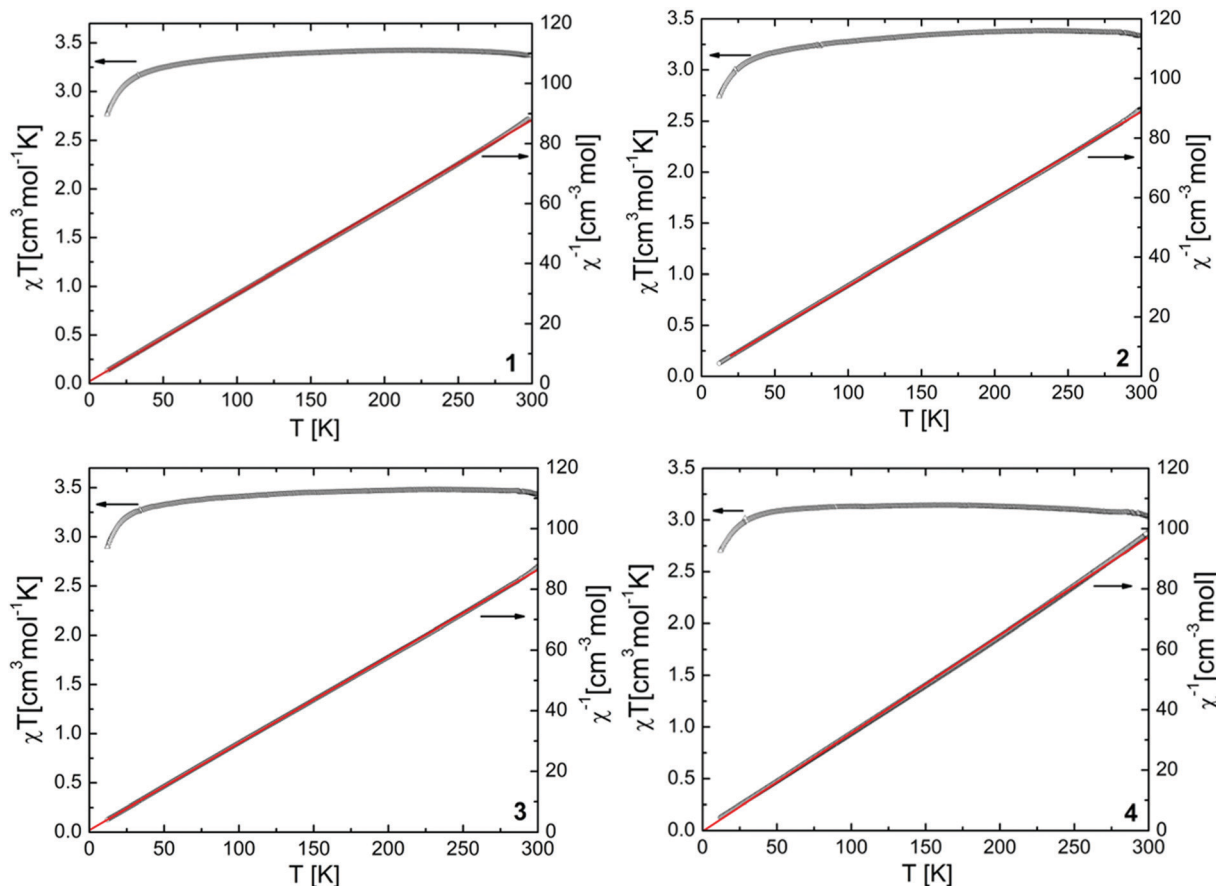


Fig. 7 χT vs. T , and χ^{-1} vs. T plots of **1–4**. The red line represents a Curie–Weiss law fit of the magnetic data.

of coordination compounds having an FeN_4O_2 coordination environment with two aromatic sulfonate anions coordinated to Fe(II) ions.⁵⁰

3.4 ^{57}Fe Mössbauer spectroscopy

^{57}Fe Mössbauer spectra of all coordination complexes are gathered in Fig. 8. The spectra were fitted to the sum of Lorentzian lines by a least-squares refinement using Recoil 1.05 Mössbauer Analysis Software (Table 1).⁵¹ A red doublet is detected in each spectrum, centred around an isomer shift of $\delta = 1.1\text{--}1.2\text{ mm s}^{-1}$ with a quadrupole splitting in the range $\Delta E_Q = 2\text{--}3\text{ mm s}^{-1}$, which is characteristic of $\text{Fe(II)}\text{ HS}$ ions. Mössbauer spectra confirm that complexes **1**, **3**, and **4** exist as whole $\text{Fe(II)}\text{ HS}$ compounds which is well supported by susceptibility measurements and single crystal X-ray diffraction. However, an additional yellow doublet was observed in the spectrum of **2** centred at $\delta = 0.14\text{ mm s}^{-1}$ with a quadrupole splitting of $\Delta E_Q = 0.51\text{ mm s}^{-1}$ which corresponds to HS Fe(III) ions.²⁸ The absence of any $\text{Fe(III)}\text{ HS}$ in SQUID measurement leads to the conclusion that **2** was synthesized as an $\text{Fe(II)}\text{ HS}$ compound but got partially oxidized to Fe(III) over a period of time needed to record the Mössbauer spectrum, which was performed under ambient air conditions. It is intriguing that only **2** got partially oxidized with time and not the other complexes. The reason may be attributed to the degree of distortion of Fe(II) octahedral geometries. This degree can be probed through the

Table 1 ^{57}Fe Mössbauer parameters of **1–4** at 298 K. Isomer shifts (δ) are given with respect to metallic $\alpha\text{-Fe}$. $\Gamma/2$ = half width of the lines

Compound	Sites	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$ (mm s^{-1})	Fraction (%)
1	$\text{Fe(II)}\text{ HS}$	1.20(1)	2.66(1)	0.27(1)	100
2	$\text{Fe(II)}\text{ HS}$	1.09(1)	2.25(1)	0.13(1)	72
	$\text{Fe(III)}\text{ HS}$	0.14(2)	0.51(5)	0.16(3)	28
3	$\text{Fe(II)}\text{ HS}$	1.21(1)	2.91(1)	0.16(5)	100
4	$\text{Fe(II)}\text{ HS}$	1.20(1)	2.50(1)	0.21(1)	100
	$[\text{Fe}(\text{pyridine})_4(\text{tos})_2]^{53}$	1.08	3.47	0.27	100

quadrupole splitting in Mössbauer spectra. Indeed, for ferrous compounds, the higher the distortion degree, the lower the quadrupole splitting. Indeed, this situation results from the presence of a lattice contribution to the electric field gradient which is negative compared to the valence contribution.⁵² If we compare the quadrupole splitting of Fe(II) complexes in Table 1, we find that **2** has the least value of ΔE_Q suggesting that **2** has the most distorted octahedral geometry. The distortion is the consequence of the appearance of oxidized iron species, which are located nearby Fe(II) ions.

No Mössbauer data are available for comparison on Fe(II) coordination complexes with two bidentate diimine ligands and two aromatic sulfonate ligands. $[\text{Fe}(\text{pyridine})_4(\text{tos})_2]$ is however the only closest coordination complex akin to our

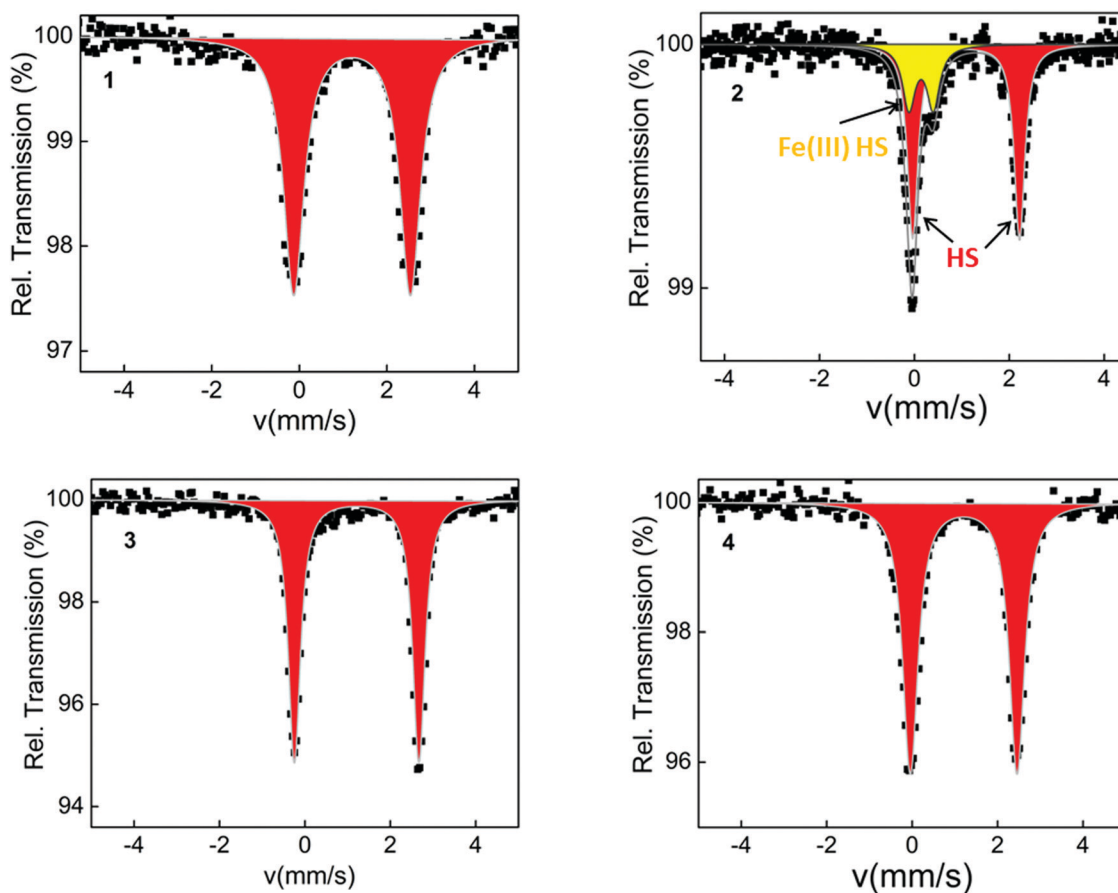


Fig. 8 Room temperature ^{57}Fe Mössbauer spectra of **1–4**.

synthesized complexes holding an FeN_4O_2 coordination sphere and two aromatic sulfonate ligands coordinated to Fe(II) .⁵³ The isomer shift is found to be of the same order but a significant difference is observed in quadrupole splitting (Table 1).

4. Conclusions

Four novel mononuclear Fe(II) coordination complexes including phenylsulfonate ligands were successfully synthesized. Single crystals could be isolated by vapour diffusing diethyl ether into the crystallization mixture, though this solvent was only observed as occluded species in the crystal structure of **4**. This solvent interfered with the self-assembly of the originally targeted $[\text{Fe}(\text{DMPP})_3]\text{X}_2$, ($\text{X} = \text{ps}, \text{tos}, \text{nitps}, \text{psca}$) compounds and instead yielded $[\text{Fe}(\text{DMPP})_2\text{X}_2]$ complexes, as shown by single-crystal X-ray diffraction analysis. Though all the complexes have the same FeN_4O_2 environment, these are not isostructural because of the different phenylsulfonate anions employed. Non-classical $\text{C-H}\cdots\text{O}$ intra- and intermolecular hydrogen bonds were observed in all complexes, whereas classical $\text{O-H}\cdots\text{O}$ type intermolecular hydrogen bonds were observed only in **4** due to the oxygen rich functional groups on both ends of *psca* molecules. Multiple intramolecular aromatic interactions were found between the aromatic rings of **DMPP** and aromatic sulfonate anions in all complexes. Intermolecular aromatic interaction was seen only in **3** between *nitps* molecules. Most interestingly, the sulfonate molecules are found to operate as ligands too, as seldom observed in iron(II) complexes.^{53–57} All synthesized complexes display an FeN_4O_2 core, which has been found in several mononuclear spin cross-over complexes.⁵⁸ Nevertheless, all of them display a permanent high-spin state, because the sulfonate coordination prevents any thermally induced spin crossover behaviour from occurring. The fact that we have obtained the same coordination environment for all the complexes suggests that the synthetic approach deployed here is reliable and could be used to design new heteroleptic coordination complexes, in the near future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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