Desolvation-Driven Thermal Spin Crossover in a Fe(II) Complex incorporating the Anthracene-2-Sulfonate Anion

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Abstract

Anions containing sulfonate groups are widely used in the construction of spin crossover complexes. In this work, we synthesized a new Fe(II) salt, $[Fe(H_2O)_6](2\text{-}As)_2$, featuring the anthracene-2-sulfonate ($2\text{-}As^-$) anion, which can be used to study the influence of anion photodimerization on the spin state. Using this salt as a precursor, we obtained a Fe(II) mononuclear complex $[Fe(3\text{-}bpp)_2](2\text{-}As)_2 \cdot 2MeOH \cdot H_2O$ (**1**, 3-bpp = 2,6-di(pyrazol-3-yl) pyridine). ^{57}Fe Mössbauer spectroscopy and magnetic measurements revealed that **1** is in the low-spin state in its solvated form but undergoes a gradual and incomplete spin crossover upon desolvation, with a narrow thermal hysteresis around 290 K.

Keywords Fe(II) complexes · ^{57}Fe Mössbauer spectroscopy · Spin crossover · Hysteresis · Spin state

1 Introduction

Spin crossover (SCO) materials are extensively studied for potential applications in data storage, sensing, molecular electronics and display technologies, owing to their ability to reversibly switch between high-spin (HS) and low-spin (LS) states in response to external stimuli, such as temperature, pressure or light [1-3].

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Light-induced spin-state control offers distinct advantages, including remote actuation, low power consumption and spatiotemporal precision [4-6]. Our group is exploring anion-driven light-induced spin change (AD-LISC) by incorporating photoresponsive counterions into Fe(II) complexes [7-9]. Anions containing sulfonate groups represent a large class of anions that frequently appear in SCO complexes [10-19]. Here, anthracene-2-sulfonate (2-As$^-$) was selected as a counterion because anthracene can undergo reversible [4+4] photocycloaddition in the solid state when co-facial stacking with an intermolecular distance below 4.2 Å is achieved, which is often difficult to realize [20-22]. We first synthesized $[Fe(H_2O)_6](2\text{-}As)_2$ as a precursor for the subsequent construction of the mononuclear Fe(II) complex $[Fe(3\text{-}bpp)_2](2\text{-}As)_2\cdot 2MeOH\cdot H_2O$ (**1**, 3-bpp = 2,6-di(pyrazol-3-yl) pyridine). ^{57}Fe Mössbauer spectroscopy and magnetic susceptibility show that complex **1** exhibits solvato-sensitive SCO behavior, i.e. remaining LS in the solvated form but showing gradual and incomplete SCO behavior with a small thermal hysteresis centered near 290 K upon desolvation.

2 Experimental

The ligand 3-bpp was prepared as described [23]. The precursor $[Fe(H_2O)_6](2\text{-}As)_2$ was synthesized by adapting a reported reference [24]. Complex **1** was prepared by reacting 3-bpp (0.12 mmol, 25.33 mg) with $[Fe(H_2O)_6](2\text{-}As)_2$ (0.06 mmol, 40.71 mg) in 7.5 mL MeOH (Fig. 1). Slow diffusion of diethyl ether (DEE) vapor into the reaction solution afforded rectangular crystals after three days. Yield: 85%. FT-IR (cm^{-1}): 3399 (w), 3117 (w), 3017 (w), 2919 (w), 1617 (m), 1464 (w), 1437 (s), 1354 (m), 1172 (s), 1114 (m), 1088 (s), 1027 (s), 767 (m), 753 (m), 721 (s), 1090 (s), 645 (s), 622 (s), 608 (m), 537 (m). Elemental analysis for $[Fe(3\text{-}bpp)_2](2\text{-}As)_2\cdot 2MeOH\cdot H_2O$: $C_{52}H_{46}FeN_{10}O_9S_2$ found, (calcd) (%): C 57.91 (58.10), H 4.20 (4.31), N 12.59 (13.03), S 5.91 (5.97).

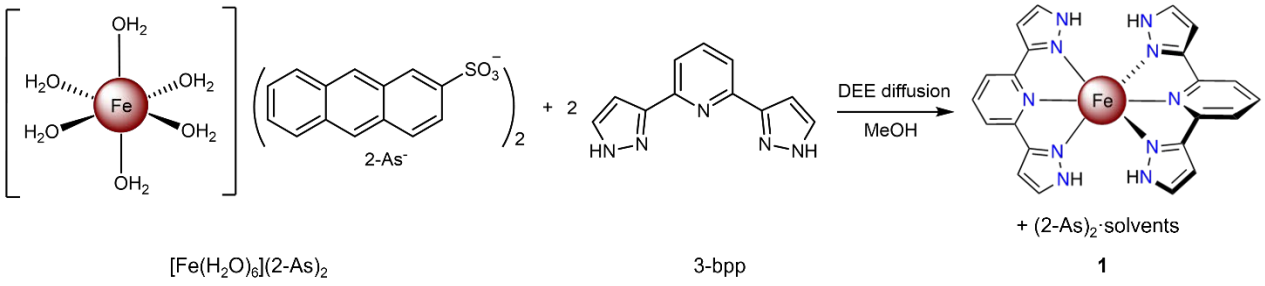

Fig.1 Schematic representation of the synthesis of complex **1**.

Fourier transformed infrared (FT-IR) spectra were performed on an Equinox 55 (Bruker) equipped with an ATR modulus and a MCT detector. Elemental analyses were performed on an Eurovector EA3000 CHNS-O elemental analyzer. ^{57}Fe Mössbauer spectra were measured in transmission geometry with a constant acceleration mode conventional spectrometer equipped with a 50 mCi ^{57}Co(Rh) source and a Reuter Stokes proportional counter. The microcrystalline samples were sealed in a cylindrical plastic sample holder and spectra were recorded at 298 K. The spectra were fitted using Recoil 1.05 Mössbauer Analysis software and isomer shift values are given with respect to α-Fe at room temperature. Magnetic susceptibility was measured on a Quantum design MPMS-5S.

3 Results and discussion

The room-temperature ^{57}Fe Mössbauer spectra of $[Fe(H_2O)_6](2\text{-}As)_2$ and complex **1** are shown in Fig. 2, and fitted parameters are summarized in Table 1. The spectrum of $[Fe(H_2O)_6](2\text{-}As)_2$ displays a dominant doublet (area fraction of 94.3%) with isomer shift δ = 1.27(1) mm s^{-1}, and quadrupole splitting ΔE_Q = 3.16(2) mm s^{-1}, parameters which are characteristic of HS Fe(II) ions stabilized by the weak ligand field generated by the six coordinated water molecules around the metal center. These parameters are indeed comparable to those reported for mononuclear complexes containing the $[Fe(H_2O)_6]^{2+}$ cation, in which the large quadrupole splitting originates from a significant electric field gradient (EFG) produced by the anisotropic distribution of the 3*d* electrons [25-29]. This anisotropy is further enhanced by a slight Jahn-Teller distortion, even though the FeO_6 octahedron deviates only marginally from ideal O_h symmetry. A minor component (5.7%) with smaller δ = 0.35(1) mm s^{-1} and ΔE_Q = 0.33(2) mm s^{-1} was also observed. The combination of reduced δ and ΔE_Q values indicates oxidation of Fe(II) to Fe(III), consistent with the removal of one 3*d* electron and the formation of half-filled, spherically symmetric d^5

configuration (high-spin Fe(III), $^6A_{1g}$). Such partial oxidation has been previously reported for another photo-switchable salt, namely $[Fe(H_2O)_6](psca)_2 \cdot 2H_2O$ (psca = *p*-sulfocinnamic acid) [9,30]. The fit of $[Fe(H_2O)_6](2\text{-}As)_2$ was carried out with an asymmetric doublet to consider texture effects arising from sample preparation [31]. In contrast, the Mössbauer spectrum of complex **1** measured at 298 K in its solvated form was well fitted by a single quadrupole doublet with δ = 0.30(1) mm s^{-1}, and ΔE_Q = 0.69(2) mm s^{-1}, indicative of LS Fe(II) ions in a pseudo-octahedral FeN_6 environment. Both isomer shift and quadrupole splitting are consistent with those reported for Fe(II) mononuclear complexes containing 3-bpp ligands, confirming the strong ligand field imposed by the 3-bpp ligands with lattice solvents [32-35]. Then, the lattice solvents were removed under dynamic vacuum on a Schlenk line by heating the sample at 400 K for 1 h. The sample was sealed in a sample holder inside a glove box and the spectrum was recorded at 298 K. The Mössbauer spectrum of the desolvated complex **1** can be fitted with three quadrupole doublets. The two outer doublets, with δ = 1.06(2) mm s^{-1}, ΔE_Q = 2.38(4) mm s^{-1} (54%), and δ = 0.79(6) mm s^{-1}, ΔE_Q = 2.35(1) mm s^{-1} (12%) correspond to HS Fe(II) sites, whereas the inner doublet with δ = 0.33(3) mm s^{-1}, ΔE_Q = 0.71(6) mm s^{-1} (34%) is attributable to LS Fe(II) centers. These parameters are in good agreement with those reported for solvent-free complex $[Fe(bpp)_2](PF_6)_2$ [33], indicating that removal of lattice solvent molecules induces a partial LS to HS transition in complex **1**. The presence of two HS doublets suggests the formation of two inequivalent HS Fe sites upon desolvation.

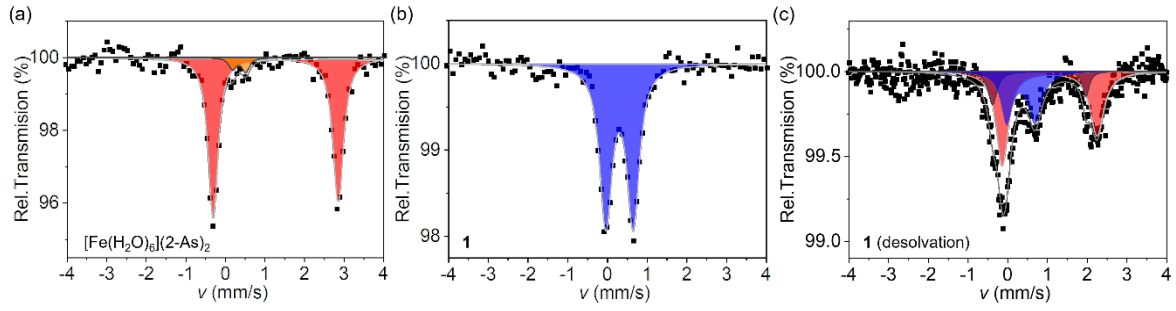

Fig. 2 ^{57}Fe Mössbauer spectra of (a) $[Fe(H_2O)_6](2\text{-}As)_2$, (b) complex **1**, and (c) complex **1** after desolvation at 298 K.

Table 1 ^{57}Fe Mössbauer parameters for $[Fe(H_2O)_6](2\text{-}As)_2$, complex **1**, and selected literature examples measured at indicated temperature. Isomer shifts (δ) are given with respect to metallic α-Fe. $\Gamma/2$ = half width of the lines.

Compound	T (K)	Spin state	Mössbauer parameters			
			δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma/2$	Fraction (%)
$[Fe(H_2O)_6](2\text{-}As)_2$	298	Fe(II) HS	1.27(1)	3.16(2)	0.14(1)	94.3
		Fe(III) HS	0.35(1)	0.33(2)	0.13(1)	5.7
$[Fe(H_2O)_6](psca)_2\cdot 2H_2O$[9]	298	Fe(II) HS	1.264(2)	3.18(4)	0.20(1)	91
		Fe(III) HS	0.143	0.43(4)	0.19(1)	9
$[Fe(H_2O)_6]SO_4\cdot H_2O$[26]	r.t.	Fe(II) HS	1.40	3.20	–	100
$[Fe(H_2O)_6]\cdot FeCl_4(H_2O)_2$[27] For $[Fe(H_2O)_6]^{2+}$	293(2)	Fe(II) HS	1.186(6)	3.03(1)	–	–
$[Fe(H_2O)_6]SiF_6$[28,29]	r.t.	Fe(II) HS	1.280	3.385	–	100
1	298	Fe(II) LS	0.30(1)	0.69(2)	0.17(1)	100
$[Fe(bpp)_2](C_8H_4O_4)\cdot 5H_2O$[32]	300	Fe(II) LS	0.32	0.66	0.31	100
$[Fe(bpp)_2](CF_3SO_3)_2\cdot 3H_2O$[33]	298	Fe(II) LS	0.36	0.70	–	100
$[Fe(bpp)_2](C_6H_8O_4)\cdot 4H_2O$[34]	295	Fe(II) LS	0.29	0.67	0.27	100
1 (desolvation)	298	Fe(II) HS1	1.06(2)	2.38(4)	0.21(7)	54
		Fe(II) HS2	0.79(6)	2.35(1)	0.10(1)	12
		Fe(II) LS	0.33(3)	0.71(6)	0.21(7)	34
$[Fe(bpp)_2](PF_6)_2$[35]	298	Fe(II) HS1	1.03	2.35	–	–
		Fe(II) HS2	1.01	1.94	–	–
		Fe(II) LS	0.33	0.69	–	–

Magnetic susceptibilities of complex **1** were measured under a 1000 Oe dc magnetic field at variable temperatures. To prevent lattice solvents loss, intact crystals were flame-sealed into a borosilicate tube with a small amount of mother liquor. Under these conditions, the $\chi_M T$ values (around 0) indicate that complex **1** remains in the LS state, as confirmed by ^{57}Fe Mössbauer spectroscopy at 298 K, with the onset of SCO occurring above 300 K (Fig. 3a). Then, the same sample was filtered and heated under vacuum at 400 K for 1 h. After this treatment, the $\chi_M T$ value

at 400 K increased to 3.13 $cm^3mol^{-1}K$, suggesting that most Fe(II) centers had converted to the HS state (Fig. 3b). Upon cooling, a gradual and incomplete SCO was observed with approximately half of the Fe(II) centers converted to the LS state at 80 K with $\chi_M T$ of 1.61 $cm^3mol^{-1}K$. This partial spin transition likely arises from one of the two inequivalent HS Fe(II) sites undergoing a HS to LS conversion, while the other Fe(II) site remains in the HS state based on Mössbauer spectrum. A sharper decline at lower temperatures is attributed to zero field splitting effects of the residual HS species [36]. Upon reheating, a small thermal hysteresis loop centered around 290 K was observed. The lattice solvent-dependent SCO behavior is consistent with other examples of the $[Fe(3\text{-bpp})_2]^{2+}$ family [37-39]. Removal of the lattice solvents disrupts the hydrogen bonding network, thereby diminishing the solvent-mediated enhancement of the ligand field strength and promoting gradual spin crossover behaviour [13, 23,40,41]. The hysteresis may arise from residual synergistic interactions mediated by hydrogen bonding between 2-As^- anion and $[Fe(3\text{-bpp})_2]^{2+}$ cation [42].

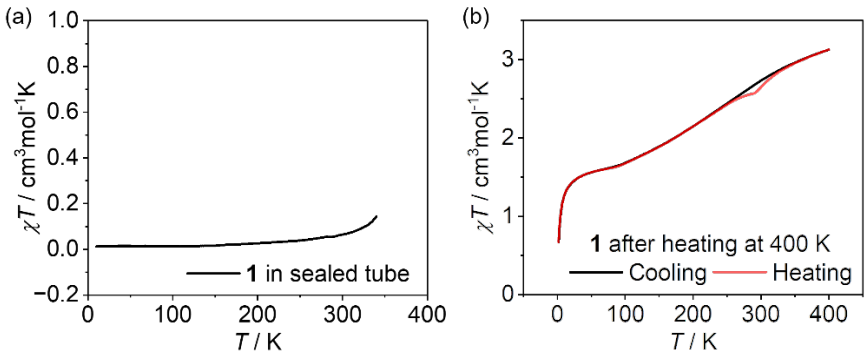

Fig. 3. $\chi_M T$ *vs*. *T* for complex **1**: (a) sample sealed with its mother liquor; (b) dried sample after heating to 400 K for 1 h under 1000 Oe dc magnetic field.

4 Conclusion

In this study, we report the synthesis and Mössbauer spectroscopy of a new Fe(II) salt $[Fe(H_2O)_6](2\text{-As})_2$, containing the 2-$As^-$ as a counter anion. This salt serves as a precursor for constructing the first Fe(II) complex with 2-As^- $[Fe(3\text{-bpp})_2](2\text{-As})_2{\cdot}2MeOH{\cdot}H_2O$ (**1**) targeting anthracene-based, anion-driven light-induced spin state change (AD-LISC) via photocyclization [7,43], which will be explored as a next field of investigation. The complex exhibits a low-spin state in the presence of lattice solvents. Upon desolvation, a gradual and incomplete spin crossover

with a small thermal hysteresis centered around 290 K is observed, which can bear importance, e.g. for civil security applications [2,44].

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Author contributions M. Wang and Y. G wrote the main manuscript text and reviewed it. J. Y. and D. P. performed magnetic measurements. M. W performed an elemental analysis.

Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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