Spin Crossover in Dinuclear N₄S₂ Iron(II) Thioether–Triazole Complexes: Access to [HS-HS], [HS-LS], and [LS-LS] States

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Supporting Information

ABSTRACT: Access to a new family of *thioether*-linked **PSRT** ligands, 4-substituted-3,5-bis{[(2-pyridylmethyl)sulfanyl]methyl}-4H-1,2,4-triazoles (analogues of the previously studied amino-linked **PMRT** ligands), has been established. Four such ligands have been prepared, **PSPhT**, **PS'BuT**, **PS'**^{*t*-Bu}**PhT**, and **PS**^{*M*e}**PhT**, with **R** = Ph, ^{*i*}Bu, ^{*t*-Bu}Ph, and ^{Me}Ph, respectively. Three dinuclear colorless to pale green iron(II) complexes, $[Fe^{II}_2(PSRT)_2](BF_4)_4$. solvent, featuring N₄S₂ donor sets, were prepared. Single-crystal structure determinations on $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ ·2MeCN·H₂O, $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ ·2MeCN, and $[Fe^{II}_2(PS^{$ *i* $}BuT)_2](BF_4)_4$. 4MeCN reveal that all four are stabilized in the [HS-HS] state



to 100 K and that both possible binding modes of the bis-terdentate ligands, *cis*- and *trans*-axial, are observed. Variable-temperature magnetic susceptibility studies of air-dried crystals (solvatomorphs of the single crystal samples) reveal the first examples of spin crossover (SCO) for a dinuclear iron(II) complex with N₄S₂ coordination. Specifically, $[Fe^{II}_2(PSPhT)_2](BF_4)_4$. $2^{1}/_2H_2O$ undergoes a multistep but complete SCO from [HS-HS] to [LS-LS], whereas $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$. $1^{1}/_2MeCN$. $2H_2O$ exhibits a half-SCO from [HS-HS] to [HS-LS]. In contrast, $[Fe^{II}_2(PS^{i}BuT)_2](BF_4)_4$. MeCN. H_2O remains [HS-HS] down to 50 K. The reflectance spectrum of pale green $[Fe^{II}_2(PSPhT)_2](BF_4)_4$. $1^{1}/_2CHCl_3$. $2^{1}/_2H_2O$ (solvatomorph A) reveals a trace of LS character (572 nm band ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$). Evans' ¹H NMR method and UV–vis spectroscopy studies revealed that on cooling dark green acetonitrile solutions of these complexes from 313 to 233 K, all three undergo SCO centered at or near room temperature. The tendency of the complexes to go LS in solution reflects the electronic impact of **R** on the σ -donor strength of the **PSRT** ligand, whereas the opposite trend in stabilization of the LS state is seen in the solid state, where crystal packing effects, of the **R** group and solvent content, dominate the SCO behavior.

INTRODUCTION

Spin crossover (SCO) complexes are an interesting class of materials exhibiting molecular bistability with potential applications in nanotechnological devices as memory storage units, sensors, or displays.^{1–5} They can be switched between two electronic states—high spin (HS) and low spin (LS)—by external stimuli, such as a change in temperature or pressure, light irradiation, or guest presence/absence, in a readily detectable and reversible way. Dinuclear complexes are of particular interest, as they can potentially have a two-step crossover, and intramolecular communication between metal centers can lead to more abrupt transitions.⁶

Ligands containing the 1,2,4-triazole moiety are well documented to have about the right field strength for SCO in iron(II) complexes, can bridge two iron centers through the two adjacent nitrogen atoms, and are versatile with respect to substitution at the N⁴, C³, and C⁵ positions.^{7,8} One such ligand previously used by us to deliberately generate dinuclear iron(II) complexes is the bis-terdentate 4-amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4H-1,2,4-triazole ligand (PMAT; Figure 1 PMRT with $R = NH_2$).⁹⁻¹⁴ The

 $[Fe^{II}_2(PMAT)_2](BF_4)_4$ ·DMF complex undergoes an abrupt half-SCO, from [HS-HS] to localized [LS-HS] at 224 K, with the [LS-LS] state inaccessible even under 1.03 GPa pressure at 4 K. Variation of the N^4 substituent to give other 4-substituted-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4H-1,2,4-triazoles (Figure 1) was shown to greatly affect the SCO properties of the analogous dinuclear iron(II) complexes, $[Fe^{II}_2(PMRT)_2]$ - X_4 , despite R being remote from the donor atoms. ^{15,16} In all of the structurally characterized dinuclear iron(II) complexes of the **PMRT** ligands to date a *cis*-axial binding mode is observed (Figure 1). In no case could the second potential SCO event, to the [LS-LS] state, be accessed, probably because of the steric restraint of having all 12 donors to the two iron(II) centers, and two N^1N^2 -triazole bridges between them, provided by just two ligands.

More recently, the Rentschler group reported a family of **PMRT**-like complexes of a thiadiazole-based ligand, 2,5-bis[(2-pyridylmethyl)amino]methyl-1,3,4-thiadiazole (**PMTD**, Figure

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Figure 1. Existing **PMRT** ligands that vary in the choice of **R**, including **PMAT**, where $\mathbf{R} = \mathbf{NH}_{2}$, and the existing **PMTD** ligand, as well as the new **PSRT** ligands described herein (in box). Also shown are the *cis*-axial (seen for **PMRT**) and *trans*-axial (seen for **PMTD**) ligand binding modes observed for the literature dinuclear iron(II) complexes of the **PMRT** and **PMTD** ligands.

1).¹⁷ In contrast to the triazole moieties in the **PMRT** ligands, the thiadiazole moiety was shown to produce $[Fe^{II}_{2}(PMTD)_{2}]$ - X_{4} complexes with a *trans*-axial binding mode (Figure 1) and to facilitate access to the fully [LS-LS] state. Indeed all three $[Fe^{II}_{2}(PMTD)_{2}]X_{4}$ complexes highly favor the [LS-LS] state and undergo a gradual SCO starting above 250 K, not reaching the [HS-LS] state (or the [HS-HS] state) at the limit of the measurement, 380 K.

All of the **PMAT**, **PMRT**, and **PMTD** complexes described above feature N₆-coordinated iron(II) centers, which are by far the dominant class of SCO compounds in the literature.¹ Mixed donor environments for SCO-active iron(II) centers are rare,¹⁸ but SCO has been reported for iron(II) with N₄C₂¹⁹ and P₂N₂Cl₂²⁰ coordination spheres, and wide thermal hysteresis^{21–24} and room-temperature bistability^{21,24,25} have been demonstrated in N₄O₂ systems.

SCO in N₄S₂-coordinated iron(II) complexes has scarcely been investigated, with only six structurally characterized examples in the literature (Chart 1), to the best of our knowledge [CSD search for Fe with 4× any bond to N, 2× any bond to S (Figure S21); CSD version 5.37 updates (November 2015); 139 hits, 6 of which are SCO active]. Five of these complexes are mononuclear, while one is polymeric, and all are of just four ligands (Chart 1), all of which are neutral, feature thioether (not thiolate) sulfur donors, and provide either N2S2 or N₂S donor sets. In 2012, McKenzie and co-workers² reported a mononuclear iron(II) complex with N₄S₂ coordination, $[Fe^{II}(bpte)(NCSe)_2]$, which crystallized in four polymorphs, two of which exhibited four-site SCO, which was attributed to cooperativity facilitated by the asymmetry of the mixed donor set at the iron(II) centers being exaggerated upon an HS \rightarrow LS transition (average Fe–S 2.54 \rightarrow 2.24 Å, average Fe-pyridine 2.18 \rightarrow 2.00 Å). More recently, they have developed a 1D polymer, {[Fe^{II}(**bpte**)(μ^2 -NC(CH₂)₄CN)]- $(BPh_4)_2 \cdot Me_2CO$, which undergoes an abrupt and hysteretic Chart 1. Only Ligands Previously Used in N_4S_2 -Coordinated Iron(II) Complexes That Are SCO-Active and Structurally Characterized^a



"All four ligands feature thioether donors. The six complexes are mononuclear (5) or polymeric (1): $[Fe^{II}(bpte)(NCSe)_2]$, $\{[Fe^{II}(bpte)(\mu^2-NC(CH_2)_4CN)](BPh_4)_2\cdot Me_2CO\}$, $[Fe^{II}(bpte)-(MeCN)_2]$, $[Fe^{II}(bptPh)(MeCN)_2]$, $[Fe^{II}(e_2)_2(CH_2SMe)]_2Fe^{II}\}$.

SCO event upon losing solvent acetone.²⁷ Prior to those reports, Britovsek and co-workers reported that the closely related N_4S_2 -coordinated iron(II) complexes [Fe^{II}(bpte)- $(MeCN)_2$] and $[Fe^{II}(bptPh)(MeCN)_2]$ undergo a gradual, almost complete SCO below room temperature in acetonitrile solution.²⁸ Finally, the N_4S_2 -coordinated iron(II) complexes $[Fe^{II}([9]aneN_2S)_2][ClO_4]_2$ and $\{[PhB(pz)_2(CH_2SMe)]_2Fe^{II}\},\$ by Gahan and co-workers²⁹ and by Weber, Holthausen, Wagner, and co-workers,³⁰ respectively, were both reported to undergo gradual, incomplete SCO. The former complex, $[Fe^{II}([9]aneN_2S)_2][ClO_4]_2$, transitions between LS in the 4– 150 K range and approximately 30% HS at 300 K (see Supporting Information) in the solid state and also shows temperature-dependent magnetic susceptibility in solution.²⁹ In the solid state the latter complex, { [PhB- $(pz)_{2}(CH_{2}SMe)]_{2}Fe^{II}$, is LS from 5 to 293 K, then undergoes an incomplete SCO to approximately 10% HS at the limit of measurement (360 K). Similarly, in toluene solution it undergoes only partial SCO, as monitored by NMR (203-298 K) and by UV-vis (283-343 K) spectroscopy.³⁰ To summarize, five of these six examples of structurally characterized, SCO-active N₄S₂-coordinated iron(II) complexes are mononuclear and one is a 1D polymer. All six feature thioether S donors.

In order to investigate SCO in *dinuclear* iron(II) complexes with mixed NS donor sets, we have incorporated thioether linkages in place of the amino linkages in the bis-terdentate **PMRT** ligand scaffold to give a new family of **PSRT** ligands (Figure 1), with two discrete N₂S-binding pockets and retaining a triazole bridge between them. The longer C–S bonds, compared to C–N bonds, are also expected to give the **PSRT** ligands greater flexibility than the amino linkages can in **PMRT**. This might give us the "best of both worlds", i.e., open up access to the [LS-LS] state in the resulting dinuclear triazolebridged complexes, as was seen for the **PMTD** systems, while retaining access to both the [LS-HS] and fully [HS-HS] states, as was seen for the **PMRT** systems. These new **PSRT** ligands remain triazole-based, so retain the advantage of having an **R** group off N^4 that can be varied. Knowing from our previous studies of the $[Fe_2^{II}(PMRT)_2](BF_4)_4$ complexes that this **R** group has a great influence on the SCO activity,¹⁵ four different **R** groups were employed in this study in order to generate a new family of $[Fe_2^{II}(PSRT)_2](BF_4)_4$ systems, thereby increasing our chances of observing and/or fine-tuning SCO.

RESULTS AND DISCUSSION

Ligand Synthesis. The key precursors to the desired bisterdentate **PSRT** ligands are the N^4 -substituted-3,5-bis(chloromethyl)-1,2,4-triazole hydrochlorides (**3R**) and the deprotonated thiol 2-pyridinemethanethiolate, as the 1:2 reaction of these precursors should generate the two thioether-linked (rather than amino-linked for **PMRT**) "arms" off the triazole (Scheme 1).



Given our established general route to 3R head units,^{15,16} four N^4 -substituents, **R**, were selected for the present study, three of which, the phenyl, *p-tert*-butylphenyl, and isobutyl N^4 substituted 3,5-bis(chloromethyl)-1,2,4-triazole hydrochlorides, were previously reported by us. The fourth 3R head unit, N^4 -ptolyl-3,5-bis(chloromethyl)-1,2,4-triazole hydrochloride, is new but was synthesized according to our general procedure, in yields consistent with those found for the other R groups. While only four such head units, 3R, are employed herein, it should be noted that there is scope for incorporation of a far wider range of R groups, as the N^4 -substituent is readily introduced in the first step by appropriate choice of a commercially available primary amine in the synthesis of triazole 1R (Scheme 1). The reasons that phenyl, tertbutylphenyl, and isobutyl N⁴-substituents were chosen for this initial foray into the development of a new range of PSRT ligands, PSPhT, PS^{t-Bu}PhT, and PSⁱBuT, respectively (Scheme 1), is that we previously found that the $[Fe_{2}^{II}(PMRT)_{2}](BF_{4})_{4}$ analogues with these R groups exhibited SCO from [HS-HS] to (mostly) [HS-LS]. The fourth R group, tolyl, was selected in order to access the PSMePhT ligand, as tolyl had been previously used by our group as an N^4 -substituent in other SCO-active iron(II) 1,2,4-triazole systems.^{31,32}

While in principle the triazole head units **3R** could be reacted with two equivalents of 2-pyridinemethanethiol, under basic conditions, to introduce the two thioether-linked "side arms" and generate the new **PSRT** ligands, thiols are prone to oxidation and often have an unpleasant odor.³³ Therefore,

instead of isolating the thiol, it was more convenient to access it via hydrolysis of the corresponding thioester, thioacetic acid *S*pyridin-2-ylmethyl ester 4, *in situ*, then add **3R** (Scheme 1). Initial attempts to isolate 4 by a literature procedure³⁴ proved unsuccessful. However, simplification of the work up removing the solid K₂CO₃ by filtration before extracting into CH₂Cl₂ (and not washing with HCl)—resulted in 4 in high yield (89%), but while clean by ¹H NMR spectroscopy and successfully used in the subsequent step, it should be noted that it was not microanalytically pure.

With thioacetic acid S-pyridin-2-ylmethyl ester 4 in hand, an analogous protocol to that reported for the synthesis of the bpte ligand by Nolan in 1970 (obtained as an oil),³⁵ and improved upon by McKenzie in 2011 (obtained as crystals),³⁶ was employed to add the two "arms" and generate the desired **PSRT** ligands (Scheme 1). Specifically, under a N₂ atmosphere in ethanol solution, two equivalents of 4 are deprotected by stirring with sodium ethoxide for 30 min. The appropriate N^4 substituted-3,5-bis(chloromethyl)-1,2,4-triazole hydrochloride 3R was then added and the mixture stirred at room temperature for 1 h, followed by a 5 h reflux, and finally by stirring at room temperature overnight. In all four cases, workup of the reaction mixtures gave brown oils, which in the case of the phenyl- and p-tolyl-substituted ligands were recrystallized from hot toluene to yield PSPhT and PSMePhT as analytically pure beige powders. After failing to successfully complex the impure oil of the *p-tert*-butylphenyl ligand $PS^{t-Bu}PhT$ with iron(II), this ligand was first purified by column chromatography, which, after recrystallization, gave PS^{t-Bu}PhT as a microanalytically pure microcrystalline solid, however in poor (13%) yield. The oil obtained in the case of the isobutyl ligand **PSⁱBuT** was clean by ¹H NMR spectroscopy but was not microanalytically pure. However, this crude material was successfully used in complexations.

Synthesis of $[Fe^{II}_2(PSRT)_2](BF_4)_4$ Complexes. Dinuclear iron(II) complexes of the form $[Fe^{II}_2(PSRT)_2](BF_4)_4$ solvent were synthesized for three of the ligands, PSPhT, PS^{Me}PhT, and PS'BuT. Unfortunately, microanalytically pure complex was not obtained from PS^{t-Bu}PhT, even after purification of the ligand (see above).

All three complexes precipitated as white to pale green powders from the 1:1 reaction of the appropriate **PSRT** ligand with iron(II) tetrafluoroborate hexahydrate under argon in MeOH or MeOH/CHCl₃ at room temperature. The solvent and ratio of solvents used in these three complexations were varied due to solubility differences between the three complexes and were chosen in order to precipitate out the desired product. However, all three powders could be recrystallized, in air, by the same protocol: vapor diffusion of THF into the respective MeCN solutions. In all three cases this resulted in the formation of colorless to pale green single crystals suitable for X-ray crystal structure determinations (see later). Solvent is present in all of these samples.

For the **PSPhT** complex, drying of the initial pale green powder under a stream of nitrogen yielded microanalytically pure $[Fe^{II}_2(PSPhT)_2](BF_4)_4$.¹/₂CHCl₃·2¹/₂H₂O (solvatomorph A), in 52% yield. Recrystallization of this powder gave colorless block-shaped single crystals of $[Fe^{II}_2(PSPhT)_2]$ - $(BF_4)_4$ ·2MeCN·H₂O (solvatomorph B, see structure description later), which after air drying lost MeCN and picked up H₂O, in the process also losing crystallinity, resulting in a third solvatomorph, $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ ·2¹/₂H₂O (solvatomorph C), obtained in 22% overall yield. An attempt at cocrystallization of the initial precipitate with TCNQ⁻ anions instead yielded colorless rod-shaped crystals of a fourth solvatomorph, $[Fe^{II}_2(PSPhT)_2](BF_4)_4 \cdot 2^1/_2MeCN \cdot 1/_2H_2O \cdot THF$ (solvatomorph D), featuring a different ligand binding mode (see Figure 1 for binding modes; also see structure description in SI); however this was obtained only on a small scale, so no other characterization could be performed.

For the other two complexes, with $\mathbf{R} = {}^{Me}Ph$ and ${}^{i}Bu$, the complexation reactions yielded impure off-white precipitates, which upon recrystallization yielded pale green block-shaped and colorless block-shaped single crystals of $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 2MeCN$ and $[Fe^{II}_{2}(PS'BuT)_{2}]-(BF_{4})_{4}\cdot 4MeCN$, respectively (see structure descriptions later). On air drying, these crystals also crumbled and lost some acetonitrile and picked up water, to give the solvatomorphs $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O$ and $[Fe^{II}_{2}(PS'BuT)_{2}](BF_{4})_{4}\cdot MeCN\cdot H_{2}O$, in 18% and 16% overall yields, respectively.

Despite our attempts to produce a set of perfect analogues, i.e., with exactly the same solvent content, the varied nature of the packing interactions of each **R** group involved led to a loss of control of solvent content; hence differing amounts of MeCN, H_2O , and/or THF were present in the single crystals of each of these complexes.

Structures of $[Fe^{II}_2(PSRT)_2](BF_4)_4$ Complexes. X-ray crystal structure determinations were carried out on all three complexes, including two solvatomorphs of the PSPhT complex (solvatomorphs B and D), at 100 K. In all four cases this confirmed that the PSRT ligands had coordinated as intended, with two of them binding in a bis-terdentate manner to the two iron(II) centers, giving both iron(II) centers an N₄S₂ donor set and providing two N^1N^2 -triazole bridges between them (Figures 2 and 3).

 $[Fe^{II}_{2}(PSPhT)_{2}](BF_{4})_{4}\cdot 2MeCN\cdot H_{2}O$ (solvatomorph B) crystallized in the C2/*c* space group with the asymmetric unit constituting half of the complex and the other half generated by a 2-fold rotation axis along the N3–C9 bond (Figure 2, top). Hence the two iron(II) centers are crystallographically identical, but half of each ligand is unique. The four BF₄⁻ counterions and the two MeCN and one H₂O solvent molecules, per complex, were disordered and could not be sensibly modeled, so SQUEEZE³⁷ was applied; the electron density included agreed with the anion and solvent content deduced by microanalysis.

The two equivalent iron(II) atoms are in a distorted octahedral N_4S_2 coordination sphere (Figure 2 and Table 1), with the two PSPhT ligands supplying all 12 donor atoms and providing two triazole bridges between them. Each bridging triazole ligand binds the two iron(II) centers in a trans-axial mode, i.e., with one pyridine arm up and one down relative to the triazole ring (Figures 1 and 2). The Fe-N bonds [2.116(16)-2.1569(17) Å] and Fe-S bonds [2.5379(6) and 2.5932(6) Å] are long, the *cis* angles of the iron(II) coordination sphere range far from 90° [79.56(5)- $108.06(7)^{\circ}$], and the octahedral distortion parameter is large $(\Sigma = 109.84^{\circ})$, all of which is consistent with the presence of HS iron(II) centers at 100 K. For both ligands, the triazole and attached N^4 -phenyl ring substituent are almost at right angles to one another, 68.22° and 78.64°. This precludes any resonance effect of the R group on the triazole. Also, as R is relatively remote from the donor atoms, any inductive effect is not expected to be strong. Hence, in the solid state, the main impact of the choice of R group is not electronic, but rather is



Figure 2. Perspective view of the cation of (top) $[Fe^{II}_2(PSPhT)_2]$ - $(BF_4)_4 \cdot 2MeCN \cdot H_2O$ (solvatomorph B), $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4 \cdot 2MeCN$ (middle), and (bottom) $[Fe^{II}_2(PS^{F}BuT)_2](BF_4)_4 \cdot 4MeCN$. Note that the **PSRT** ligands are coordinated in different modes: (top and middle) "up–down", i.e., *trans*-axial mode (see Figure 1) with a 2-fold symmetry axis along N3–C9···N6; and (bottom) *cis*-axial mode (see Figure 1) with an inversion center between the two iron centers. Color codes: iron, orange; nitrogen, royal blue; sulfur, yellow; carbon, gray/black (so that the two ligands are easily identified). Hydrogen atoms are omitted.

on the crystal packing. In this case there is no evidence of $\pi - \pi$ interactions between the aromatic rings of neighboring complex cations. The central portion of this complex is relatively flat, with the two triazole ring planes almost coplanar, intersecting at an angle of just 4.37°.

In a failed attempt to cocrystallize $[Fe^{II}_{2}(PSPhT)_{2}]^{4+}$ complex cations with TCNQ⁻ anions, colorless rod-shaped crystals of $[Fe^{II}_{2}(PSPhT)_{2}](BF_{4})_{4}\cdot 2^{1}/_{2}MeCN\cdot 1/_{2}H_{2}O\cdot THF$ (solvatomorph D) crystallized in the $P\overline{1}$ space group (see the SI for full description and figures).

Figure 3. Perspective view showing the solvent/anion– π interactions (red dashed lines) and nonclassical hydrogen bonds (green dashed lines to main residue, blue dashed lines to neighboring complex cations) for $[Fe^{II}_{2}(PS^{i}BuT)_{2}](BF_{4})_{4}\cdot 4MeCN$. For image clarity only the two unique MeCN and two unique anions are shown (B2 is "twirl" disordered about the B2–F5 bond; only the 0.6 occupancy component is shown). Color codes: iron, orange; nitrogen, royal blue; sulfur, yellow; carbon, gray; fluorine, green; boron, tan; selected hydrogen atoms, black. Red spheres represent ring centroids.

 $[Fe_{2}^{II}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 2MeCN$ (Figure 2, middle) also crystallized in the C2/*c* space group with half of the complex in the asymmetric unit and the other half generated by a C₂ axis through the C9–N3 bond. Indeed it is isomorphous with $[Fe_{2}^{II}(PSPhT)_{2}](BF_{4})_{4}\cdot 2MeCN\cdot H_{2}O$ (solvatomorph B) (Figure 2, top), so again the iron(II) centers are in an N₄S₂ distorted octahedral environment (Table 1), and the bridging triazole ligands bind in the *trans*-axial mode (Figure 1). Again SQUEEZE was used to account for the disordered counterions and solvent molecules: the electron density included agreed with the anion and solvent content deduced by microanalysis. The Fe–N bonds [2.0885(30)-2.1171(35) Å] and Fe–S bonds [2.4996(12) and 2.5159(14) Å] are shorter than those in $[\text{Fe}^{II}_2(\text{PSPhT})_2](\text{BF}_4)_4\cdot 2\text{MeCN}\cdot\text{H}_2\text{O}$ (solvatomorph B) but are still within the range expected for HS iron(II). The *cis* angles of the iron(II) coordination sphere deviate slightly less from 90° $[79.95(9)-104.83(14)^\circ]$, and Σ is slightly lower, at 87.16°, but these remain consistent with the presence of two HS iron(II) centers at 100 K. Similar to the previous structures, the tolyl–triazole angles are near 90° $(76.46^\circ \text{ and } 70.45^\circ)$, and there is no evidence of $\pi-\pi$ interactions between complex cations. The central portion of the complex is significantly more twisted than $[\text{Fe}^{II}_2(\text{PSPhT})_2](\text{BF}_4)_4\cdot 2\text{MeCN}\cdot\text{H}_2\text{O}$ (solvatomorph B), with the triazole ring planes at a greater angle $(23.83^\circ \text{PS}^{\text{Me}}\text{PhT} \text{ vs } 4.37^\circ \text{PSPhT})$.

 $[Fe^{II}_{2}(PS^{i}BuT)_{2}](BF_{4})_{4}$ ·4MeCN crystallized in the $P2_{1}/c$ space group. The asymmetric unit contains one iron(II) center, one complete ligand, two anions, and two MeCN solvent molecules, with the other half of the complex generated by an *inversion center* between the two iron(II) centers (Figures 2 and 3). Hence the two **PS'BuT** ligands sandwich the two iron(II) centers in a *cis*-axial mode; that is, the pyridine arms of each ligand bind the iron(II) centers from the *same face* of the triazole ring (Figure 1).

In common with the other three structures, the iron(II) centers are in a distorted octahedral N_4S_2 coordination sphere (Table 1) comprising two heterocyclic nitrogen donors and one thioether sulfur donor from each of the two **PS'BuT** ligands. The Fe–N [2.1273(45)–2.1683(45) Å] and Fe–S [2.5448(14) and 2.5822(21) Å] bond distances, *cis* donor–Fe– donor angles [79.54(11)–103.16(5)°], and Σ (97.14°) are all consistent with the complex being in the [HS-HS] state at 100 K. The central portion of this complex is very flat with the triazole planes parallel by symmetry and offset by just 0.340 Å.

In this structure the anions and solvent molecules were successfully included in the refinement. As a result, a number of solvent/anion- π (Figure 3, red dashed lines) and nonclassical hydrogen bonding (Figure 3, green dashed lines) interactions

Table 1. Comparison of Selected Bond Distances (Å), Angles (deg), and Other Data for the Four [HS-HS] PSRT Complexes

selected parameters ^a	[Fe ^{II} ₂ (PSPhT) ₂](BF ₄) ₄ ·2MeCN·H ₂ O solvatomorph B (SQUEEZE applied)	$\begin{array}{l} [Fe^{II}_{2}(PSPhT)_{2}](BF_{4})_{4}\cdot\\ 2^{1}/_{2}MeCN\cdot^{1}/_{2}H_{2}O\cdot THF\\ \text{solvatomorph }D \ (\text{see the SI}) \end{array}$	$[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4} \cdot 2MeCN$ (SQUEEZE applied)	$[Fe^{II}_{2}(PS'BuT)_{2}](BF_{4})_{4} \cdot 4MeCN$
spin state at 100 K	HS-HS	HS-HS	HS-HS	HS-HS
PSRT binding mode	trans-axial	<i>cis</i> -axial	<i>trans</i> -axial	<i>cis</i> -axial
Fe…Fe	4.216	4.231	4.190	4.218
Fe-N _t	2.1166(16), 2.1348(16)	2.1326(52), 2.1564(47)	2.0885(30), 2.0923(33)	2.1273(45), 2.1418(42)
Fe-N _{py}	2.1382(17), 2.1569(17)	2.1665(51), 2.1726(50)	2.0892(34), 2.1171(35)	2.1683(45), 2.1578(43)
Fe-S	2.5379(6), 2.5932(6)	2.5397(16), 2.5779(16)	2.4996(12), 2.5159(14)	2.5448(14), 2.5822(21)
cis-N _t -Fe-N _t	96.57(6)	96.95(18)	95.26(12)	96.89(15)
cis-N _t -Fe-N _{py}	87.07(6)-108.06(7);]	91.87(18)-105.37(19);	88.51(12)-104.83(14);	88.91(16)-100.86(16);
range; [av]	[98.17]	[98.16]	[95.86]	[96.79]
cis-S-Fe-N _t	79.90(4), 79.62(4)	79.79(13), 78.99(13)	81.09(9), 79.95(9)	79.82(11), 80.12(11)
cis-S-Fe-N _{py}	79.56(5)-88.85(5);	78.79(14)-85.83(14);	81.31(11)-90.08(9);	79.54(11)-91.33(11);
range; [av]	[82.58]	[82.49]	[84.69]	[83.64]
cis-S-Fe-S	104.60(2)	104.41(5)	103.97(4)	103.16(5)
<i>trans</i> -N _{py} -Fe-N _{py}	155.21(7)	155.37(19)	162.35(14)	158.87(17)
trans-S-Fe-N _t	171.43(5), 173.51(4)	174.43(13), 175.97(14)	172.84(9), 174.48(9)	176.69(11), 177.01(12)
Σ	109.84	105.25	87.16	97.54

 ${}^{a}N_{t} = N$ donor atom on triazole; $N_{py} = N$ donor atom on pyridine; $\Sigma =$ octahedral distortion parameter, defined as the sum of the absolute values of the difference of each of the 12 *cis* angles from 90°.

Table 2. Comparison of Value or Range [Average] of Selected Bond Distances (Å) and Angles (deg) for the Iron(II) Coordination Spheres in the Average of the Four [HS-HS] PSRT Complexes Reported Herein (See Table S5 for Data on Each), with that of the [HS-HS] and [LS-HS] PMAT Complex,¹⁰ and the [LS-LS] PMTD Complex^{17ab}

selected parameters ^a	combined PSRT data (4 structures herein)	[Fe ^{II} ₂ (PMAT) ₂](BF ₄) ₄ ·DMF at 298 K	$[Fe^{II}_{2}(PMAT)_{2}](BF_{4})_{4} \cdot DMF$ at 123 K ^b	$[Fe^{II}_{2}(PMTD)_{2}](BF_{4})_{4}\cdot DMF \cdot \frac{3}{4}MeOH \cdot \frac{1}{2}H_{2}O^{b}$
spin state	HS-HS	HS-HS	LS-HS	LS-LS
av. C–X	1.807	1.482	1.488	1.483
cis-X-Fe-Nt	78.99–81.09; [79.91]	75.92(16), 75.93(16)	81.79(14), 81.86(14) / 75.14(15), 75.24(13)	82.73(9), 82.55(10) / 81.52(10), 82.76(10)
cis-X–Fe–X	103.16–104.60; [104.04]	115.90(17)	101.11(15) / 121.65(14)	97.86(10)/99.39(11)
<i>cis</i> -X–Fe–N _{py} range; [av.]	78.79(14)–91.33(11); [83.35]	76.13(18)–94.91(18); [85.00]	81.99(15)-92.26(15) / 75.13(13)-93.98(14); [87.12 / 83.75]	82.66(10)-92.48(10) / 80.62(11)-89.83(11) [87.32 / 85.86]
cis-N _t -Fe-N _t	96.42	92.80(15)	95.43(14) / 87.92(13)	97.07(9)/96.63(10)
<i>cis</i> -N _t -Fe-N _{py} range; [av.]	87.07(6)–108.06(7); [97.25]	93.84(16)–100.17(17); [96.43]	91.25(14)-94.84(14) / 93.58(13)-107.13(14); [93.04 / 99.19]	90.09(9)-94.47(10) / 92.86(11)-94.84(11) [92.70 / 94.25]
trans-X-Fe-Nt	171.43–177.01; [174.55]	166.40(16), 167.66(17)	175.38(14), 175.92(15) / 162.72(13), 163.15(13)	175.26(10), 177.41(11) / 175.33(11), 175.80(11)
trans-N _{py} -Fe-N _{py}	157.78	161.26(18)	170.96(14) / 154.24(14)	171.77(10) / 167.10(11)
$ au_4$	0.0774	0.184	0.0617 / 0.242	0.0520 / 0.0629
Σ	99.95	117.5	65.0 / 133.1	58.36 / 65.40

 ${}^{a}N_{t} = N$ donor atom on triazole or thiadiazole; $N_{py} = N$ donor atom on pyridine; X = S or amino N donor atom; $\Sigma =$ octahedral distortion parameter, defined as the sum of the absolute values of the difference of each of the 12 *cis* angles from 90°, τ_{4} is the four-coordinate geometry index for the Fe-X-X-N_t-N_t-Ph_t plane of the octahedron, where $\tau_{4} = 0$ for square planar and $\tau_{4} = 1$ for a tetrahedron. Data for HS centers in red text; data for LS centers in blue text. ${}^{b}Fe1/Fe2$.

between them and the cation were able to be identified, and a sandwiching of a triazole ring, by a solvent lone pair…triazole… counteranion interaction, was observed. Specifically, there is a solvent- π interaction^{15,16,38,39} between the N2 triazole ring and N7 of a MeCN molecule [centroid…N7 = 3.106 Å; \angle (nitrile CN…centroid) = 169.87°]. On the other face of the triazole ring there is an anion- π interaction^{15,16,39-43} with a tetrafluoroborate counteranion [F2...centroid = 3.199 Å; F4... centroid = 3.403 Å], where the counteranion sits almost directly above the triazole ring $\left[\angle (B1 - F2 - centroid) \right]$ = 107.34° ; $\angle(B1-F4-centroid) = 97.55^{\circ}$]. The B1 BF₄⁻ counterion is also involved in nonclassical hydrogen bonding to two of the pyridine rings $[C2-H\cdots F3 = 3.246(7) \text{ Å}, \angle (C2 H \cdots F3$ = 125.8°; C15- $H \cdots F3$ = 3.192(7) Å, \angle (C15- $H \cdots F3$) = 123.1°] and to one of the side arm CH₂ groups [C10-H10a…F4 = 3.086(7) Å, ∠(C−H…F) = 130.7°]. The B2 BF₄⁻ anion is "twirl" disordered about the B2-F5 bond. Nevertheless it is involved in nonclassical hydrogen bonding [C11-H11b...F5 = 3.286(7) Å, \angle (C11-H11b...F5) = 157.0° ; C6-H6a…F11 = 3.346(13) Å, ∠(C6-H6a…F11) = 173.4°]. Both tetrafluoroborate counterions are also involved in extensive nonclassical hydrogen bonding to neighboring complex cations throughout the lattice (Figure 3, blue dashed lines; Figures S5 and S6; Tables S3 and S4). The N6 MeCN molecule interacts with a CH₂ group through a nonclassical hydrogen bond [C- $H \cdots N = 3.418(8) \text{ Å}, \angle (C - H \cdots N) = 150.2^{\circ}].$

All four of the structurally characterized **PSRT** complexes, including $[Fe^{II}_2(PSPhT)_2](BF_4)_4 \cdot 2^1/_2MeCN \cdot 1/_2H_2O \cdot THF$ (described in the SI), are stabilized in the [HS-HS] state at 100 K (Table 1). Interestingly, unlike the case for the related

PMRT and PMTD complexes, both of the possible binding modes, cis- and trans-axial (Figure 1), are observed, with two examples of complexes adopting each mode: evidently both modes are possible for at least the PSPhT ligand. Analysis of the octahedral distortion parameter, Σ_{i} of the iron(II) centers in these PSRT complexes reveals no clear relationship to the binding mode (*cis*-axial, $\Sigma = 97.54^{\circ}$ or 105.25°; *trans*-axial, $\Sigma =$ 87.16° or 109.84°). However, the HS iron(II) centers in these **PSRT** complexes are in more regular octahedral environments, with significantly smaller Σ values in all cases (87.16–109.84°), than for the HS iron(II) centers in $[Fe_{2}^{II}(PMAT)_{2}](BF_{4})_{4}$. DMF in either the [HS-HS] ($\Sigma = 117.5^{\circ}$) or [HS-LS] state (Σ = 133.1°) structures (Table 2, red data). Examining this more closely, both the X-Fe-X and X-Fe-N_t (where X = S for **PSRT**, X = NH for **PMAT** and **PMTD**; $N_t = triazole$ or thiadiazole) angles are significantly closer to 90° for PSRT than for HS iron(II) in PMAT (Figure 4) and are in fact more similar to the corresponding angles of the LS iron(II) centers of PMAT and PMTD (Table 2, blue data). However, the N_t-Fe-N_t angles of **PSRT** are further from right angles than in the HS centers of PMAT, but interestingly they are similar to those of LS iron(II) in **PMAT** and **PMTD**. For the remaining *cis* angles, there is no significant difference between the HS iron(II) centers of PSRT and PMAT. The trans X-Fe-Nt angles are closer to 180° in the **PSRT** complexes than for the HS iron(II) in the PMAT complexes and are in fact similar to the LS iron(II) centers in both the PMAT and PMTD complexes. Thus, the PSRT complexes are in a more square planar environment through the sulfur and triazole donor atoms, with the four-coordinate geometry index⁴⁴ (τ_4) for **PSRT** being

Figure 4. Schematic showing the average cis-X-Fe-X and cis-S-Fe-N_t angles in the [HS-HS] structures (left) $[Fe^{II}_2(PSRT)_2](BF_4)_4$. solvents and (right) $[Fe_{2}^{II}(PMAT)_{2}](BF_{4})_{4}$ ·DMF at 298 K. These angles, in the iron(II) complexes of these thioether linked (PSRT) and amino-linked (PMRT) ligands, show the greatest differences. For clarity, one pyridine donor in each of these N₄X₂ octahedral iron(II) coordination spheres is not shown.

closer to a perfect square plane than for the HS PMRT complexes (Figure 4, Table 2).

In summary, as intended, greater flexibility has been achieved in these bis-terdentate ligands by attaching the arms by thioether linkages rather than amino linkages, due to the longer C–X bonds (av C–S = 1.807 Å in **PSRT**, av C–NH = 1.488 Å in [HS-HS] PMAT) and smaller C-X-C angles (Table S6; av C-S-C in PSRT 102.0°, av C-N(H)-C in PMAT and PMTD 112.0-114.5°). This has resulted in less constrained ligand binding in these dinuclear complexes of PSRT, with both possible ligand-binding modes observed and iron(II) centers that are more regularly octahedral in the HS state than was the case for the previously reported amino-linked PMRT ligands.

Magnetic Characterization of $[Fe^{II}_{2}(PSRT)_{2}](BF_{4})_{4}$ Complexes in the Solid State. Initially, variable-temperature magnetic susceptibility measurements were performed on the three air-dried crystal samples, which analyzed as $[Fe^{II}_{2}(PSPhT)_{2}](BF_{4})_{4}\cdot 2^{1}/_{2}H_{2}O$ (solvatomorph C), $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O, \text{ and}$ $[Fe^{I_2}(PS^iBuT)_2](BF_4)_4$ ·MeCN·H₂O. These studies revealed that both $\text{Fe}^{\text{II}}_{2}(\text{PSPhT})_{2}](\text{BF}_{4})_{4}\cdot 2^{1}/_{2}\text{H}_{2}\text{O}$ (solvatomorph C) and $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O$ are SCO active, while $[Fe_{2}^{II}(PS'BuT)_{2}](BF_{4})_{4}$ ·MeCN·H₂O remains in the [HS-HS] state (Figure 5).

At 350 K, the $\chi_m T$ value of $[Fe^{II}_2(PSPhT)_2](BF_4)_4 \cdot 2^1/_2H_2O$ (solvatomorph C) is 6.0 cm³ K mol⁻¹ per dinuclear complex, which is consistent with the [HS-HS] state (Figure 5, red). As it is cooled, a gradual SCO occurs, between about 300 and 150 K, with $\chi_m T$ dropping in two steps from 5.5 cm³ K mol⁻¹ to 2.0 cm³ K mol⁻¹. The latter value corresponds to about two-thirds of the iron(II) centers being in the LS state and the remaining third remaining in the HS state. This gradual transition appears to occur in two steps, with the first derivative of $\chi_{\rm m}T$ with respect to temperature giving $T_{1/2}$ values of approximately 265 and 210 K (Figure S8). A second SCO event is observed between 100 and 70 K, with the value of $\chi_{\rm m}T$ decreasing from 1.7 cm³ K mol⁻¹ to 1.0 cm³ K mol⁻¹ ($T_{1/2} = 87$ K), consistent with almost all of the iron(II) centers having transitioned to the LS state.

 $[Fe_{2}^{II}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O$ appears to be [HS-HS] at room temperature with $\chi_m T = 6.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K (Figure 5, green). Upon cooling, an SCO is observed between 140 and 85 K, with $\chi_m T$ decreasing from 5.9 cm³ K

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Figure 5. $\chi_m T$ per dinuclear complex vs temperature for the samples of air-dried crystals, $[Fe_{2}^{II}(PSPhT)_{2}](BF_{4})_{4}\cdot 2^{1}/_{2}H_{2}O$ (solvatomorph C), $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O, \text{ and } [Fe^{II}_{2}(PS^{i}BuT)_{2}] (BF_4)_4 \cdot MeCN \cdot H_2O.$

 mol^{-1} to 3.9 cm³ K mol⁻¹, with $T_{1/2} = 109$ K, then leveling out at 3.5 cm³ K mol⁻¹ at 40 K, consistent with SCO to the [HS-LS] state.

 $[Fe^{II}_2(PS^iBuT)_2](BF_4)_4$ ·MeCN·H₂O has a $\chi_m T$ value of 6.4 cm³ K mol⁻¹ at 350 K, which only slightly decreases, to 5.3 cm³ K mol⁻¹ at 50 K, consistent with the complex remaining mainly [HS-HS] to low temperatures (Figure 5, blue). This is in good agreement with the crystallographic data for the ·4MeCN solvatomorph of this complex (Figure 2, bottom).

Next, fresh crystals of $[Fe^{II}_2(PSPhT)_2](BF_4)_4 \cdot 2MeCN \cdot H_2O$ (solvatomorph B) and $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 2MeCN$ were studied magnetically to investigate the effects of lattice solvent content on the solid-state magnetic behavior (see the SI). Recording susceptibility vs temperature data, on samples both fresh out of the crystallization mother liquor and after drying in the magnetometer, revealed that loss of MeCN activates SCO for the former complex and further stabilizes the LS state for the latter complex. In contrast, $[Fe_{2}^{II}(PS^{i}BuT)_{2}](BF_{4})_{4}$. 4MeCN remains [HS-HS] regardless of whether studied fresh out of solution or after air drying (see the SI). Unfortunately, due to the highly disordered nature of the MeCN solvent molecules, a detailed structural analysis of the interactions between MeCN and the complex for the two SCOactive complexes could not be performed, and so the effects of solvent on the SCO that we have described above (and in more detail in the SI) cannot be fully explained. However, similar solvent dependence of SCO has been seen for the PMRT complex $[Fe^{II}_{2}(PMPh^{tBu}T)_{2}](BF_{4})_{4}$, which is SCO *inactive* with a solvent content of $\cdot 3CH_3CN \cdot 1/2(C_4H_{10}O)$ but after air drying becomes SCO active (with scan-rate-dependent thermal hysteresis) with a solvent content of $3^{1/2}H_{2}O$.¹⁶

Magnetic Characterization of $[Fe^{II}_{2}(PSRT)_{2}](BF_{4})_{4}$ Complexes in Acetonitrile Solution. In order to avoid the complicating effects of the impact of crystal packing and solvent of crystallization effects on SCO, noted in the previous section, the magnetic behavior of the three iron(II) complexes was also investigated in acetonitrile solution. These solution phase studies facilitate probing the electronic effects of the R substituent in these complexes on the SCO events. Evans' method NMR spectroscopy and UV-vis spectroscopy have been employed, vs

temperature, to probe the spin state vs temperature profile for each of these three complexes dissolved in acetonitrile solution (Figures 6 and 7).

Figure 6. $\chi_m T$ per dinuclear complex cation vs temperature for CD₃CN solutions of $[Fe^{II}_2(PSPhT)_2](BF_4)_4$, $[Fe^{II}_2(PS'^{Me}PhT)_2]-(BF_4)_4$, and $[Fe^{II}_2(PS'BuT)_2](BF_4)_4$, as determined by Evans' method.^{45–48} For modern NMR instruments (with superconducting magnets) there is an amendment to the original Evans' method formula^{49,50} (see Experimental Section for details).

Evans' Method NMR Study. Magnetic susceptibility determinations were carried out using Evans' method.^{45–48} In CD₃CN, all three complexes appear to undergo gradual incomplete SCO in the measured temperature range, 264–313 K (Figure 6, see Experimental Section for details).

Of the three complexes studied in CD₃CN solution (Figure 6), $[Fe^{II}_{2}(PSPhT)_{2}]^{4+}$ maintains the largest $\chi_{m}T$ values across the studied temperatures, 313 to 264 K (dropping from 6.3 to 4.8 cm³ K mol⁻¹), so appears to have the lowest $T_{1/2}$. $[Fe^{II}_{2}(PS^{Me}PhT)_{2}]^{4+}$ undergoes a similar transition, however with lower $\chi_{m}T$ values (5.5 to 4.1 cm³ K mol⁻¹), which are indicative of a greater proportion of LS species being present in solution across all temperatures. Similarly, $[Fe^{II}_{2}(PS^{IB}uT)_{2}]^{4+}$ has a still greater proportion of LS (4.6 to 2.9 cm³ K mol⁻¹), so appears to have the highest $T_{1/2}$.

In summary, the relative tendency of these three complexes in MeCN solution to go LS, is in the *reverse order* of that seen in the solid state. This is consistent with *crystal packing and solvent content effects dominating in the solid state*. In contrast, the solution results are free from the influence of those factors and are instead able to reveal the electronic impact of the choice of **R**: the results are consistent with the more electron donating the **R** substituent at the N^4 position on the triazole (ⁱBu > ^{Me}Ph > Ph), the more the LS state is favored, the octahdedral ligand field increased, and the $T_{1/2}$ raised. Hence it appears that for these complexes *in solution the \sigma-donor strength of the ligand is the largest contributor to the octahedral ligand field strength*.

UV–Vis Spectroscopy (Solid and MeCN Solution). In the solid state $[Fe^{II}_2(PSPhT)_2](BF_4)_4 \cdot \frac{1}{2}CHCl_3 \cdot \frac{21}{2}H_2O$ (solvatomorph A), $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4 \cdot \frac{11}{2}MeCN \cdot 2H_2O$, and $[Fe^{II}_2(PS^{IB}uT)_2](BF_4)_4 \cdot MeCN \cdot H_2O$ are all pale green, but when dissolved in acetonitrile, they give intense dark green solutions (Figures S13–S15, Figure 7).

Considering the UV-vis spectrum of $[Fe^{II}_{2}(PSPhT)_{2}]$ -(BF₄)₄, in MeCN, bands are observed at $\lambda_{max} = 586$ and 930 nm with extinction coefficients (per mole of dinuclear

Figure 7. Variable-temperature UV-vis absorption spectra of MeCN solutions of (top) $[Fe^{II}_2(PSPhT)_2](BF_4)_4$, (middle) $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$, and (bottom) $[Fe^{II}_2(PS^{FB}uT)_2](BF_4)_4$, Note: ε is calculated per mole of dinuclear complex in all cases. For the ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ band, at 574–586 nm, the observed ε value is related to the product of the LS fraction multiplied by ε of the pure [LS-LS] state, and therefore indicates the amount of LS Fe(II) present.

complex) of 34 and 9 L mol⁻¹ cm⁻¹, respectively, at 293 K (Figure 7, top). By comparison to typical iron(II) octahedral complexes, ^{51–55} including those with an N₄S₂ coordination sphere, ^{28–30} the band at 586 nm can be attributed to the Laporte-forbidden, spin-allowed d–d transition ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ of the LS state, and the weak, broad band at 930 nm to the spin-allowed d–d transition state.

Temperature dependence of the band at 586 nm indicates that a partial spin crossover occurs in solution over this temperature range (Figure 7, top), as the extinction coefficient per mole of dinuclear complex steadily increases with decreasing temperature, from 34 L mol⁻¹ cm⁻¹ at 293 K to 68 L mol⁻¹ cm⁻¹ at 233 K, which is consistent with an increased proportion of LS iron centers. At 930 nm there is no significant change in extinction coefficient with temperature, with $\varepsilon = 9$ L mol⁻¹ cm⁻¹ at all measured temperatures: however, this absorption band of the HS state is very weak and noisy, even at the solubility limit of the complex in MeCN; thus no spin-state monitoring can be achieved in this region of the spectrum. The LS band seen in MeCN solution is also evident in the solidstate spectrum ($\lambda_{max} = 572$ nm) at room temperature (Figures S13, S14).

Partial SCO also occurs for both of the other complexes in MeCN as the temperature is lowered (Figure 7). For $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$ the extinction coefficient of the 574 nm ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ band of the iron(II) centers present in the LS state increases from 53 to 92 L mol⁻¹ cm⁻¹ (per mole of complex) on cooling from 293 to 233 K (Figure 7, middle). The position of this band is almost identical to that of $[Fe^{II}_2(PSPhT)_2](BF_4)_4$, however with greater extinction coefficients at each temperature, consistent with a greater proportion of LS iron(II) centers. The very weak and broad band centered at ca. 900 nm remains at 14 L mol⁻¹ cm⁻¹ across all studied temperatures.

For $[Fe^{II}_2(\mathbf{PS}^{iB}\mathbf{uT})_2](BF_4)_4$, the LS band is centered at 580 nm (Figure 7, bottom). The extinction coefficients (per mole of complex) are greater than for the other two complexes and again increase with decreasing temperature (61 L mol⁻¹ cm⁻¹ at 288 K to 139 L mol⁻¹ cm⁻¹ at 233 K). In this spectrum the HS ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ band centered at 920 nm was more resolved, and a slight decrease in extinction coefficient from 7 L mol⁻¹ cm⁻¹ to 5 L mol⁻¹ cm⁻¹ is observed with decreasing temperature.

Four of the temperature points at which UV–vis spectra were collected also have corresponding Evans' method data. The $\chi_m T$ values, and associated HS fraction, γ_{HS} , obtained from the Evans' method data allow us to "calibrate" the observed ε values (assigning them γ_{HS} values) at these temperatures for each of the three complexes in MeCN solution. From this we can go on to estimate the γ_{HS} for each complex at the lower temperatures studied only by UV–vis spectroscopy (see the SI for details, Table S9, Figures S16 and S17). Overall this analysis indicates that on cooling these MeCN solutions from 313 K to 233 K, $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ undergoes SCO from $\gamma_{HS} \approx 0.9$ to $\gamma_{HS} \approx 0.6$, $[Fe^{II}_2(PS^{IB}ehT)_2](BF_4)_4$ from $\gamma_{HS} \approx 0.7$ to $\gamma_{HS} \approx 0.2$. Fitting of the UV–vis 54,56 and Evans' NMR^{46,47,57,58} data to

Fitting of the OV = Vis and EVans (Wirk data to the thermodynamic parameters of the spin equilibrium (see the SI for details, Tables S10–S12, Figures S18–S20) indicates that in MeCN solution both $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ and $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$ probably undergo a half SCO, $[HS-HS] \leftrightarrow [HS-LS]$, whereas $[Fe^{II}_2(PS'BuT)_2](BF_4)_4$ appears to undergo a full SCO, $[HS-HS] \leftrightarrow [LS-LS]$. This is consistent with the estimated high spin fractions, γ_{HS} , noted in the previous paragraph. Determining $T_{1/2}$ values from these thermodynamic parameters reveals that the SCO for each complex in MeCN solution is centered at or near room temperature (see the SI). From these tentative fits, it also appears that the actual ε values per mole of dinuclear complex, for the LS ${}^{1}A_{1g}$ $\rightarrow {}^{1}T_{1g} d-d$ band seen at 574–586 nm, are about 200 and 100 L mol⁻¹ cm⁻¹ for the [LS-LS] and [LS-HS] states, respectively.

CONCLUSIONS

An unusual N_4S_2 coordination environment has been successfully introduced to the iron(II) centers of a family of dinuclear **PMRT**-like complexes by incorporation of thioether donors into the "arms", giving rise to the new family of **PSRT** ligands. Not only has SCO activity been retained (from the **PMRT** systems), but for the first time in complexes of this kind, all three of the possible spin states—[HS-HS], [HS-LS], and [LS-LS]—are accessible for the new **PSRT** systems.

In contrast, in previous studies of dinuclear iron(II) complexes of **PMAT/PMRT** it has not been possible to access the [LS-LS] state due to the highly constrained nature of the these amino-linked ligands: on SCO from [HS-HS] to [HS-LS] in $[Fe^{II}_2(PMAT)_2](BF_4)_4$ ·DMF, the iron(II) center, which remains HS, becomes more distorted (HS in [HS-HS] at 293 K has $\Sigma = 117.5^{\circ}$; HS in [HS-LS] at 123 K has $\Sigma = 133.1^{\circ}$), which inhibits this center from also transitioning to the LS state. The **PSRT** complexes are less constrained due to the incorporation of a more flexible thioether group, which gives a more regular octahedral environment at the iron(II) centers in the HS state, facilitating complete SCO to the [LS-LS] state.

Previously, dinuclear iron(II) systems based on the PMAT ligand have been observed to bind in either the *cis*-axial (PMAT and PMRT) or *trans*-axial (PMTD) binding modes. Here, the more flexible nature of the PSRT ligands has given access to both the *cis*- and *trans*-axial binding modes. Interestingly for the PSRT systems that were studied magnetically, only the *trans*axial binding mode complexes exhibited SCO in the solid state. However, the sample size is too small to be able to draw firm conclusions on this point.

Subtle variation of the **R** substituent at the N^4 triazole position of the **PSRT** ligands results in a dramatic change in the magnetic properties of the dinuclear iron(II) complexes in the solid state. Although the site of variation is relatively remote from the iron(II) coordination environment, and the aromatic **R** groups are far from coplanar with the triazole ring, the variation of **R** was still expected to influence the magneto-chemistry based on our previous **PMRT** studies. As for those **PMRT** studies, the effects of *crystal packing and solvato-morphism on the solid state SCO* are again seen to be *dominant* in these new **PSRT** systems.

In contrast to the solid-state magnetic behavior, the UV-vis and Evans' method data obtained on the three complexes in MeCN solution show that all three undergo partial, gradual, SCO events in the measurable temperature range (313-233 K), with $T_{1/2}$ values close to room temperature. In solution, the effects of crystal packing and lattice solvent are eliminated, and instead the electronic effects of varying the R are able to be probed. As the magnetic behavior observed in solution is very different from that seen in the solid state, these studies confirm that in the solid state the impact of changing R is indeed dominated by associated changes in the crystal packing and solvent content. Indeed these effects are so dominant in the solid state that the complexes actually have the reverse tendency to go LS, to the order seen in solution. More importantly, these solution studies also show that the more electron donating the **R** substituent at the N^4 position on the triazole (^{*i*}Bu > ^{Me}Ph > Ph), the more the LS state is favored; so for these complexes in solution the σ -donor strength of the ligand is the largest contributor to the octahedral ligand field strength.

Finally, we note that these are the first dinuclear iron(II) complexes featuring N_4S_2 coordination to show SCO and that

all three possible spin states can be accessed; so this new ligand class shows great promise for further elaboration. Such studies are currently under way.

EXPERIMENTAL SECTION

General Instrument Details. NMR spectra were recorded on a Varian 400-MR spectrometer at 400 MHz (¹H) or 100 MHz (¹³C) or on a Varian 500 MHz VNMRS spectrometer at 500 MHz (¹H) or 125 MHz (¹³C). Mass spectra were recorded on a Bruker MicrOTOF-Q spectrometer. TGA was recorded on a TA Instruments Q50 with the samples in a platinum pan heated at 2 °C min⁻¹. Nitrogen gas flow was set to 40 mL min⁻¹ over the balance and 60 mL min⁻¹ over the sample. Microanalysis was performed by the Campbell Microanalytical Laboratory at the University of Otago.

Solid-state visible reflectance data were recorded on a PerkinElmer Lambda 950 UV–vis/NIR spectrometer in the range 200–1500 nm. Samples were attached to a solid support of Labsphere reflectance standard using double-sided tape (Sellotape double-sided).

Solution UV–vis spectra were recorded on a PerkinElmer Lambda 950 UV–vis/NIR equipped with a JANIS Research model VNF-100 cryostat and Lake Shore Cryotronics model 335 temperature controller. Solutions were all in HPLC grade MeCN of concentrations (at room temperature) as follows: $[Fe^{II}_2(PSPhT)_2](BF_4)_4$, 32.66 mmol L^{-1} ; $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$, 3.913 mmol L^{-1} ; $[Fe^{II}_2(PS^iBuT)_2](BF_4)_4$, 6.238 mmol L^{-1} . Temperatures are accurate to ±0.5 K. The data were corrected for concentration changes arising from the temperature dependence of the density of acetonitrile.

X-ray crystallographic data were collected on an Oxford Diffraction SuperNova diffractometer with an Atlas CCD, equipped with a Cryostream N₂ open-flow cooling device, using mirror monochromated microfocus Mo or Cu K α radiation at 100 K. Scans were performed in such a way as to collect a complete set of unique reflections to a maximum resolution of 0.80 Å. Raw frame data (including data reduction, interframe scaling, unit cell refinement, and absorption corrections) for all structures were processed using CrysAlis Pro.⁵⁹ Structures were solved using SUPERFLIP⁶⁰ and refined against all F^2 data using SHELXL-2014.⁶¹ Hydrogen atoms were inserted at calculated positions with U(H) = 1.2U(attachedatom) and rode on the atoms to which they were attached. SQUEEZE³⁷ was used for $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$ ·2MeCN·H₂O (solvatomorph B) and $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$ ·2MeCN, as the counteranions and solvent molecules were badly disordered (details below). High-resolution pictures were prepared using Mercury⁶² and POVray⁶³ software. CCDC 1439744–1439747.

 $[\text{Fell}'_2(\text{PSPhT})_2](\text{BF}_4)_4\cdot 2\text{MeCN}\cdot\text{H}_2\text{O}$ (Solvatomorph B). Colorless block-shaped crystal. Data were collected using Mo K α radiation. Disorder of the counteranions and solvent molecules could not be modeled well (large Q peaks could not be sensibly assigned), so all of them were removed and SQUEEZE³⁷ was applied. This greatly improved the difference map and (not surprisingly) lowered the R_1 (on $[I > 2\sigma(I)]$ data) from 0.053 (for the best model achieved; one MeCN molecule disordered over two sites of half-occupancy each and a half water molecule disordered over two sites of quarter-occupancy each per asymmetric unit, so 2 MeCN and 1 H₂O per complex) to 0.047. The missing electron density found by SQUEEZE was 837 electrons/cell, i.e., 209 electrons per complex (Z = 4), which agrees very well with the four BF₄⁻ anions and the proposed solvent content of two acetonitrile and one water molecule per complex determined by microanalysis (210 electrons/complex).

 $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$:2MeCN. Pale green block-shaped crystal. Data were collected using Mo K α radiation. Disorder of the counteranions and solvent molecules could not be modeled well (large Q peaks could not be sensibly assigned), so all of them were removed and SQUEEZE³⁷ was applied. This greatly improved the difference map and (not surprisingly) lowered the R_1 (on $[I > 2\sigma(I)]$ data) from 0.080 (for the best model achieved; three one-quarter occupancy MeCN molecules per asymmetric unit, so $1^{1}/_2$ MeCN per complex) to 0.077. The missing electron density found by SQUEEZE was 816 electrons/cell, i.e., 204 electrons per complex (Z = 4), which agrees very well with the four BF_4^- anions and the proposed solvent content of two acetonitrile molecules per complex determined by microanalysis (200 electrons/complex).

 $[Fe^{II}_2(PS^{i}BuT)_2](BF_4)_4$ -4MeCN. Colorless block-shaped crystal. Data were collected using Cu K α radiation. All non-H atoms were assigned anisotropic thermal displacement parameters, with the exception of the C_2 -rotationally disordered BF₄⁻ anion: the shared boron atom and fluorine atom were refined anisotropically, and the three rotationally disordered fluorine atoms, over two sites of occupancy 60:40, were refined isotropically.

Magnetic data for $[FeII_2(PSPhT)_2](BF_4)_4 \cdot 2^{1/2}H_2O$ (solvatomorph C) were collected on a Quantum Design SQUID magnetometer under an applied field of 0.1 T at Callaghan Innovation, Lower Hutt, NZ. The data were collected between 350 and 4 K in settle mode at 5 K intervals.

Magnetic data for $[Fe_2^{II}(PS^{Me}PhT)_2](BF_4)_4\cdot 1^1/_2MeCN\cdot 2H_2O$ were recorded using a Quantum Design PPMS susceptometer equipped with a vibrating sample mount, under an applied field of 0.1 T at Callaghan Innovation, between 300 and 4 K, in sweep mode with a scan rate of 5 K min⁻¹.

Magnetic data for $[Fe^{II}_2(PS^iBuT)_2](BF_4)_4$ ·MeCN·H₂O were collected in-house on a Quantum Design Versalab, a cryogen-free PPMS susceptometer, equipped with a vibrating sample mount under an applied field of 0.1 T. Data were collected in the temperature range 350–50 K in sweep mode with a scan rate of 5 K min⁻¹.

Samples were mounted for the PPMS and Versalab in a polyethylene capsule, and for the SQUID in a gelatin capsule. Data were corrected for the diamagnetism of the sample according to the approximation that $\chi_{\rm M}^{\rm dia}({\rm sample}) = -0.5M \times 10^{-6} \, {\rm cm}^3 \, {\rm mol}^{-1}$ (where M = molecular weight of complex),⁶⁴ and a background correction for the sample holder was also applied.

Solution magnetic susceptibility data were measured in the temperature range 264–313 K in CD₃CN by ¹H NMR spectroscopy on a Varian 500 MHz VNMRS spectrometer using Evans' method.⁴⁸ Samples were prepared by dissolving a precisely known mass in 0.700 mL of CD₃CN. Pure CD₃CN was placed in a special capillary NMR tube insert, and the paramagnetic solution was placed in the outer tube. Temperatures are accurate to ± 1 K. The shift of the CD₃CN peak in the paramagnetic solution compared to pure CD₃CN, Δf in Hz, can be used to calculate the mass susceptibility of the complexes by eq 1.

$$\chi_{\rm g} = \frac{3\Delta f}{4\pi m f} + \chi_0 + \chi_0 \frac{d_0 - d_{\rm s}}{m}$$
(1)

where *m* is the concentration of the paramagnetic solution in g cm⁻³ and this was corrected for the temperature dependence of the density of acetonitrile, *f* is the spectrometer frequency in Hz, and d_0 and d_s are the densities of the solvent and solution, respectively. χ_0 is the mass susceptibility of the solvent in cm³ g⁻¹. However, eq 1 can be simplified by taking an approximation that $d_s = d_0 + m$. This is reasonable because the solutions used were dilute^{49,54} (2.5–5.3 mmol L⁻¹). This approximation leads to the second and third terms in eq 1 canceling out, giving eq 2, which was used in the present analysis.

$$\chi_{\rm g} = \frac{3\Delta f}{4\pi m f} \tag{2}$$

Note that the original Evans' method was developed using early generations of NMR spectometers in which the sample axis was perpendicular to the magnetic field, whereas in modern superconducting NMR spectrometers the sample axis is parallel to the magnetic field. Hence there is a factor of $3/4\pi$ in eqs 1 and 2, rather than the original factor of $-3\pi/2$.^{49,50}

Multiplying χ_g by the molecular weight (*M*) gave the molar susceptibility χ_M . These χ_M values were then corrected for the diamagnetic contributions of each sample according to $\chi_M^{\text{dia}}(\text{sample}) = -0.5M \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1.64}$

General Experimental Details. Ethanol was dried by distillation over magnesium turnings and iodine. LiTCNQ was synthesized

Table 3. Crystal Data and Structure Refinement Details for the Complexes $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ ·2MeCN·H₂O (Solvatomorph B), $[Fe^{II}_2(PSPhT)_2](BF_4)_4$ ·2I/₂MeCN·I/₂H₂O·THF (Solvatomorph D), $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$ ·2MeCN, and $[Fe^{II}_2(PS^{IB}uT)_2](BF_4)_4$ ·4MeCN

	$[\text{Fe}^{\text{II}}_{2}(\text{PSPhT})_{2}](\text{BF}_{4})_{4} \cdot \\ 2\text{MeCN} \cdot \text{H}_{2}\text{O}$	$[\mathrm{Fe^{II}}_{2}(\mathrm{PSPhT})_{2}](\mathrm{BF_{4}})_{4} \cdot 2^{1} / _{2}\mathrm{MeCN} \cdot ^{1} / _{2}\mathrm{H_{2}O} \cdot \mathrm{THF}$	$[\mathrm{Fe}^{\mathrm{II}}_{2}(\mathbf{PS}^{\mathrm{Me}}\mathbf{PhT})_{2}](\mathrm{BF}_{4})_{4}\cdot\\2\mathrm{Me}\mathrm{CN}$	$[Fe^{II}_{2}(\mathbf{PS^{i}BuT})_{2}](BF_{4})_{4}\cdot 4MeCN$
empirical formula	$C_{44}H_{42}Fe_2N_{10}S_4$	$C_{53}H_{58.50}B_4F_{16}Fe_2N_{12.50}O_{1.50}\ S_4$	$C_{46}H_{46}Fe_2N_{10}S_4$	$C_{48}H_{62}B_4F_{16}Fe_2N_{14}S_4\\$
$M_{ m r}$	950.81	1481.80	978.87	1422.29
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	C2/c	$P\overline{1}$	C2/c	$P2_1/c$
a [Å]	15.8987(2)	9.9850(2)	16.0419(6)	10.6772(16)
<i>b</i> [Å]	27.4992(4)	11.9087(3)	27.6191(11)	24.8009(12)
c [Å]	14.3082(2)	15.1801(4)	14.6634(6)	16.296(2)
$\alpha [deg]$	90	104.568(2)	90	90
$\beta [deg]$	108.9212(18)	97.7804(19)	110.472(4)	134.03(3)
γ [deg]	90	108.767(2)	90	90
V [Å]	5917.52(15)	1607.40(7)	6086.5(4)	3102.6(12)
Ζ	4	1	4	2
T [K]	100(2)	100(2)	100(2)	100(2)
$\rho_{\rm calcd} [{\rm g/cm^3}]$	1.067	1.531	1.068	1.522
$\mu \; [\mathrm{mm}^{-1}]$	0.665	5.688	0.648	5.853
F(000)	1968	756	2032	1456
cryst size (mm)	$0.270 \times 0.170 \times 0.090$	$0.270 \times 0.076 \times 0.070$	$0.400 \times 0.200 \times 0.200$	$0.160 \times 0.130 \times 0.110$
heta range for data collection	2.963 to 29.670	3.095 to 76.311	3.215 to 29.593	4.173 to 62.619
reflns collected	78 405	23 901	20 288	18 322
indep reflns	7974	6655	7460	4897
R(int)	0.0386	0.1213	0.0376	0.1256
max. and min. transmn	1.0 and 0.797 44	1.000 00 and 0.577 12	1.00 and 0.69	1.000 and 0.363 27
data/restraints/params	7974/0/274	6655/55/449	7460/0/284	4897/0/398
Goof (F^2)	1.048	1.058	1.035	1.001
$R_1 \left[I > 2\sigma(I) \right]$	0.0467	0.1068	0.0765	0.0731
wR ₂ [all data]	0.1331	0.2750	0.2004	0.1979
max./min. res. e density [e∙ Å ^{−3}]	1.302 and -0.555	2.365 and -1.923	1.364 and -1.528	0.974 and -0.648

following the reported procedure.⁶⁵ All other chemicals were purchased from commercial suppliers and were used as received.

Stepwise Synthesis of the Ligands. N,N-Dimethylformamide azine was prepared according to the literature method.⁶⁶ N^4 -Substituted-1,2,4-triazoles 1R, N^4 -substituted-3,5-bis(hydroxymethyl)-1,2,4-triazoles 2R, and N^4 -substituted-3,5-bis(chloromethyl)-1,2,4-triazole hydrochlorides 3R were prepared according to the reported general procedure,¹⁵ with the exception of $1^{Me}Ph$, $2^{Me}Ph$, and $3^{Me}Ph$, which are detailed below.

N⁴-p-Tolyl-1,2,4-triazole (1^{Me}Ph). N,N-Dimethylformamide azine dihydrochloride (4.00 g, 18.6 mmol) and p-toluidine (1.33 g, 12.4 mmol) were refluxed in pyridine (50 mL) for 48 h. After cooling to room temperature the pyridine was removed in vacuo, and trace amounts were azeotroped with toluene (50 mL) then methanol (50 mL). The resulting yellow-brown oil was taken up in CH₂Cl₂ (50 mL), washed with water $(2 \times 50 \text{ mL})$, saturated aqueous NaHCO₃ (50 mL), and then brine (50 mL), followed by drying with MgSO4 and taking to dryness in vacuo to give a beige powder. Recrystallization in hot toluene afforded N⁴-p-tolyl-1,2,4-triazole as a brown crystalline solid (1.36 g, 69%). Anal. Calcd for C₉H₉N₃: C 67.91, H 5.70, N 26.40. Found: C 68.12, H 5.69, N 26.50. δH (400 MHz, CDCl₃): 8.52 (s, 2H, trH), 7.33-7.35 (m, 2H, phH3/5), 7.26-7.29 (m, 2H, phH2/ 6), 2.44 (s, 3H, CH₃). δC (100 MHz, CDCl₃): 141.5 (tr), 139.4 (PhC4), 131.3 (PhC1), 130.8 (PhC3/5), 122.2 (PhC2/6), 21.1 (CH_3)

 N^{4} -p-Tolyl-3,5-bis(hydroxymethyl)-1,2,4-triazole ($2^{Me}Ph$). N^{4} -p-Tolyl-1,2,4-triazole (0.956 g, 6.01 mmol) was dissolved in xylenes (50 mL) with heating to 110 °C. The reaction vessel was placed under an argon atmosphere, and paraformaldehyde (1.80 g, 60.0 mmol) was quickly added by briefly removing the condenser, while argon was flowed into the reaction vessel. The resulting suspension was heated at 125 °C for 2.5 h before a second portion of paraformaldehyde (1.80 g,

60.0 mmol) was added. After a further 6 h of heating the product had precipitated and excess paraformaldehyde had sublimed up the condenser. Hot filtration of the reaction mixture yielded a white solid contaminated with paraformaldehyde. This mixture was taken up in boiling ethanol (100 mL), and solid paraformaldehyde removed by hot filtration. The filtrate was left to cool to room temperature, and white crystalline N^4 -*p*-tolyl-3,5-bis(hydroxymethyl)-1,2,4-triazole was isolated by filtration (1.09 g, 83%). Anal. Calcd for C₁₁H₁₃N₃O₂: C 60.26, H 5.98, N 19.17. Found: C 60.26, H 5.99, N 19.17. δ H (400 MHz, *d*₆-DMSO): 7.32–7.36 (m, 4H, PhH2/6 and PhH3/5), 5.35 (t, 2H, *J* = 5.4 Hz, OH), 4.36 (d, 4H, *J* = 5.3 Hz, CH₂), 2.37 (s, 3H, CH₃). δ C (125 MHz, *d*₆-DMSO): 154.9 (tr), 139.2 (PhC4), 131.6 (PhC1), 130.2 (PhC3/5), 127.3 (PhC2/6), 53.6 (CH₂), 21.2 (CH₃).

 N^4 -*p*-Tolyl-3,5-bis(chloromethyl)-1,2,4-triazole·1/₂HCl (3^{Me}Ph). N⁴-*p*-Tolyl-3,5-bis(hydroxymethyl)-1,2,4-triazole, 2^{Me}Ph (1.059 g, 4.83 mmol), was dissolved in 10 mL of SOCl₂ and stirred for 2 h. The reaction mixture was dried first by evaporating SOCl₂ under a stream of compressed air, then *in vacuo*. Recrystallization from hot ethanol afforded N⁴-*p*-tolyl-3,5-bis(chloromethyl)-1,2,4-triazole hydrochloride as a beige powder (1.050 g, 79%). Anal. Calcd for C₁₁H_{11.5}N₃Cl_{2.5}: C 48.16, H 4.22, N 15.32. Found: C 48.51, H 4.19, N 15.41. δH (400 MHz, CDCl₃): 7.37–7.43 (m, 4H, PhH2/6 and PhH3/5), 4.61 (s, 4H, CH₂), 2.50 (s, 3H, CH₃). δC (125 MHz, CDCl₃): 152.5 (tr), 141.8 (PhC4), 130.9 (PhC3/5), 128.7 (PhC1), 127.1 (PhC2/6), 32.7 (CH₂), 21.4 (CH₃).

Thioacetic Acid S-Pyridin-2-ylmethyl Ester (4). Compound 4 was prepared using an adapted method from the literature.³⁴ A suspension of potassium thioacetate (2.30 g, 20.1 mmol), K_2CO_3 (5.06 g, 36.6 mmol), and 2-picolyl chloride hydrochloride (3.00 g, 18.3 mmol) in dry DMF (40 mL) was stirred overnight under argon in the dark. The white precipitate was filtered and washed with CH₂Cl₂ (50 mL), and the filtrate was taken to dryness. The dried filtrate was azeotroped with

toluene (2 × 40 mL) to remove residual DMF. The resulting brown oil was taken up in CH_2Cl_2 (40 mL) and washed with water (2 × 40 mL) and brine (40 mL). Drying with MgSO₄ before removing the solvent *in vacuo* gave 4 as a brown oil (2.72 g, 89%). δ H (400 MHz, CDCl₃): 8.54 (d, 1H, *J* = 5.0 Hz, pyH6), 7.64 (td, 1H, *J* = 7.7, 1.8 Hz, pyH4), 7.35 (d, 1H, *J* = 7.9 Hz, pyH3), 7.17 (ddd, 1H, *J* = 7.5, 4.9, 1.1 Hz, pyH5), 4.26 (s, 2H, CH₂), 2.36 (s, 3H, CH₃). δ C (125 MHz, CDCl₃): 195.0 (C=O), 157.3 (pyC2), 149.5 (pyC6), 136.8 (pyC4), 123.3 (pyC3), 122.2 (pyC5), 35.4 (CH₂), 30.3 (CH₃). ESI-MS (+): $m/z = 168.0453 [4 + H]^+$ (calcd = 168.0478), 190.0282 [4 + Na]⁺ (calcd = 190.0297).

General Procedure for the Preparation of Thioether Ligands. Sodium (6–8.5 equiv) was dissolved in dry ethanol at 0 °C, and a solution of 4 (2 equiv) in dry ethanol was added and stirred at 0 °C under N₂ for 30 min. N⁴-Substituted-3,5-bis(chloromethyl-1,2,4-triazole hydrochloride (1 equiv) was added and stirred at room temperature for 1 h, refluxed for 5 h, then stirred at room temperature overnight, all under N₂. Water was added and the ethanol removed *in vacuo*. The resulting suspension was extracted with CH₂Cl₂ then washed with water, then brine, followed by drying with MgSO₄ before taken to dryness *in vacuo*. Any deviation from this procedure is detailed below.

PSPhT. Sodium (0.40 g, 17 mmol), 4 (0.954 g, 5.74 mmol), and **3Ph** (0.799 g, 2.87 mmol) were reacted in 50 mL of dry ethanol, then worked up according to the general procedure. Recrystallization of the brown oily solid in boiling toluene gave **PSPhT** as a beige powder (0.979 g, 81%). Anal. Calcd for $C_{22}H_{21}N_5S_2$: C 62.98, H 5.05, N 16.69, S 15.28. Found: C 63.25, H 5.16, N 16.61, S 15.21. δ H (500 MHz, CDCl₃): 8.55 (d, 2H, *J* = 4.9 Hz, pyH6), 7.67 (td, 2H, *J* = 7.7, 1.8 Hz, pyH4), 7.50–7.53 (m, 3H, phH3/5 and phH4), 7.49 (d, 2H, *J* = 7.9 Hz, pyH3), 7.34–7.36 (m, 2H, phH2/6), 7.19 (ddd, 2H, *J* = 7.7, 4.9, 1.2 Hz, pyH5), 3.93 (s, 4H, py-CH₂-S), 3.59 (s, 4H, tr-CH₂-S). δ C (125 MHz, CDCl₃): 157.3 (pyC2), 152.6 (tr), 149.3 (pyC6), 137.0 (pyC4), 132.9 (phC1), 130.2 (phC4), 129.9 (phC3/5), 127.7 (phC2/6), 123.9 (pyC3), 122.2 (pyC5), 37.1 (py-CH₂-S), 24.1 (tr-CH₂-S). ESI-MS (+): *m/z* = 442.1104 [(**PSPhT**) + Na]⁺ (calcd = 442.1131).

PS'BuT. Sodium (0.30 g, 13 mmol), 4 (0.675 g, 4.06 mmol), and **3'Bu** (0.525 g, 2.03 mmol) were reacted in 40 mL of dry ethanol, then worked up according to the general procedure to yield **PS'BuT** as a brown oil, which was used for complexation without further purification (0.649 g, 80%). δH (500 MHz, CDCl₃): 8.58 (d, 2H, *J* = 4.9 Hz, pyH6), 7.65 (td, 2H, *J* = 7.6, 1.8 Hz, pyH4), 7.42 (d, 2H, *J* = 7.8 Hz, pyH3), 7.17 (ddd, 2H, *J* = 7.6, 4.9, 1.1 Hz, pyH5), 3.84 (s, 4H, py-CH₂-S), 3.82 (s, 2H, 'BuCH₂) 3.80 (s, 4H, tr-CH₂-S), 2.05 (septet, 1H, *J* = 7.0 Hz, 'BuCH), 0.87 (d, 6H, *J* = 6.6 Hz, 'Bu(CH₃)₂). δC (125 MHz, CDCl₃): 157.2 (pyC2), 152.2 (tr), 148.9 (pyC6), 137.6 (pyC4), 124.1 (pyC3), 122.4 (pyC5), 51.0 ('BuCH₂) 36.7 (py-CH₂-S), 29.1 ('BuCH), 24.8 (tr-CH₂-S), 19.9 ('Bu(CH₃)₂). ESI-MS (+): *m*/*z* = 400.1617 [(**PS'BuT**) + H]⁺ (calcd = 400.1624).

PS^{t-Bu}PhT. Sodium (0.37 g, 16 mmol), 4 (0.892 g, 5.37 mmol), and $3^{t-Bu}Ph$ (0.898 g, 2.68 mmol) were reacted in 50 mL of dry ethanol, then worked up according to the general procedure. Column chromatography using silica gel and eluting with CH2Cl2 followed by 5% then 10% MeOH in CH2Cl2 and recrystallization of the resulting brown oily solid in boiling toluene gave PS^{t-Bu}PhT as a beige microcrystalline solid (0.171 g, 13%). Anal. Calcd for C₂₆H₂₉N₅S₂: C 65.65, H 6.15, N 14.72, S 13.48. Found: C 65.78, H 6.34, N 14.71, S 13.25. δ H (500 MHz, CDCl₃): 8.55 (d, 2H, J = 4.9 Hz, pyH6), 7.64 (td, 2H, J = 7.6, 1.8 Hz, pyH4), 7.47–7.51 (m, 2H, phH3/5), 7.46 (d, 2H, J = 7.7 Hz, pyH3), 7.24-7.27 (m, 2H, phH2/6), 7.15 (ddd, 2H, J = 7.5, 4.9, 1.2 Hz, pyH5), 3.93 (s, 4H, py-CH₂-S), 3.57 (s, 4H, tr-CH₂-S), 1.36 (s, 9H, t-Bu(CH₃)₃). δC (125 MHz, CDCl₃): 157.2 (pyC2), 153.5 (phC4), 152.8 (tr), 148.9 (pyC6), 137.4 (pyC4), 130.0 (phC1), 127.2 (phC2/6), 126.9 (pyC3), 124.1 (phC3/5), 122.3 (pyC5), 36.8 (py-CH₂-S), 34.9 (t-BuC), 31.2 (t-Bu(CH₃)₃), 24.1 (tr-CH₂-S). ESI-MS (+): $m/z = 476.1901 [(\mathbf{PS}^{t-\mathbf{Bu}}\mathbf{PhT}) + \mathbf{H}]^+$ (calcd = 476.1937).

 $PS^{Me}PhT$. Sodium (0.19 g, 8.3 mmol), 4 (0.279 g, 1.68 mmol), and $3^{Me}Ph$ (0.238 g, 0.813 mmol) were reacted in 30 mL of dry ethanol, then worked up according to the general procedure. Recrystallization of the brown oily solid in boiling toluene gave $PS^{Me}PhT$ as a beige

powder (0.122 g, 35%). Anal. Calcd for $C_{23}H_{23}N_5S_2$: C 63.71, H 5.35, N 16.15, S 14.79. Found: C, 63.82, H 5.41, N 16.15, S 14.79. δ H (500 MHz, CDCl₃): 8.56 (d, 2H, *J* = 5.1 Hz, pyH6), 7.66 (td, 2H, *J* = 7.6, 1.9 Hz, pyH4), 7.48 (d, 2H, *J* = 7.8 Hz, pyH3), 7.28–7.31 (m, 2H, phH3/5), 7.20–7.23 (m, 2H, phH2/6), 7.17 (ddd, 2H, *J* = 7.6, 4.9, 1.1 Hz, pyH5), 3.92 (s, 4H, py-CH₂-S), 3.58 (s, 4H, tr-CH₂-S), 2.44 (s, 3H, CH₃). δ C (125 MHz, CDCl₃): 157.5 (pyC2), 152.7 (tr), 149.6 (pyC6), 140.4 (phC4), 136.7 (pyC4), 130.5 (phC3/5), 130.2 (phC1), 127.4 (phC2/6), 123.8 (pyC3), 122.1 (pyC5), 37.3 (py-CH₂-S), 24.1 (tr-CH₂-S), 21.3 (CH₃). ESI-MS (+): *m*/*z* = 434.1439 [(**PS^{Me}PhT**) + H]⁺ (calcd = 434.1468).

Synthesis of the Iron(II) Complexes. $[Fe^{II}_{2}(PSPhT)_{2}](BF_{4})_{4}$. To a clear yellow solution of PSPhT (122 mg, 0.291 mmol) in 20 mL of CHCl₃ was added a solution of $Fe(H_2O)_6(BF_4)_2$ (98 mg, 0.29 mmol) in 10 mL of MeOH. This was stirred under argon at room temperature for 2 h, during which time the clear yellow solution turned cloudy white. The pale green precipitate was collected by filtration under a nitrogen stream to yield solvatomorph A, $[Fe^{II}_2(PSPhT)_2]$ - $(BF_4)_4 \cdot \frac{1}{2}CHCl_3 \cdot \frac{2^1}{2}H_2O$ (99 mg, 0.076 mmol, 52%), and the solid was promptly stored under argon. Anal. Calcd for [Fe^{II}₂(PSPhT)₂]-(BF₄)₄·¹/₂CHCl₃·2¹/₂H₂O: C 38.10, H 3.41, N 9.99, S 9.14. Found: C 38.17, H 3.32, N 9.72, S 9.11. TGA: calcd 7.5%, found 7.6%. ESI-MS (+): $m/z = 1211.1295 \{ [Fe^{II}_2(PSPhT)_2] (BF_4)_3 \}^+$ (calcd = 1211.1280). A solution of $[Fe_{2}^{II}(PSPhT)_{2}](BF_{4})_{4} \cdot \frac{1}{2}CHCl_{3} \cdot \frac{2^{1}}{2}H_{2}O$ (59 mg, 0.042 mmol) in 3 mL of MeCN was exposed to THF vapor. After 1 week, colorless block-shaped crystals of solvatomorph B, $[Fe^{II}_{2}(PSPhT)_{2}](BF_{4})_{4} \cdot 2MeCN \cdot H_{2}O$ (25 mg, 43%), had formed. One such experiment gave single colorless block crystals suitable for X-ray crystallography. Anal. Calcd for $[Fe_{2}^{II}(PSPhT)_{2}](BF_{4})_{4}\cdot 2MeCN\cdot H_{2}O:$ C 41.23, H 3.60, N 12.02, S 9.17. Found: C 41.29, H 3.54, N 11.95, S 9.03. Upon air drying $[Fe_{2}^{II}(PSPhT)_{2}](BF_{4})_{4}\cdot 2MeCN\cdot H_{2}O_{2}$, the crystals crumbled and the solvent content changed to give solvatomorph C, $[Fe^{II}_2(PSPhT)_2](BF_4)_4 \cdot 2^1/_2H_2O_1$ as a pale green powder. Anal. Calcd for $[Fe_2^{II}(PSPhT)_2](BF_4)_4 \cdot 2^1/_2H_2O: C 39.35, H$ 3.53, N 10.43, S 9.55. Found: C 39.34, H 3.29, N 10.46, S 9.80. TGA: calcd 3.35%, found 3.40%.

 $[Fe^{II}_{2}(PS^{i}BuT)_{2}](BF_{4})_{4}$. To a clear yellow solution of $PS^{i}BuT$ (139 mg, 0.348 mmol) in 10 mL of MeOH was added a 5 mL solution of $Fe^{II}(H_{2}O)_{6}(BF_{4})_{2}$ (117 mg, 0.348 mmol) in MeOH. Stirring overnight at room temperature resulted in a brown solution with a white precipitate. The precipitate was isolated and taken up in 4 mL of MeCN to give a green solution, which was exposed to THF vapor diffusion to yield colorless block-shaped crystals. At this point a single crystal was collected for X-ray diffraction, before the bulk crystalline sample was air-dried to give $[Fe^{II}_{2}(PS^{i}BuT)_{2}](BF_{4})_{4}$ ·MeCN·H₂O (37 mg, 16%). Anal. Calcd for $[Fe^{II}_{2}(PS^{i}BuT)_{2}](BF_{4})_{4}$ ·MeCN·H₂O: C 38.30, H 4.21, N 11.70, S 9.74. Found: C 38.20, H 4.29, N 11.98, S 9.35. TGA: calcd 4.48%, found 4.34%. ESI-MS (+): m/z = 1171.1976 { $[Fe^{II}_{2}(PS^{i}BuT)_{2}](BF_{4})_{3}^{+}$ (calcd = 1171.1905).

 $[Fe^{H}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}$. To a clear yellow solution of $PS^{Me}PhT$ (49) mg, 0.11 mmol) in 15 mL of CHCl3 was added a 5 mL solution of $Fe^{II}(H_2O)_6(BF_4)_2$ (38 mg, 0.11 mmol) in MeOH. Stirring overnight at room temperature resulted in a brown solution with a white precipitate. The precipitate was isolated and taken up in 3 mL of MeCN to give a green solution, which was exposed to THF vapor diffusion for 1 week to yield pale green block-shaped crystals. At this point a few milligrams of single crystals of $[Fe^{II}_2(PS^{Me}PhT)_2](BF_4)_4$. 2MeCN was collected for X-ray diffraction and microanalysis, before the bulk crystalline sample was air-dried to give $[Fe^{II}_{2}(PS^{Me}PhT)_{2}]$ - $(BF_4)_4 \cdot 1^1/_2 MeCN \cdot 2H_2O$ (15 mg, 18%; actual yield higher than this, as a large portion was lost on finding a suitable single crystal for X-ray analysis). Anal. Calcd for [Fe^{II}₂(PS^{Me}PhT)₂](BF₄)₄·2MeCN: C 42.65, H 3.72, N 11.94, S 9.11. Found: C 42.73, H 3.77, N 11.66, S 8.95. Anal. Calcd for $[Fe^{II}_{2}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O: C 41.34,$ H 3.86, N 11.31, S 9.01. Found: C 41.29, H 3.71, N 11.05, S 9.02. TGA $[Fe_{2}^{II}(PS^{Me}PhT)_{2}](BF_{4})_{4}\cdot 1^{1}/_{2}MeCN\cdot 2H_{2}O:$ calcd 6.43%, found 6.85%. ESI-MS (+): $m/z = 1239.1737 \{ [Fe_2^{II}(PS^{Me}PhT)_2] (BF_4)_3 \}^{+1}$ (calcd = 1239.1594).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02851.

CSD search details (CIF)

Additional X-ray crystallographic tables and figures, magnetic data, UV-vis spectra, and experimental setup (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

Gütlich, P.; Goodwin, H. A. Top. Curr. Chem. 2004, 233, 1–47.
 Spin Crossover in Transition Metal Compounds, I-III; Gütlich, P.;

Goodwin, H. A., Eds.; Top. Curr. Chem. 2004; Vol. 233-235.

- (3) Halcrow, M. A. Spin-Crossover Materials: Properties and Applications, 1st ed.; John Wiley & Sons, Ltd, 2013.
- (4) Gütlich, P.; Gaspar, A. B.; Garcia, Y. Beilstein J. Org. Chem. 2013, 9, 342–391.
- (5) Brooker, S. Chem. Soc. Rev. 2015, 44, 2880–2892. , and front cover feature.
- (6) Olguín, J.; Brooker, S. In *Spin-Crossover Materials: Properties and Applications*, 1st ed.; Halcrow, M. A., Ed.; John Wiley & Sons, Ltd, 2013; pp 77–120.
- (7) Haasnoot, J. G. 1,2,4-Triazoles as Ligands for Iron(II) High Spin-Low Spin Crossovers; Kluwer Academic Publishers: Dordrecht, 1996.
- (8) Kitchen, J. A.; Brooker, S. Coord. Chem. Rev. 2008, 252, 2072-2092.
- (9) Klingele, M. H.; Moubaraki, B.; Murray, K. S.; Brooker, S. Chem. -Eur. J. 2005, 11, 6962–6973.
- (10) Klingele, M. H.; Moubaraki, B.; Cashion, J. D.; Murray, K. S.; Brooker, S. Chem. Commun. 2005, 987–989 and front cover feature.
- (11) Grunert, C. M.; Reiman, S.; Spiering, H.; Kitchen, J. A.; Brooker, S.; Gütlich, P. Angew. Chem., Int. Ed. 2008, 47, 2997–2999 and front

cover feature. (12) Bhattacharjee, A.; Ksenofontov, V.; Kitchen, J. A.; White, N. G.;

- Brooker, S.; Gütlich, P. Appl. Phys. Lett. 2008, 92, 174104.
- (13) Kitchen, J. A.; White, N. G.; Jameson, G. N. L.; Tallon, J. L.; Brooker, S. *Inorg. Chem.* **2011**, *50*, 4586–4597.
- (14) Bhattacharjee, A.; Roy, M.; Ksenofontov, V.; Kitchen, J. A.; Brooker, S.; Gütlich, P. *Eur. J. Inorg. Chem.* **2013**, 2013, 843–849.

(15) Kitchen, J. A.; Olguín, J.; Kulmaczewski, R.; White, N. G.; Milway, V. A.; Jameson, G. N. L.; Tallon, J. L.; Brooker, S. *Inorg. Chem.* **2013**, *52*, 11185–11199.

(16) Kulmaczewski, R.; Olguín, J.; Kitchen, J. A.; Feltham, H. L. C.; Jameson, G. N. L.; Tallon, J. L.; Brooker, S. J. Am. Chem. Soc. **2014**, 136, 878–881.

(17) Herold, C. F.; Carrella, L. M.; Rentschler, E. Eur. J. Inorg. Chem. 2015, 2015, 3632–3636.

(18) Weber, B. In Spin-Crossover Materials; John Wiley & Sons Ltd, 2013; pp 55-76.

(19) Costa, J. S.; Balde, C.; Carbonera, C.; Denux, D.; Wattiaux, A.; Desplanches, C.; Ader, J.-P.; Gütlich, P.; Létard, J.-F. *Inorg. Chem.* **2007**, *46*, 4114–4119.

(20) Holzhacker, C.; Calhorda, M. J.; Gil, A.; Carvalho, M. D.; Ferreira, L. P.; Stöger, B.; Mereiter, K.; Weil, M.; Müller, D.; Weinberger, P.; Pittenauer, E.; Allmaier, G.; Kirchner, K. *Dalton Trans.* **2014**, *43*, 11152–11164.

- (21) Weber, B.; Bauer, W.; Obel, J. Angew. Chem., Int. Ed. 2008, 47, 10098–10101.
- (22) Weber, B.; Kaps, E. S.; Obel, J.; Achterhold, K.; Parak, F. G. Inorg. Chem. 2008, 47, 10779–10787.

(23) Bauer, W.; Schlamp, S.; Weber, B. Chem. Commun. 2012, 48, 10222-10224.

(24) Lochenie, C.; Bauer, W.; Railliet, A. P.; Schlamp, S.; Garcia, Y.; Weber, B. *Inorg. Chem.* **2014**, *53*, 11563–11572.

(25) Iasco, O.; Rivière, E.; Guillot, R.; Buron-Le Cointe, M.; Meunier, J.-F.; Bousseksou, A.; Boillot, M.-L. *Inorg. Chem.* **2015**, *54*, 1791–1799.

(26) Lennartson, A.; Bond, A. D.; Piligkos, S.; McKenzie, C. J. Angew. Chem. 2012, 124, 11211–11214.

(27) Lennartson, A.; Southon, P.; Sciortino, N. F.; Kepert, C. J.; Frandsen, C.; Mørup, S.; Piligkos, S.; McKenzie, C. J. Chem. - Eur. J. 2015, 21, 16066–16072.

(28) England, J.; Gondhia, R.; Bigorra-Lopez, L.; Petersen, A. R.; White, A. J. P.; Britovsek, G. J. P. *Dalton Trans.* **2009**, 5319–5334.

(29) Grillo, V. A.; Gahan, L. R.; Hanson, G. R.; Stranger, R.; Hambley, T. W.; Murray, K. S.; Moubaraki, B.; Cashion, J. D. J. Chem. Soc., Dalton Trans. **1998**, 2341–2348.

(30) Reus, C.; Ruth, K.; Tüllmann, S.; Bolte, M.; Lerner, H.-W.; Weber, B.; Holthausen, M. C.; Wagner, M. *Eur. J. Inorg. Chem.* **2011**, 2011, 1709–1718.

(31) Hogue, R. W.; Miller, R. G.; White, N. G.; Feltham, H. L. C.; Jameson, G. N. L.; Brooker, S. Chem. Commun. 2014, 50, 1435–1437.

- (32) Miller, R. G.; Brooker, S. Chem. Sci. 2016, 7, 2501.
- (33) Brooker, S. Coord. Chem. Rev. 2001, 222, 33-56.
- (34) van Bommel, K. J. C.; de Jong, M. R.; Metselaar, G. A.;

Verboom, W.; Huskens, J.; Hulst, R.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. Chem. - Eur. J. 2001, 7, 3603-3615.

- (35) Livingstone, S. E.; Nolan, J. D. Aust. J. Chem. 1970, 23, 1553-1558.
- (36) Lennartson, A.; McKenzie, C. J. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 2011, 67, 0354–0358.

(37) van der Sluis, P.; Spek, A. L. Acta Crystallogr., Sect. A: Found. Crystallogr. **1990**, A46, 194–201.

- (38) Mooibroek, T. J.; Teat, S. J.; Massera, C.; Gamez, P.; Reedijk, J. *Cryst. Growth Des.* **2006**, *6*, 1569–1574.
- (39) Gamez, P.; Mooibroek, T. J.; Teat, S. J.; Reedijk, J. Acc. Chem. Res. 2007, 40, 435-444.
- (40) Schottel, B. L.; Chifotides, H. T.; Dunbar, K. R. Chem. Soc. Rev. 2008, 37, 68-83.
- (41) Salonen, L. M.; Ellermann, M.; Diederich, F. Angew. Chem., Int. Ed. 2011, 50, 4808–4842.
- (42) Frontera, A. Coord. Chem. Rev. 2013, 257, 1716-1727.
- (43) Brooker, S.; White, N. G.; Bauzá, A.; Deyà, P. M.; Frontera, A. *Inorg. Chem.* **2012**, *51*, 10334–10340.
- (44) Yang, L.; Powell, D. R.; Houser, R. P. Dalton Trans. 2007, 955–964.
- (45) Yatsunyk, L. A.; Walker, F. A. Inorg. Chem. 2004, 43, 757-777.
- (46) Weber, B.; Walker, F. A. Inorg. Chem. 2007, 46, 6794-6803.

(47) Weber, B.; Obel, J.; Henner-Vasquez, D.; Bauer, W. Eur. J. Inorg. Chem. 2009, 36, 5527-5534.

- (48) Evans, D. F. J. Chem. Soc. 1959, 2003–2005.
- (49) Piguet, C. J. Chem. Educ. 1997, 74, 815–816.
- (50) Shores, M. P.; Klug, C. M.; Fiedler, S. R. In Spin-Crossover
- Materials; John Wiley & Sons Ltd, 2013; pp 281–301. (51) Hauser, A. Top. Curr. Chem. 2004, 233, 49–58.
- (51) Hadder, H. 10p. Curr. Chem. 2004, 255, 49 58. (52) Blakesley, D. W.; Payne, S. C.; Hagen, K. S. Inorg. Chem. 2000,
- (5) blaces(y, D. W., Tayle, C. C., Hagen, R. G. Inorg. Chem. 2000, 39, 1979–1989.

(53) Hinek, R.; Spiering, H.; Schollmeyer, D.; Gütlich, P.; Hauser, A. *Chem. - Eur. J.* **1996**, *2*, 1427–1434.

(54) Turner, J. W.; Schultz, F. A. Inorg. Chem. 2001, 40, 5296-5298.

(55) Tafili-Kryeziu, M.; Weil, M.; Muranaka, T.; Bousseksou, A.; Hasegawa, M.; Jun, A.; Linert, W. Dalton Trans. **2013**, 42, 15796– 15804.

(56) Martin, L. L.; Martin, R. L.; Sargeson, A. M. Polyhedron 1994, 13, 1969–1980.

(57) Ortega-Villar, N.; Thompson, A.; Muñoz, M. C.; Ugalde-Saldívar, V. M.; Goeta, A. E.; Moreno-Esparza, R.; Real, J. A. *Chem. - Eur. J.* **2005**, *11*, 5721–5734.

(58) Slichter, C. P.; Drickamer, H. G. J. Chem. Phys. 1972, 56, 2142–2160.

(59) CrysAlisPro; Agilent Technologies Yarnton: Oxfordshire.

(60) Palatinus, L.; Chapuis, G. J. Appl. Crystallogr. 2007, 40, 786-790.

(61) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, A64, 112–122.

(62) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de

Streek, J.; Wood, P. A. J. Appl. Crystallogr. 2008, 41, 466–470.
(63) POVray; Persistence of Vision Raytracer (Version 3.6); 2004.

(64) Kahn, O. *Molecular Magnetism*; VCH Publishers Inc.: New York, 1993.

(65) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. J. Am. Chem. Soc. **1962**, 84, 3374.

(66) Bartlett, R. K.; Humphrey, I. R. J. Chem. Soc. C 1967, C, 1664–1666.