Marquette University

e-Publications@Marquette

Chemistry Faculty Research and Publications

Chemistry, Department of

6-24-2019

Selective Isomer Formation and Crystallization-Directed Magnetic Behavior in Nitrogen-Confused C-Scorpionate Complexes of $\text{Fe}(\text{O}_3\text{SCF}_3)_2$

James R. Gardinier
Marquette University, james.gardinier@marquette.edu

Kristin J. Meise
Marquette University

Fathiya Jahan
Marquette University

Denan Wang
Marquette University

Sergey V. Lindeman
Marquette University, sergey.lindeman@marquette.edu

Follow this and additional works at: https://epublications.marquette.edu/chem_fac

Part of the [Chemistry Commons](#)

Recommended Citation

Gardinier, James R.; Meise, Kristin J.; Jahan, Fathiya; Wang, Denan; and Lindeman, Sergey V., "Selective Isomer Formation and Crystallization-Directed Magnetic Behavior in Nitrogen-Confused C-Scorpionate Complexes of $\text{Fe}(\text{O}_3\text{SCF}_3)_2$ " (2019). *Chemistry Faculty Research and Publications*. 992.

https://epublications.marquette.edu/chem_fac/992

Marquette University

e-Publications@Marquette

Chemistry Faculty Research and Publications/College of Arts and Sciences

This paper is NOT THE PUBLISHED VERSION; but the author's final, peer-reviewed manuscript. The published version may be accessed by following the link in the citation below.

Inorganic Chemistry, Vol. 58, No. 14 (June 24, 2019): 8953-8968. [DOI](#). This article is © American Chemical Society Publications and permission has been granted for this version to appear in [e-Publications@Marquette](#). American Chemical Society Publications does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from American Chemical Society Publications.

Selective Isomer Formation and Crystallization-Directed Magnetic Behavior in Nitrogen-Confused C-Scorpionate Complexes of $\text{Fe}(\text{O}_3\text{SCF}_3)_2$

James R. Gardinier

Department of Chemistry, Marquette University, Milwaukee, Wisconsin

Kristin J. Meise

Department of Chemistry, Marquette University, Milwaukee, Wisconsin

Fathiya Jahan

Department of Chemistry, Marquette University, Milwaukee, Wisconsin

Denan Wang

Department of Chemistry, Marquette University, Milwaukee, Wisconsin

Sergey V. Lindeman

Department of Chemistry, Marquette University, Milwaukee, Wisconsin

Abstract

The complex $[\text{Fe}(\text{HL}^*)_2](\text{OTf})_2$, **1**, where $\text{HL}^* = \text{bis}(3,5\text{-dimethylpyrazol-1-yl})(3\text{-}1H\text{-pyrazole})\text{methane}$, was prepared in order to compare its magnetic properties with those of the analogous parent complex, $[\text{Fe}(\text{HL})_2](\text{OTf})_2$, that lacks methyl groups on pyrazolyl rings and that undergoes spin crossover (SCO) from the low spin (LS) to the high spin (HS) form above room temperature. It was anticipated that this new semibulky derivative should favor the HS state and undergo SCO at a lower temperature range. During this study, six crystalline forms of **1** were prepared by controlling the crystallization conditions. Thus, when reagents are combined in CH_3CN , an equilibrium mixture of *cis* and *trans* isomers is established that favors the latter below 311 K. The *trans* isomer can be isolated exclusively as a mixture of solvates, LS *trans*-**1**·2 CH_3CN and HS *trans*-**1**·4 CH_3CN , by cooling CH_3CN solutions to -20°C with the former being favored at high concentrations and short crystallization times. Subsequently, vapor diffusion of Et_2O into CH_3CN solutions of pure *trans*-**1**·2 CH_3CN gives solvate-free HS *trans*-**1**. Subjecting *trans*-**1**·2 CH_3CN to vacuum at room temperature gives microcrystalline *trans*-**1**· CH_3CN , identified by elemental analysis and its distinct powder X-ray diffraction pattern. If an isomeric mixture of **1** is subject to room-temperature vapor diffusion, then a crystalline mixture of HS isomers *cis*-**1** and *trans*-**1** is obtained. Finally, slowly cooling hot acetonitrile solutions of isomeric mixtures of **1** to room temperature gives large prisms of HS *co*-**1**, a species with both *cis* and *trans* isomers in the unit cell. The complexes *trans*-**1**, *trans*-**1**· CH_3CN , *cis*-**1**, and *co*-**1** undergo SCO below 250 K while *trans*-**1**· $x\text{CH}_3\text{CN}$ ($x = 2, 4$) solvates do not undergo SCO before desolvation.

Synopsis

The complex, $[\text{Fe}(\text{HL}^*)_2](\text{OTf})_2$, **1**, where $\text{HL}^* = \text{bis}(3,5\text{-dimethylpyrazol-1-yl})(3\text{-}1H\text{-pyrazole})\text{methane}$, can be coerced to crystallize in one of four different forms from CH_3CN solutions under normal laboratory conditions where each form has distinctive magnetic properties.

Introduction

Transition metal complexes that have metal centers with d^4 to d^7 electron configurations and ligands that impart intermediate fields to the metal can be provoked to undergo reversible spin crossover (SCO) [\(1,2\)](#) between low spin (LS) and high spin (HS) electronic states via controlled perturbations to temperature, applied pressure, or various forms of electromagnetic radiation. [\(3–11\)](#) Since a given SCO complex in each of its electronic spin states exhibits different size, color, magnetic properties, and bulk solid-state electrical resistivity, there has been great interest in their potential employment for various technological applications. [\(12–20\)](#) The temperature dependence of bulk molar magnetic susceptibility (χ_M) is most often used to characterize SCO behavior since it is simple to measure and because χ_M directly correlates to the high spin fraction (γ_{HS}) in the sample. The temperature with $\gamma_{\text{HS}} = 0.5$, or $T_{1/2}$, is generally used as a descriptive reference. The full χ_M versus T plots reveal whether or not the SCO is complete, if SCO occurs in one or more steps, and whether there is cooperativity in

the form of either a large $\delta\chi_M/dT$ or a hysteresis (where $T_{1/2}\uparrow$ (heating) is different than $T_{1/2}\downarrow$ (cooling)), or both.⁽²¹⁾ The requisite conditions (T , P , $h\nu$, etc.) for the initiation and progression of SCO in the solid state depend not only on the metal ion and the ligand field strength, but also, critically, on the nature of the crystal packing. Thus, each polymorph⁽²²⁾ or solvatomorph⁽²³⁾ of a given complex typically exhibits magnetic behavior that is different than that of its relative. A longstanding research challenge in SCO compounds is to use molecular design and/or crystal engineering approaches to identify structure–property relationships with the goal of imparting a specific magnetic behavior ($T_{1/2}$, $\delta\chi_M/dT$, number of SCO steps, etc.) into the bulk solid.

Within the profuse collection of transition metal complexes that exhibit SCO behavior, octahedral iron(II) complexes of organoamine and/or N-heterocyclic donors represent one of the largest and most intensely studied classes.^(24–29) Of these, complexes of scorpionate ligands,^(30,31) poly(pyrazolyl)borates or poly(pyrazolyl)methanes (C-scorpionates), have received increased scrutiny because of their interesting SCO behavior^(32–39) and their attractive physical properties that are useful for materials processing.^(40–47) While the SCO behavior of iron(II) scorpionates has shown some evidence of tunability via ligand modifications,^(48–52) there is a need for elaboration in order to more fully understand the impact of substituent changes on fine-tuning ligand field strength and crystal packing, and, hence, controlling SCO behavior in this class of compounds.

We recently introduced a new class of C-scorpionate, the nitrogen-confused C-scorpionate, where the connectivity of one of the three heterocycles bound to the central methine carbon occurs at the 3-carbon ring position instead of the more usual N-1 position. The iron(II) complexes $[\text{Fe}(\text{}^{\text{H}}\text{L})_2](\text{X})_2$ ($\text{X} = \text{BF}_4$,⁽⁵³⁾ OTf ⁽⁵⁴⁾), where $\text{}^{\text{H}}\text{L}$ is a ligand with two unsubstituted pyrazolyls and a “confused” pyrazolyl with an N–H moiety, were studied. Both complexes are low spin (LS) at room temperature and undergo SCO with $T_{1/2}$ near 360 K, but the triflate (OTf) derivative exhibited a more cooperative SCO than the BF_4 derivative due to stronger intermolecular charge-assisted hydrogen-bonding interactions between the pyrazolyl-NH donor and anion acceptor (O versus F). It is known for iron(II) complexes of normal scorpionates that introducing methyl substituents at the 3-pyrazolyl ring positions dramatically reduces $T_{1/2}$ of SCO presumably because interligand steric interactions of six methyl groups near the metal center favor the longer bond distances associated with the HS state. For instance, $\{\text{Fe}[\text{HC}(3,5\text{-Me}_2\text{pz})_3 = \text{Tpm}^*]_2\}(\text{BF}_4)_2$ has $T_{1/2}$ near 200 K⁽⁵⁵⁾ while $\{\text{Fe}[\text{HC}(\text{pz})_3 = \text{Tpm}]\}(\text{BF}_4)_2$ has $T_{1/2}$ near 400 K.⁽⁵⁶⁾ Lowering the number of methyls at the 3-pyrazolyl position gives $T_{1/2}$ between these two extremes as in the cases of $[\text{Fe}\{\text{HC}(3\text{-Mepz})_2(5\text{-Mepz})\}_2](\text{BF}_4)_2$ ($T_{1/2} = 250$ K)⁽⁵⁷⁾ or $[\text{Fe}(\text{Tpm}^*)(\text{Tpm})](\text{BF}_4)_2$ ($T_{1/2}$ (polymorph 1) ~ 228 K; $T_{1/2}$ (polymorph 2) ~ 310 K).⁽⁵⁸⁾ Given these results and the current interest in discovering new examples of species that undergo thermal SCO with $T_{1/2}$ near room temperature,⁽⁵⁹⁾ we initiated a study of the SCO behavior of iron(II) complexes of $\text{}^{\text{H}}\text{L}^*$, a N-confused C-scorpionate ligand with two 3,5-dimethylpyrazolyl rings and an unsubstituted “confused” pyrazolyl; such complexes would have four methyl groups near the metal center. During the course of these studies, we discovered that the iron(II) triflate complex showed unexpectedly rich structural chemistry that was responsible for the unusual thermal SCO behavior as evaluated by magnetometry measurements. This paper details the coordination chemistry, crystallization behavior, and resultant magnetic properties of $[\text{Fe}(\text{}^{\text{H}}\text{L}^*)_2](\text{OTf})_2 \cdot x\text{CH}_3\text{CN}$, $\mathbf{1} \cdot x\text{CH}_3\text{CN}$, where $x = 0, 1, 2$, or 4.

Experimental Section

General Considerations

Commercial solvents were dried by conventional means and distilled under a nitrogen atmosphere prior to use. Anhydrous $\text{Fe}(\text{OTf})_2$ was purchased from commercial sources and was purified by low temperature crystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ to give $\text{Fe}(\text{OTf})_2 \cdot 2\text{CH}_3\text{CN}$ that was stored under argon in a drybox.⁽⁵⁴⁾ The compound $\text{}^{\text{H}}\text{L}^*$ was prepared as described elsewhere.⁽⁵⁴⁾ The iron(II) complex was prepared under argon using

Schlenk line techniques; however, after isolation, it was stored and manipulated under normal laboratory atmospheric conditions.

Instrumentation

Midwest MicroLab, LLC, Indianapolis, IN, performed all elemental analyses. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded for samples as KBr pellets in the 4000–500 cm^{-1} region on a Nicolet Magna-IR 560 spectrometer or on solid samples using a Thermo Scientific Nicolet iS5 IR spectrometer equipped with an iD3 attenuated total reflection (ATR) accessory. ^1H NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts were referenced to the residual CD_2HCN resonance⁽⁶⁰⁾ at δ_{H} 1.94 for CD_3CN . Solution magnetic moments were measured by the Evans method.⁽⁶¹⁾ Magnetic susceptibility data were collected on a Quantum Design MPMS3 SQUID magnetometer. Raw moment data were corrected for sample shape and radial offset corrections using the MPMS 3 Sample Geometry Simulator.⁽⁶²⁾ Diamagnetic corrections of -372×10^{-6} emu/mol for each *trans*-**1**, *cis*-**1**, and *co*-**1** calculated from tabulated Pascal's constants⁽⁶³⁾ were applied to the measured susceptibility data, as appropriate. Electronic absorption (UV–vis/NIR) measurements were made on a Cary 5000 instrument. Powder X-ray diffraction patterns were collected with an Oxford Diffraction Ltd. Supernova equipped with a 135 mm Atlas CCD detector or with a Rigaku Miniflex II instrument using Cu K α radiation.

Synthetic Protocol

$[\text{Fe}(\text{H}^{\text{L}}^*)_2](\text{OTf})_2$, **1**

A solution of 0.854 g (3.15 mmol) of H^{L}^* in 20 mL of CH_3CN was added to a solution of 0.654 g (1.50 mmol) of $\text{Fe}(\text{OTf})_2 \cdot 2\text{CH}_3\text{CN}$ in 10 mL of CH_3CN . The flask originally containing H^{L}^* was washed with 5 mL of CH_3CN , and the washings were transferred to the reaction medium to ensure quantitative transfer of reagent. After the pale violet solution had been stirred 1 h at room temperature, solvent was removed under vacuum distillation with an external room-temperature water bath to facilitate evaporation. The pale lavender pink residue was washed with Et_2O (3×10 mL) and was dried under vacuum to leave 1.073 g (80%) of **1** as a nearly colorless powder. Mp, did not melt below 200 °C. Anal. Calcd (Found) for **1**, $\text{C}_{30}\text{H}_{36}\text{F}_6\text{FeN}_{12}\text{O}_6\text{S}_2$: C, 40.28 (40.29); H, 4.06 (4.08); N, 18.79 (18.79). μ_{eff} (Evans, CD_3CN) = 4.9 μ_{B} . IR: ν_{NH} (Nujol/KBr) = 3139. IR for triflate (Nujol/KBr, s to vs): 1286 (ν_{as} , SO_3), 1256 (ν_{s} , CF_3), 1160 (ν_{as} , CF_3), 1033 (ν_{s} , SO_3), 638 (δ_{s} , SO_3) cm^{-1} . UV–vis [CD_3CN] λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 800 (20), 467 sh (90), 374 sh (280), 338 (600), 320 (640). See below for ^1H NMR data.

cis- $[\text{Fe}(\text{H}^{\text{L}}^*)_2](\text{OTf})_2$, *cis*-**1**

This isomer has not yet been obtained pure in a bulk form. The greatest amounts of this isomer as a powder admixed with small amounts of *trans*-**1** are obtained by boiling a CH_3CN solution of **1** to dryness with the aid of an external 90 °C oil bath (see [Figure S6b](#) for PXRD and [Figure S11](#) for NMR). Single crystals of *cis*-**1** could be selected (at random) from mixtures with *trans*-**1** (see below) and analyzed by single crystal X-ray diffraction (scXRD), as follows. Room-temperature vapor diffusion of Et_2O into a filtered 0.025 M CH_3CN solution of **1** gave colorless plate-like needles which are a mixture of isomers, *trans*-**1** and *cis*-**1**. One of the latter was hand-selected and used for scXRD. The bulk colorless needle crystals were collected by decanting the mother liquor, washing with Et_2O , and drying under vacuum for 20 min. ^1H NMR (CD_3CN) analysis confirms the bulk crystals to be a mixture of isomers (see [Figure S10](#)). The resonances attributed to the *cis* isomer are δ_{H} 50.7 (2 H), 48.0 (2 H), 44.8 (2 H), 44.2 (6 H), 35.6 (4 H), 21.5 (6 H), 20.3 (6 H), 19.3 (6 H), -41.6 (2 H) ppm.

co- $[\text{Fe}(\text{H}^{\text{L}}^*)_2](\text{OTf})_2$, *co*-**1**

Crystallization by cooling a hot (60 °C) CH_3CN solution of **1** (200 mg/1 mL CH_3CN , ca. 0.22 M) to room temperature overnight gave 52 mg of large, pale blue-green block-like prisms of *co*-**1**. An additional 47 mg fraction was obtained by evaporating the mother liquor to 1/2 the original volume by heating to 60 °C under a nitrogen stream and then allowing the mother liquor to cool to room temperature for 2 h. It then was cooled at

4 °C for 12 h, followed by decanting and drying under nitrogen. A final 20 mg crop of crystals was obtained by concentrating and cooling a second time as above. Anal. Calcd (Found) for *co-1*, C₃₀H₃₆F₆FeN₁₂O₆S₂: C, 40.28 (40.07); H, 4.06 (4.04); N, 18.79 (18.66). ¹H NMR (CD₃CN) δ_H 50.7, 50.5, 48.0, 44.7, 44.2, 37.5, 36.6, 35.6, 21.5, 20.4, 19.6, 19.3, 2.22, -41.0, -41.7 ppm.

trans-[Fe(^HL*)₂(CH₃CN)_x](OTf)₂·xCH₃CN (x = 1, 2, or 4), trans-1·xCH₃CN (x = 1, 2, or 4)

A solution of 500 mg of **1** in 7 mL of CH₃CN was placed in a freezer at -20 °C, and the solution became light violet on cooling. Large violet square plates of *trans-1*·2CH₃CN formed over 14 h. The violet crystals of *trans-1*·2CH₃CN (251 mg) were separated from the mother liquor by decanting and drying under a N₂ stream. Evaporating the mother liquor to about 1/3 the volume and cooling another 14 h gave a second crop (42 mg) of *trans-1*·2CH₃CN. Total: 293 mg of *trans-1*·2CH₃CN. Note that if any trace colorless powder of *trans-1*·4CH₃CN is present in the bulk crystallization, it can be removed by shaking and decanting the cold suspension from the larger violet crystals. Then, after drying under a nitrogen stream, the violet crystals of the disolvate are then separated mechanically from any opaque, pale aqua crystals of the (now desolvated) tetrasolvate. Longer crystallization times (4–7 days) or more dilute solutions produced a mixture of *trans-1*·2CH₃CN and colorless prisms of *trans-1*·4CH₃CN. If the crystallization time is extended to 2 weeks or more, then the violet crystals transform completely into colorless prisms of *trans-1*·4CH₃CN. The crystals of *trans-1*·4CH₃CN rapidly desolvate under a N₂ stream to give approximately 45 mg of desolvated *trans-1* per 100 mg of **1**. The following ¹H NMR data are for violet *trans-1*·2CH₃CN. ¹H NMR (CD₃CN, 295 K) δ_H 50.5 (4 H), 37.5 (2 H), 36.6 (12 H), 19.5 (16 H), 2.22 (6 H), -41.0 (2 H) ppm.

Samples of **1**·2CH₃CN desolvate to **1**·CH₃CN during shipping to the combustion analysis laboratory. Samples of **1**·CH₃CN can be prepared intentionally by subjecting **1**·2CH₃CN to an oil pump vacuum (0.1 mTorr) at room temperature for 1 h. Anal. Calcd (Found) for *trans-1*·CH₃CN, C₃₂H₃₉F₆FeN₁₃O₆S₂: C, 41.07 (41.31); H, 4.20 (4.29); N, 19.46 (19.70).

trans-[Fe(^HL*)₂](OTf)₂, trans-1

For method A, a 100 mg (0.102 mmol) sample of *trans-1*·2CH₃CN dissolved in 2 mL of CH₃CN at room temperature (avoid heating) is immediately precipitated with 6 mL of Et₂O. The colorless powder, 81 mg (0.091 mmol, 89%), is collected after filtering and drying under a nitrogen stream. For method B, a 65 mg (0.067 mmol) sample of *trans-1*·2CH₃CN is heated at 70 °C for 4 h under vacuum to give 46 mg (0.051 mmol, 76%) of *trans-1* as a colorless powder. Anal. Calcd (Found) for *trans-1*, C₃₀H₃₆F₆FeN₁₂O₆S₂: C, 40.28 (40.34); H, 4.06 (4.04); N, 18.79 (18.70).

X-ray Crystallography

X-ray intensity data from a violet prism of *cis-1*, a violet needle of *trans-1*, a violet irregular crystal of *co-1*, a violet prism of *trans-1*·2CH₃CN, and a colorless prism of *trans-1*·4CH₃CN were collected at 100.0(1) K with an Oxford Diffraction Ltd. Supernova equipped with a 135 mm Atlas CCD detector. The data for *trans-1*, *cis-1*, and *co-1* were also collected at 250 K (a temperature where the latter two crystals were colorless but the former was light violet/pink). Cu Kα radiation, λ = 1.54184 Å, was used for all experiments except for *trans-1* which used Mo Kα radiation, λ = 0.71073 Å. Raw data frame integration and Lp corrections were performed with Crysalis Pro (Oxford Diffraction, Ltd.).⁽⁶⁴⁾ Final unit cell parameters were determined by least-squares refinement of 18 495 (100 K) and 14 400 (250 K) reflections from the data set of *cis-1*, 22 417 (100 K) and 17 127 (250 K) reflections from the data set of *co-1*, 10 392 (100 K) reflections from the data set of *trans-1*·2CH₃CN, 13 813 (100 K) reflections from the data set of *trans-1*·4CH₃CN, and 15 651 (100 K) and 10 071 (250 K) reflections from the data set of *trans-1*, with *I* > 2σ(*I*) for all cases. Analysis of the data showed negligible crystal decay during collection in each case. Direct methods structure solutions were performed with Olex2.solve⁽⁶⁵⁾ while difference Fourier calculations and full-matrix least-squares refinements against *F*² were performed with SHELXTL.⁽⁶⁶⁾ Empirical absorption corrections were applied using spherical harmonics implemented in the

SCALE3 ABSPACK scaling algorithm. The hydrogen atom bound to nitrogen of the pyrazol-3-yl group in *cis*-**1**, *trans*-**1** (100 K), and *trans*-**1**·2CH₃CN was located and refined. All other hydrogen atoms were placed in idealized positions and included as riding atoms.

Special details follow. For *cis*-**1**, one of the triflate anions is well-ordered while the other is unequally disordered, 67%:33%, over two nearby positions. At high temperature the extreme disorder causes an A-level alert in the checkcif program; this alert is resolved in the 100 K structure. Also, a modulated phase with **q**-vector (0.077 0 0.171) was found at 100 K; no satellites were detected at 250 K. For *co*-**1**, one of the triflate ions is disordered over two nearby positions. The major component (84%) is hydrogen-bonded to the pyrazolyl. The minor component occupies an alternative position in a cavity. The content of the cavity could not be elucidated but may involve a small amount of unidentified solvent and/or a third orientation of the anion. The crystal of *trans*-**1** at 100 K was a twin where component two is rotated 180° around [−0.01 −0.02 1.00] (reciprocal space) or [0.00 0.00 1.00] (direct space). The crystal of *trans*-**1**·2CH₃CN was an 87/8/5 triplet where component 2 was rotated by −170.9° around [−0.05 1.00 −0.01] (reciprocal space) or [−0.05 1.00 −0.02] (direct space) while component 3 was rotated by −174.6° around [−0.02 1.00 0.00] (reciprocal space) or [−0.01 1.00 −0.00] (direct space).

Computational Details

General Considerations

Geometry optimizations were performed using Handy's optimized exchange (OPTX) with the PBE correlation (OPBE functional)^[67] in combination with the def2-SV(P) double- ζ basis set for light atoms and def2-QZVPP for Fe^[68] because we have previously found^[69] (and find again here) that this method provides excellent agreement (within 0.09 Å) with solid-state structures. Moreover, such an approach has been found to successfully determine spin-state splitting in other iron complexes that undergo spin crossover phenomena.^[70] Solvent effects were accounted for by using the polarizable continuum model IEFPCM,^[71] as implemented in Gaussian 16.^[72] Analytical vibrational frequency calculations were carried out to verify that optimized geometries were stationary points. [Table S7](#) summarizes the results of these studies. Cartesian coordinates are contained within the FeConf_DFT.xyz file found in the [Supporting Information](#).

Results and Discussion

The reaction between Fe(OTf)₂ and 2 equiv of ^HL* in CH₃CN gives the desired complex [Fe(^HL*)₂](OTf)₂, **1**, in high yield. Recrystallization of **1** under different conditions led to the different crystal types pictured in [Figure 1](#). Recrystallization of **1** by room-temperature vapor diffusion of Et₂O into CH₃CN solutions produced plate-like needles that are a mixture of *cis* and *trans* isomers, as defined by the relative disposition of the confused pyrazolyl ring on each ligand about iron's coordination sphere. The unit cell parameters of the crystals of each isomer at 250 K are nearly identical, so it is very difficult to distinguish these crystals by visual inspection. The *trans* isomer can be isolated by alternate means (vide infra). This mixture of needles was sometimes accompanied by large isometric crystalline blocks (left of [Figure 1](#)) that were found to contain both *cis*- and *trans*-[Fe(^HL*)₂]²⁺ cations in the same unit cell, so this crystal form is referred to as *co*-**1**. Crystals of *co*-**1** are also formed predominantly in a mixture along with smaller amounts of plate-like needle mixtures of *trans*-**1** and *cis*-**1** by slow evaporation of CH₃CN solutions of **1**. Crystals of *co*-**1** are best isolated (giving the highest quality crystals without contamination of needles) by slowly cooling hot concentrated (ca. > 0.2 M) CH₃CN solutions to room temperature or to 4 °C (at the sacrifice of crystal quality). Recrystallization of lower concentrations of **1** in CH₃CN (≤ca. 0.10 M) at low temperature (−20 °C) gave different CH₃CN solvates of *trans*-**1**. More specifically, when dilute solutions are placed directly in a −20 °C freezer, violet crystals of a hydrogen-bonded bis-acetonitrile solvate *trans*-[Fe(^HL*)₂](OTf)₂·2CH₃CN, *trans*-**1**·2CH₃CN, form ([Figure 1](#), center) after about 1 day, followed by colorless block-like prisms of the tetrasolvate, *trans*-**1**·4CH₃CN ([Figure 1](#), right). If

crystallization chambers are left for extended periods (2 weeks to 1 month), the initially formed violet crystals eventually transform to colorless *trans*-**1**·4CH₃CN. Alternatively, when more dilute (<0.02 M) solutions are cooled in a –20 °C freezer, the resulting crystal mixture is composed mainly of *trans*-**1**·4CH₃CN with minor amounts of the disolvate. If crystals of *trans*-**1**·*x*CH₃CN (*x* = 2, 4) are subject to recrystallization by vapor diffusion of Et₂O into CH₃CN solutions at 4 °C, then a mixture of *trans*-**1** and *trans*-**1**·2CH₃CN is obtained.

Figure 1. Left: Photograph of the mixture of crystals obtained after recrystallizing **1** by vapor diffusion of Et₂O into a 0.025 M CH₃CN solution, filtering, and drying under vacuum, producing a mixture of large blocks of *co*-**1** and smaller plate-like needles of *cis*-**1** and *trans*-**1**. Center: Photograph of crystals of *trans*-**1**·2CH₃CN obtained after cooling a CH₃CN solution of **1** to –20 °C, after decanting the mother liquor, and (immediately) after drying under a nitrogen stream. Right: Crystals of *trans*-**1**·4CH₃CN in their mother liquor. Each photograph was taken under the same magnification.

Solid-State Structures

Crystals of *trans*-**1**·*x*CH₃CN (*x* = 2 or 4) maintained their color over the temperature range 298–100 K while *trans*-**1**, *cis*-**1**, and *co*-**1** changed from colorless at room temperature to violet at 100 K. Thus, the crystal structures of the former two complexes were determined at 100 K while those of the latter complexes were determined at two temperatures (250 K (colorless) and 100 K (violet)). The structures of the *trans*-**1**·*x*CH₃CN solvates (*x* = 2 or 4) will be described briefly first, and then the structures of the other compounds are described in more detail because unusual features of their crystal packing dictate their peculiar magnetic behavior.

Views of the structure of *trans*-**1**·2CH₃CN are shown in [Figure 2](#) while selected bond distances and angles are listed in [Table 1](#). The asymmetric unit consists of an iron(II) ion located on an inversion center, one κ³N-ligand, one triflate anion, and one CH₃CN molecule. The crystal symmetry gives a pseudo-octahedral FeN₆ kernel with an average Fe–N bond length of 1.97(3) Å. This distance is characteristic of low spin (LS) iron(II) and is identical to that previously found in [Fe(^HL)₂](BF₄)₂ that possessed a dication with unsubstituted “normal” pyrazolyls and that was shown to be 100% LS iron(II) by magnetometry.⁽⁵³⁾ In the dication of *trans*-**1**·2CH₃CN, the Fe–N distance associated with the “confused” pyrazolyl is much shorter (Fe–N2 1.936(2) Å) than those of the other two pyrazolyls (Fe–N11, 1.991(2) Å; Fe–N21 1.997(2) Å). The ligand is relatively strain-free with no discernible distortions⁽⁵²⁾ which normally manifest in pyrazolyl ring twisting (pz twist = average of the absolute value of the two torsion angles, |FeN–NC_{methine}|, and the corresponding confused pyrazolyl’s torsion |FeN–CC_{methine}| ≥ 0° (untwisted value); here, pz twist = 1.4°) and pyrazolyl ring tilting (pz tilt = average of the two |FeN–NC_{pz}| torsions and “confused” pz ring equivalent |FeN–C_{pz}C_{pz}| torsion ≤ 180° (untilted value); here, the pz tilt = 177.8°). Finally, the “confused” pyrazolyl N–H was located and refined (N1–H1n 0.86(3) Å) and is, somewhat surprisingly, hydrogen-bonded⁽⁷³⁾ to the solvate acetonitrile [N1H1n⋯N3 2.03(3) Å, 172(2)°, N3⋯N1 2.884(3) Å] rather than to the triflate anions. The triflate anions are instead associated with acidic methine and pyrazolyl ring hydrogens⁽⁷⁴⁾ and with solvate methyl hydrogens on neighboring dications to give the three-dimensional supramolecular structure, as detailed more fully in the [Supporting Information](#).

Figure 2. Left: Asymmetric unit of *trans*-1·2CH₃CN, minor disorder component of anion and solvate atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability. Right: View of the dication showing *trans*-disposition of the “confused” pyrazolyls, with most hydrogen atoms omitted for clarity.

Table 1. Selected Bond Distances (Å), Angles (deg), and Torsions (deg) for *trans*-1·*x*CH₃CN (*x* = 2, 4)

	1·2CH ₃ CN	1·4CH ₃ CN
Bond Distances (Å)		
Fe–N2	1.9364(17)	2.1297(10)
Fe–N11	1.9908(18)	2.1799(11)
Fe–N21	1.9964(16)	2.2147(11)
N1–H1n	0.86(3)	0.88
Bond Angles (deg)		
N2–Fe–N11	87.93(6)	83.85(4)
N2–Fe–N21	87.71(6)	83.61(4)
N11–Fe–N21	86.95(7)	83.28(4)
N2–Fe1–N2'	180.00(8)	180.00(6)
N2–Fe–N11'	92.07(6)	96.15(4)
N11–Fe–N21'	93.05(7)	96.72(4)
Bond Torsions (deg)		
FeN2–C3C4	–0.3(2)	10.15(15)
FeN11–N12C4	–1.7(2)	7.89(14)
FeN21–N22C4	–2.0(2)	12.92(14)
FeN2–C3C2	–179.47(13)	–171.42(8)
FeN11–N12C13	177.51(13)	–173.03(8)
FeN21–N22C23	176.40(13)	–161.71(8)

The structure of *trans*-1·4CH₃CN at 100 K contrasts that of the disolvate in that the dication in the tetrasolvate is HS iron(II) as opposed to LS iron(II) found in the disolvate, a difference that can be attributed to the crystal packing, as described below. A comparison of bond distances and angles between the tetra- and disolvates is found in [Table 1](#). Thus, the average Fe–N distance of 2.17 Å in the tetrasolvate is characteristic for HS iron(II) versus 1.97 Å for LS iron(II) in the disolvate. Moreover, the ligand in the tetrasolvate is significantly distorted ([Figure 3](#), left) but is not very distorted in the disolvate. That is, the tetrasolvate has both greater pyrazolyl ring twisting (10.3° vs 1.4°) and pyrazolyl ring tilting (168.7° vs 177.8°) than the disolvate. In fact, the large pz twist in the tetrasolvate is close to the previously identified empirical 11° pz twist limit([52](#)) whereby spin crossover has never been observed for an iron(II) scorpionate. This empirical limit presumably reflects that any large distortion(s) caused by crystal packing imparts an insurmountable kinetic barrier (especially at low temperature) for reorganization to a hypothetical undistorted low spin form. In *trans*-1·4CH₃CN, two of the acetonitriles are hydrogen-bonded to the dication (N1⋯N3 2.8796(18) Å, N1–H1n⋯N3, 168°) with a geometry quite similar to

that in *trans*-1·2CH₃CN, vide supra (center of [Figure 3](#)). However, the other two acetonitrile molecules of solvation in 1·4CH₃CN are loosely held in pockets along the *c*-axis ([Figure 3](#), right) by CH···O([74](#)) weak hydrogen-bonding interactions with the triflate anions (C9H9a···O1, 2.51 Å, 166°). These latter acetonitrile molecules are, in turn, pressed against the most distorted pz* ring (with N21) to give a short CH···π interaction([75](#)) between the acetonitrile methyl donor and pyrazolyl acceptor (CH9b···Ct(N21) 2.73 Å, 132°).

Figure 3. Left: View of the dication of *trans*-1·4CH₃CN down the C_{methine}–Fe vector with most H atoms and all CH₃CN and triflate atoms removed for clarity to emphasize pyrazolyl ring twisting. Center: Comparison of dications in *trans*-1·4CH₃CN (cyan) versus in *trans*-1·2CH₃CN (violet). Right: View of crystal packing of *trans*-1·4CH₃CN showing half of the acetonitrile molecules (as larger black ball and sticks) in channels/pockets along the *c*-axis.

Single crystal X-ray diffraction data was obtained for a colorless needle of *cis*-1 at 250 K and then after cooling to 100 K when the needle was violet ([Figure 4](#)). A listing of selected bond distances and interatomic angles for *cis*-1 at different temperatures is provided in [Table 2](#). The compound crystallizes in the space group *P*2₁/*c* where the asymmetric unit is composed of one cation, one well-ordered triflate anion, and another triflate anion that is disordered unequally (2:1) over two nearby positions. The FeN₆ coordination environment is distorted octahedral since the Fe–N bonds of the confused pyrazolyl are at least 0.02 Å shorter than those of the (inequivalent) pz* groups. At 250 K, the average Fe–N bond distance of the six bonds is 2.17(2) Å which is aligned with expectations for HS iron(II). At 100 K, the average distance shortens to 2.11(2) Å, indicative of an increasing portion (ca. 33%) of LS iron(II). For reference, the compound [Fe(^{Bn}L)₂](BF₄)₂·2CH₃CN (with an N-benzyl on the “confused” pyrazolyl and unsubstituted “normal” pyrazolyls) had an average Fe–N bond distance of 2.14 Å at 250 K (partly LS) and 1.99 Å at 100 K (fully LS).([53](#)) In *cis*-1, the average pyrazolyl ring twist is 6° at both temperatures; thus, spin crossover behavior is expected and is observed in this case, vide infra.

Figure 4. Left: Structure of *cis*-[Fe(^{HL*})₂](OTf)₂, *cis*-1, at 100 K. Middle: Photographs of a crystal at different temperature. Right: Overlay of structures obtained at 250 K (light blue) and 100 K (violet).

Table 2. Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for *cis*-1

	250 K	100 K
Bond Distances (Å)		

Fe1–N2	2.146(2)	2.0849(17)
Fe1–N11	2.173(2)	2.1089(14)
Fe1–N21	2.192(2)	2.1356(15)
Fe1–N2a	2.146(2)	2.0833(16)
Fe1–N11a	2.196(2)	2.1404(16)
Fe1–N21a	2.177(2)	2.1242(17)
Bond Angles (deg)		
N2–Fe1–N11	82.57(9)	83.46(6)
N2–Fe1–N21	83.77(9)	84.47(6)
N11–Fe1–N21	85.25(9)	86.14(5)
N2a–Fe1–N11a	82.36(9)	83.52(6)
N2a–Fe1–N21a	83.75(9)	84.29(6)
N11a–Fe1–N21a	85.52(9)	86.59(6)
Bond Torsions (deg)		
C4C3–N2Fe1	–9.3(3)	–8.3(2)
C4N12–N11Fe1	2.3(3)	1.7(2)
C4N22–N21Fe1	–9.7(3)	–9.1(2)
C4aC3a–N2aFe1	–2.7(3)	–3.9(2)
C4aN12a–N11aFe1	5.5(3)	3.2(2)
C4aN22a–N21aFe1	–8.3(3)	–10.8(2)

The three-dimensional supramolecular structure of *cis*-**1** is constructed from N–H $\cdots$ O,⁽⁷³⁾ C–H $\cdots$ O,⁽⁷⁴⁾ and C–H $\cdots$ F⁽⁷⁶⁾ weak charge-assisted hydrogen-bonding interactions involving hydrogen donors of the dications and either oxygen or fluorine acceptors of the triflate anions (Table3 and Figure 5). One of the triflate anions is disordered in a 2:1 ratio over two positions; thus, the discussion will first focus on the well-ordered triflate anion with atoms O1, O2, and O3. A sheet of cations is formed in the *ac*-plane by the N–H $\cdots$ O and C–H $\cdots$ O weak hydrogen-bonding interactions involving these well-ordered triflate anions (contact nos. 1 and 4–8 in Table3). That is, a dimer is formed by a pair of triflate anions bridging two dications where O1 of the triflate interacts with the N–H of the confused pyrazolyl (N1–H1n $\cdots$ O1, 1.98 Å) on one cation and O2 interacts with the methine hydrogen, H4a, of the neighboring dication. This hydrogen-bonding interaction is in the range found for other hydrogen-bonded iron(II) SCO compounds: for instance, N–H $\cdots$ O interactions in [Fe(2,6-bis(pyrazol-3-yl)pyridine)₂](*cis*,*cis*-1,3,5-cyclohexanetricarboxylate dianion)·5.5H₂O ranging from 1.73 to 1.86 Å,⁽⁷⁷⁾ those in [Fe(2,6-bis[5-methyl-1*H*-pyrazol-3-yl]pyridine)₂](ClO₄)₂·solvate (solvate = H₂O, MeOH, or MeNO₂) ranging from 1.80 to 2.26 Å,⁽⁷⁸⁾ or those in [Fe(2-(pyrazol-1-yl)-6-(pyrazol-3-yl)pyridine)₂](ClO₄)₂ of 1.93 and 2.03 Å.⁽⁷⁹⁾ The dimers are organized into sheets parallel with the *ac*-plane (containing the two dications in the middle of the unit cell in Figure 5b) by interactions of O2 and O3 of one dimer with the hydrogens at the 4-positions of the dimethylpyrazolyl groups of neighboring dimers (interactions 7 and 8, Table3). The *ac*-sheets are stacked along the *b*-axis by hydrogen-bonding interactions with oxygen atoms of the disordered triflate (major disorder component, contact nos. 2, 9, 11, and 13; minor disorder component, contact nos. 3, 10, and 12 in Table3). Importantly, each contact with the disordered triflate falls well below the limits for NH $\cdots$ O or CH $\cdots$ O interactions and is in the range of that for medium-strength hydrogen bonds.⁽⁶⁷⁾ Similarly, the acidic methine hydrogen, H4, of one *ac*-sheet acts as a donor to triflate oxygens from an adjacent sheet (67% involve contact 9, and 33% involve contact 10, Table3) where both associated C $\cdots$ O distances are well within the accepted limits for a CH $\cdots$ O interaction.⁽⁶⁸⁾ The minor component of the disordered triflate also has a number of CH $\cdots$ F weak hydrogen-bonding interactions that serve to support the structure but will not be discussed further. The overall supramolecular structure is retained at 250 K, but all contacts are elongated versus those at 100 K.

Table 3. Geometries of Main N–H···O and C–H···O Weak Hydrogen-Bonding Interactions in *cis*-1 at 100 K

contact	donor (D)(–H)···acceptor (A)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (deg)
1	N1–H1n···O1	0.83(3)	1.98(3)	2.795(2)	170(3)
2	N1a–H1na···O1a	0.83(3)	1.96(3)	2.678(3)	143(2)
3	N1a–H1na···O1b	0.83(3)	2.29(3)	3.103(5)	165(3)
4	C2a–H2a···O2	0.95	2.55	3.243(3)	130
5	C4a–H4a···O2	1.00	2.26	3.188(2)	154
6	C24a–H24a···O2	0.98	2.48	3.401(3)	156
7	C12–H12···O2	0.95	2.56	3.445(2)	156
8	C22–H22···O3	0.95	2.48	3.190(2)	132
9	C4–H4···O2a	1.00	2.23	3.157(14)	154
10	C4–H4···O2b	1.00	2.42	3.34(3)	153
11	C2–H2···O2a	0.95	2.54	3.22(2)	128
12	C2–H2···O2b	0.95	2.57	3.29(3)	133
13	C20a–H20b···O3a	0.98	2.44	3.420(5)	176

Figure 5. Noncovalent interactions of *cis*-1. (a) Labeling of atoms involved in interactions. Hanging and completed contacts are red and green dashed lines, respectively. Pink spheres represent a minor triflate disorder component. (b) View down the *c*-axis of the unit cell with noncovalent interactions labeled in accord with [Table 3](#).

The structure of *trans*-1 was determined at 250 and 100 K; at these temperatures the crystal was light pink and violet, respectively. The crystal undergoes a reversible phase transition over this temperature range, as it is monoclinic ($P2_1/c$) at 250 K but triclinic (PT) at 100 K. In the 250 K structure, the asymmetric unit ([Figure 6a](#)) contains one well-ordered (containing S1) and one disordered triflate (containing S1a) anion in general positions and two independent Fe^{HL} units where the iron center in each is located on an inversion center thereby guaranteeing each is the *trans* isomer. The average Fe–N bond distance about Fe1a ([Table 4](#)) of 2.18(3) Å is typical of HS iron(II) whereas that about Fe1 of 2.12(3) Å is indicative of partial LS character (HS/LS). The confused pyrazolyl N–H groups in each serve as hydrogen-bond donors to oxygen atoms of triflate anions ([Figure 6b](#)). The HS complex has N–H···O interactions with the well-ordered triflate (N1aH1na···O1, 1.94 Å, 169°) while the HS/LS complex interacts with the disordered triflate (N1H1n···O3a, 2.17 Å, 167°). The well-ordered triflate also interacts with the acidic methine hydrogen of the partially LS complex (C4H4···O3, 2.30 Å, 157°) to form a chain of complexes with alternating (HS/LS) Fe1 and HS Fe1a centers along the [101] direction. A more complete analysis of the supramolecular structure is given in the [Supporting Information](#), and further discussion of the structure will continue after discussion of the 100 K structure.

Figure 6. (a) Asymmetric unit of the 250 K structure of $trans\text{-}[\text{Fe}(\text{H}^*\text{L})_2](\text{OTf})_2$, *trans*-1, with partial atom labeling, and (b) view showing the shortest three hydrogen-bonding interactions (Σ van der Waals radii $-0.4 \text{ \AA}$, cyan dotted lines) forming chains. Color key: black sticks = well-ordered triflate ion, green sticks = disordered triflate ion, pale blue sticks = HS dication with central Fe1a, pink sticks = partial HS/LS dication with central Fe1.

Table 4. Bond Distances ($\text{\AA}$), Angles (deg), and Torsion Angles (deg) for *trans*-1

250 K			100 K		100 K
Bond Distances ($\text{\AA}$)					
Fe1–N2	2.082(4)	Fe1–N2	1.942(3)	Fe1b–N2b	2.143(2)
Fe1–N12	2.129(4)	Fe1–N12	2.010(2)	Fe1b–N12b	2.172(3)
Fe1–N22	2.151(4)	Fe1–N22	1.990(2)	Fe1b–N22b	2.216(3)
Fe1a–N2a	2.145(4)	Fe1a–N2a	2.063(3)	Fe1c–N2c	2.146(3)
Fe1a–N12a	2.216(4)	Fe1a–N12a	2.125(3)	Fe1c–N12c	2.214(3)
Fe1a–N22a	2.173(3)	Fe1a–N22a	2.139(3)	Fe1c–N22c	2.179(3)
Bond Angles (deg)					
N2–Fe1–N12	84.52(16)	N2–Fe1–N12	87.77(10)	N2b–Fe1b–N12b	83.42(10)
N2–Fe1–N22	84.66(15)	N2–Fe1–N22	87.68(11)	N2b–Fe1b–N22b	83.49(10)
N12–Fe1–N22	85.17(14)	N12–Fe1–N22	87.28(10)	N12b–Fe1b–N22b	82.84(10)
N2a–Fe1–N12a	83.82(15)	N2a–Fe1a–N12a	84.98(11)	N2c–Fe1c–N12c	83.49(10)
N2a–Fe1–N22a	83.60(14)	N2a–Fe1a–N22a	84.57(10)	N2c–Fe1c–N22c	83.37(10)
N12a–Fe1–N22a	82.79(15)	N12a–Fe1a–N22a	85.62(10)	N12c–Fe1c–N22c	82.04(11)
Bond Torsions (deg)					
C4C3–N2Fe1	–3.3(6)	C4C3–N2Fe1	0.8(4)	C4bC3b–N2bFe1b	7.3(4)
C4N11–N12Fe1	–7.7(5)	C4N11–N12Fe1	0.5(3)	C4bN11b–N12bFe1b	3.9(4)
C4N21–N22Fe1	–0.8(5)	C4N21–N22Fe1	3.9(3)	C4bN21b–N22bFe1b	8.4(4)
C4aC3a–N2aFe1a	–6.7(5)	C4aC3a–N2aFe1a	–8.6(4)	C4cC3c–N2cFe1c	–5.8(4)
C4aN11a–N12aFe1a	–6.0(5)	C4aN11a–N12aFe1a	–12.5(3)	C4cN11c–N12cFe1c	–5.5(4)
C4aN21a–N22aFe1a	–3.0(5)	C4aN21a–N22aFe1a	–4.5(3)	C4cN21c–N22cFe1c	–3.0(4)

In the 100 K structure, the asymmetric unit ([Figure 7a](#)) contains three well-ordered triflate ions (containing S1, S1a, and S1b) and one disordered triflate (over two nearby positions in a 2:1 S1c:S1d ratio) on general positions and four independent Fe(^HL*) units whose metal centers are on inversion centers generating *trans* isomers by symmetry. Inspection of the Fe–N distances reveals that two of the dications with Fe1b and Fe1c are HS (av Fe–N = 2.18(4) and 2.18(3) Å, respectively) and that the dication with a central Fe1 is LS (av Fe–N = 1.98(3) Å). The last dication with Fe1a has an average Fe–N distance of 2.11(4) Å that corresponds to approximately 25–33% LS character, so is labeled HS/LS. As with the 250 K structure, the triflate ions are hydrogen-bonded to the dications via N–H...O interactions (cyan dashed lines [Figure 7b](#)). Three interactions involve well-ordered triflate ions (N1H1n...O2b, 1.81(5) Å, 176(4)°; N1bH1nb...O2b, 2.03(4) Å, 168(4)°; N1cH1nc...O1, 2.07(4) Å, 176(4)°) while the remaining interaction involves the partly LS complex and the disordered triflate (major component, N1aH1na...O3c, 2.07(4) Å, 134(4)°; minor component, N1aH1na...O1d 2.12(4) Å, 170(4)°). Two of the well-ordered triflate ions also interact with methine hydrogen on neighboring dications (C4H4...O2a 2.26 Å, 154° and C4aH4a...O3 2.21 Å, 154°) to form two separate chains. One chain along the [2 2 0] direction has alternating dications of HS Fe1c and (LS/HS) Fe1a while the other chain along the [1 1 0] direction has alternating dications of HS Fe1b and (LS) Fe1. Further details of crystal packing in the 100 K structure are found in the [Supporting Information](#). [Figure 8](#) provides comparative views of the crystal packing diagrams in the 250 K (left) and 100 K (right) structures. The crystal packing is quite similar at both temperatures, with layers of HS complexes stacked alternately with layers of complexes with partially (LS/HS) or fully LS (100 K case) complexes along the *a*-direction (250 K) or *c*-direction (100 K), or colloquially, the SCO layer. The well-ordered triflates (black sticks, [Figure 8](#)) are found in the HS layers at each temperature. The main differences in the structures occur in the SCO layers. At 250 K, the SCO layers contain partly HS/LS complexes (25–33% LS character from bond distances) and disordered triflate ions. At 100 K, one-half of the complexes in the SCO layer (25% overall) have converted to fully LS (dark violet sticks, right of [Figure 8](#)). The other half of the complexes in this layer remain (HS/LS) (25–33% LS character). So, on the basis of an estimation from bond distances, the entire sample is approximately 31–33% LS at 100 K. Coincidentally, at 100 K one-half of the triflate ions in the SCO layer (75% overall) are now fully ordered (red arrows bottom of [Figure 8](#)). Decreasing the temperature from 250 to 100 K, and the associated SCO contracts the unit cell sufficiently to lock one of the triflate ions into one position. The remaining 25% of the triflate ions are disordered. If the minor disorder component (34% occupancy) is associated with the LS component of the partial SCO, then 33.5% (25% LS + 34% occupancy × 25% HS/LS) of the total complexes in the unit cell would be LS *trans*-1 at 100 K.

(a)

(b)

Figure 7. (a) Asymmetric unit of the 100 K structure of $trans\text{-}[Fe(H^*L^*)_2](OTf)_2$, *trans*-**1**, with partial atom labeling. (b) View showing some of the shortest hydrogen-bonding interactions (Σ van der Waals radii $-0.45 \text{ \AA}$, cyan dotted lines) forming two chains. Color key: black sticks = well-ordered triflate ion, green sticks = disordered triflate ion, pale blue sticks = HS dication with central Fe1b or Fe1c, pink sticks = partial HS/LS dication with central Fe1a, dark violet sticks LS dication with central Fe1.

Figure 8. Comparison of a portion of the crystal packing diagrams in the 250 K (left) and 100 K (right) structures of *trans*-**1**. Top left: view down *c*-axis. Top right: view down *a*-axis. Bottom left: view down *a*-axis. Bottom right: view down *b*-axis. Axes color scheme: *a*-axis (red), *+b*-axis (green), and *+c*-axis (blue). Red arrows highlight transition in disorder/well-ordered triflate types upon changing temperature.

Crystals of *co*-**1** turn violet on cooling to 77 K, so single crystal X-ray diffraction experiments were performed at two temperatures, 250 K (colorless/pale blue) and 100 K (violet). Views of the 100 K structure are found

in [Figure 9](#) while bond distances and interatomic angles are listed in [Table 5](#). The asymmetric unit ([Figure 9a](#)) consists of one well-ordered triflate (with terminal atoms bound to the S1–C5 unit), one triflate that is disordered unequally over two nearby positions (84% containing S1a–C5a and 16% containing S1b–C5b), and two Fe(^HL*) moieties (one with Fe1 on an inversion center and one with Fe2 on a 2-fold rotation axis). By crystallographic symmetry, the dication with Fe1 is the *trans* isomer (angle between iron-bound “confused” nitrogens, N2–Fe1–N2' = 180.0(1)°) whereas that with Fe2 is the *cis* isomer (N2–Fe2–N2' = 92.5(2)°), [Figure 9b](#). At 250 K, the average Fe–N bond distances indicate that both the *trans* (2.17 Å) and *cis* (2.16 Å) components are HS Fe(II). At 100 K, the *trans* isomer remains HS (Fe–N_{av} 2.14 Å) while the *cis* isomer has Fe–N_{av} of 2.06(3) Å, a distance between HS (2.18 Å) and LS (ca. 1.98 Å) roughly corresponding to about 38 ± 12% HS character (overall 69% HS or 31 ± 6% SCO). It is noteworthy not only that the *trans* component has longer bond distances than the *cis* component but also that the ligand is more distorted with greater pyrazolyl ring twisting (5.8° vs 4.4° at 250 K or 4.8° vs 4.5° at 100 K) and ring tilting (171° vs 175° at 250 K or 172° vs 176° at 100 K), [Figure 9c](#). In other words, the *cis* isomer with a less distorted ligand and shorter bonds at room temperature undergoes SCO on cooling (albeit incomplete over this temperature range).

Figure 9. Views of the structure of a crystal with a 1:1 ratio of *cis*-1²⁺:*trans*-1²⁺, a crystal form called *co*-1. (a) Asymmetric unit with partial atom labeling and most hydrogen atoms removed for clarity. (b) View of the *trans* (left) and *cis* (right) dication components. (c) View of the dications down the C(methine)–H bond showing greater pz ring tilting in the *trans* isomer (left) than the *cis* isomer (right).

Table 5. Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for *co*-1

	250 K	100 K
Bond Distances (Å)		
Fe1–N2	2.1321(19)	2.103(3)
Fe1–N11	2.2059(18)	2.163(3)
Fe1–N21	2.1850(18)	2.154(3)
Fe2–N2a	2.132(2)	2.032(4)
Fe2–N11a	2.178(2)	2.087(3)
Fe2–N21a	2.156(2)	2.064(3)
Bond Angles (deg)		
N2–Fe1–N11	85.32(7)	85.68(11)
N2–Fe1–N21	84.10(7)	84.82(11)
N11–Fe1–N21	82.38(7)	83.07(10)
N2a–Fe2–N11a	85.83(8)	86.83(13)
N2a–Fe2–N21a	82.26(8)	84.35(13)
N11a–Fe2–N21a	85.94(8)	87.11(13)
Bond Torsions (deg)		
C4C3–N2Fe1	–6.1(3)	–6.1(4)

C4N12–N11Fe1	–4.9(2)	–5.0(4)
C4N22–N21Fe1	–2.2(2)	–3.2(4)
C4aC3a–N2aFe2	–6.9(3)	–5.4(4)
C4aN12a–N11aFe2	–4.5(3)	–3.8(4)
C4aN22a–N21aFe2	5.9(3)	4.4(4)

An examination of the three-dimensional supramolecular structure provides insight into why the *cis* component of *co-1* undergoes SCO but the *trans* component does not. Views of the crystal packing arrangement are found in [Figure 10](#), while [Table 6](#) lists the short noncovalent interactions that help organize the structure. The three-dimensional structures of *co-1* at 250 and 100 K are only slightly different, so the 100 K structure is discussed first. As stated above, there are two triflate anions, one well-ordered and one disordered. The three-dimensional structure can be described by only considering charge-assisted C–H $\cdots$ O weak hydrogen-bonding interactions([74](#)) with the well-ordered triflate where interactions with the disordered triflate further support the structure. The C–H $\cdots$ O interactions assemble each of the *cis* (colored orange in [Figure 10](#)) or *trans* (colored black in [Figure 10](#)) isomers into separate polymeric chains (that contain only one type of isomer) that run parallel with the *c*-axis ([Figure 10b,c](#)). The *cis* chain is organized via a trifurcated C–H $\cdots$ O interaction involving O1 as a bridging acceptor to a 5-methyl hydrogen donor (H24e) on one complex and both a methine (H4a) and a nearby 5-methyl hydrogen (H24f) donor on a neighboring complex (contacts 3, 6, and 7, [Table 6](#)). The interaction of O3 of the triflate ions attached to the *cis* chain with the methine hydrogen of the *trans* isomer (H4, contact 2, [Table 6](#)) also places *trans* isomers in chains parallel to *c* (and gives bilayer sheets parallel to the *ac*-plane), [Figure 10b,c](#). The *trans* chains are further supported by their confused pyrazolyl hydrogens as donors (H1n, H1) and oxygen atoms of disordered triflate ions (contacts 9 and 10, [Table 6](#)). The *ac*-bilayer sheets are stacked along the *b*-direction by the interaction between O2 on one sheet and a 5-methyl hydrogen of a pz* group (H24b) on an adjacent sheet (contact 5, [Table 6](#)). The other noncovalent interactions listed in [Table 6](#) further secure this structure. This packing arrangement places the minor disorder triflate component within voids of the supramolecular framework. The minor component is still hydrogen-bonded to the *trans* isomer but does not bridge neighboring *trans* isomers within the polymer chain. Moreover, there is no hydrogen bonding to the *cis* isomer. It is further noted that, at 250 K, the overall connectivity is retained but noncovalent interactions lengthen. Also, the minor triflate disorder component is not observed. Instead, there are solvent accessible voids 162 Å³ in the same location as in the 100 K structure. Thus, the *cis* component of *co-1* is more loosely packed than the *trans* component at both temperatures and presumably is freer to adopt an LS configuration at low temperature.

Figure 10. Supramolecular structure of *co-1*. (a) View of important noncovalent interactions with atom labeling. The *cis* isomer has light orange carbons as capped sticks while the *trans* isomer shows carbon as black capped sticks. Hanging and completed contacts are red and green dashed lines, respectively. Pink spheres represent a minor triflate disorder component. (b) View of unit cell down *b* with contact no. from [Table 6](#) labeled. (c) View of unit cell down *c* with contacts labeled as per [Table 6](#).

Table 6. Geometries of Selected Weak Hydrogen-Bonding Interactions in *co-1* at 100 K

contact	donor (D)(-H)⋯acceptor (A)	D–H (Å)	H⋯A (Å)	D⋯A (Å)	D–H⋯A (deg)
Ordered Triflate					
1	C2–H2⋯O3	0.95	2.60	3.286(5)	130
2	C4–H4⋯O3	1.00	2.24	3.182(5)	157
3	C4a–H4a⋯O1	1.00	2.26	3.211(4)	158
4	C14–H14a⋯O3	0.98	2.57	3.434(5)	147
5	C24–H24b⋯O2	0.98	2.46	3.366(5)	154
6	C24–H24e⋯O1	0.98	2.55	3.477(5)	158
7	C24–H24f⋯O1	0.98	2.42	3.279(5)	145
Disordered Triflate					
8	N1a–H1na⋯O3a	0.88	1.96	2.807(5)	162
9	N1–H1n⋯O1a	0.88	1.93	2.744(5)	154
10	C1–H1⋯O2a	0.95	2.45	3.395(6)	173
11	C1–H1⋯O2b	0.95	2.53	3.40(2)	153
12	C1a–H1a⋯O3b	0.95	2.54	3.20(2)	120
13	C10a–H10e⋯O2b	0.98	2.59	3.34(2)	133
14	C22a–H22e⋯F1b	0.98	2.48	3.269(18)	137
15	C22a–H22e⋯F2b	0.98	2.25	2.868(18)	122
16	C2–H2⋯F1b	0.95	2.48	2.977(18)	113

Powder X-ray Diffraction

The multiple crystal forms of **1** identified by single crystal X-ray diffraction studies prompted an investigation into the structural nature of the bulk crystalline and powder samples. First, it was found that the PXRD patterns of freshly ground bulk crystalline samples of *trans-1* or *co-1* matched those calculated from their single crystal X-ray diffraction data. The data for ground, air-dried crystals of *trans-1*·2CH₃CN mostly matched the calculated pattern but had reflections for desolvated forms, [Figure 11a,b](#). If the initially violet *trans-1*·2CH₃CN is subjected to room-temperature evacuation, samples become colorless and PXRD data shows a new phase ([Figure 11c,d](#)) for *trans-1*·CH₃CN, as suggested by NMR and combustion analysis. This new phase only very slowly (several hours) converts with heating at 70 °C under vacuum to *trans-1* ([Figure 11e–g](#)). In contrast, samples of *trans-1*·4CH₃CN readily lose solvent even at room temperature (neither heating nor evacuation is necessary) to give PXRD patterns identical with that of *trans-1* ([Figure S5](#)). Samples of as-formed powders of **1** crystallized at room temperature by Et₂O vapor diffusion had PXRD patterns that were consistent with an admixture of crystalline phases *cis-1* and *trans-1*. It is noted that because of the similarity in unit cells at room temperature these two PXRD patterns are strikingly similar ([Figure S6](#)) but are distinguishable by peaks at 2θ (deg) = 7.3 (*trans*), 14.5 and 14.7 (*cis*) versus 14.4 and 14.8 (*trans*), 19.4 (*cis*) versus 19.6 (*trans*), 25.0 (*cis*) versus 25.2 (*trans*), 27.8 (*trans*), and 29.4 (*cis*). Finally, the PXRD patterns reveal that the Et₂O-washed, colorless, as-formed powders of **1** are mixtures *trans-1*, *cis-1*, and sometimes *co-1*. As described more fully in the [Supporting Information](#), the relative composition of the mixture depends on the temperature of the reaction mixture and that at which solvent was removed under vacuum; both are controlled by solution isomerization equilibrium (vide infra)

where high temperatures favor greater proportions of *cis*-**1** and/or *co*-**1** whereas room-temperature reactions and distillations gave mixtures that favored *trans*-**1** (Figures S6 and S7).

Figure 11. Calculated (blue dashed traces) and experimental (black traces) powder X-ray diffractograms (Cu K α radiation, 295 K) for various stages of desolvation of [Fe(ᐢL^*) $_2$](OTf) $_2$ ·2CH $_3$ CN, *trans*-**1**·2CH $_3$ CN. (a) Calculated pattern for *trans*-**1**·2CH $_3$ CN. (b) Air-dried, ground crystals of *trans*-**1**·2CH $_3$ CN. (c) Crystals of *trans*-**1**·2CH $_3$ CN dried under vacuum at 295 K for 5 min to give pink powder. (d) Crystals of *trans*-**1**·2CH $_3$ CN dried under vacuum at 295 K for 1 h to give colorless powder. (e) Crystals of *trans*-**1**·2CH $_3$ CN dried under vacuum at 343 K 1 h. (f) Crystals of *trans*-**1**·2CH $_3$ CN dried under vacuum at 343 K for 12 h. (g) Calculated pattern of *trans*-**1** from 250 K single crystal X-ray diffraction experiment.

Magnetometry

The temperature dependences of the magnetic properties of air-dried crystals of *co*-**1**, a powder sample of *cis*-**1** contaminated with minor amounts of *trans*-**1**, and phase pure powders of *trans*-**1** and *trans*-**1**·CH $_3$ CN were investigated by SQUID magnetometry. Figure 12 gives the magnetic data, plotted as $\chi_m T$ versus T . The magnetic data for *co*-**1** (Figure 12a) shows a gradual SCO beginning near 300 K ($\chi_m T = 3.2 \text{ cm}^3 \text{ K mol}^{-1}$, 100% HS; theor $\chi_m T = 3.25 \text{ cm}^3 \text{ K mol}^{-1}$ with orbital angular momentum contribution to spin-only moment) that stops after $\chi_m T$ reaches $1.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 80 K (68% HS, 32% SCO). This behavior is aligned with the crystallographic data that showed that only the *cis* component undergoes partial SCO. The $\chi_m T$ value at 100 K of $2.2 \text{ cm}^3 \text{ K mol}^{-1}$ indicates 23% SCO which is on par with $31 \pm 6\%$ SCO estimated from bond distance analysis. As shown in Figure 12b, $\chi_m T$ in *cis*-**1** maintains a constant value from 300 K to about 165 K of $3.2 \text{ cm}^3 \text{ K mol}^{-1}$ consistent with 100% HS Fe(II). Between 80 and 20 K, the $\chi_m T$ value drops to a constant value of $2.0 \text{ cm}^3 \text{ K mol}^{-1}$, indicating about 72% HS Fe(II). Given the X-ray structural data that showed a rather long average Fe–N bond distance of 2.11(2) Å at 100 K (consistent with an incomplete $30 \pm 5\%$ spin crossover) and a triflate disordered in a near 2:1 ratio over two sites, we tentatively ascribe the unusual magnetic behavior as the result of the spin crossover of the minor disorder component in *cis*-**1**; the majority of the sample remains HS. The subtle “hump” in the curve near 100 K is due to *trans*-**1**, as described next. For *trans*-**1**, $\chi_m T$ at 300 K is $3.1 \text{ cm}^3 \text{ K mol}^{-1}$ and reduces to a constant value of $2.0 \text{ cm}^3 \text{ K mol}^{-1}$ upon cooling to 80 K or below, in accord with about 28% SCO on cooling, similar to the behavior for *cis*-**1**. As opposed to the gradual transition in *cis*-**1**, that of *trans*-**1** occurs in two unequal steps at $T_1 = 250 \text{ K}$ (18% SCO) and $T_2 = 105 \text{ K}$ (10% SCO) with the former being more gradual (temperature range of transition, ΔT , $\sim 78 \text{ K}$) than the latter ($\Delta T \sim 22 \text{ K}$). The monoclinic/triclinic crystal phase transition is responsible for the abruptness of the low temperature SCO transition. In particular, the 10% SCO of this second step observed from the magnetometry data is similar to the 8.5% minor component of the disordered triflate associated with the LS component of the HS/LS iron site in the 100 K structure. Finally, the sample of *trans*-**1**·CH $_3$ CN of unknown structure undergoes a complete but gradual SCO with $T_{1/2}$ of 156 K.

Figure 12. Magnetic susceptibility data obtained from hand-separated crystals of (a) *co-1*, (b) *cis-1*, (c) *trans-1*, and (d) *trans-1*·CH₃CN.

Solution Properties

The properties of the various crystalline forms in solution were investigated first by their crystallization behavior and then by ¹H NMR spectroscopy. First, dissolution of any of the crystalline forms followed by either evaporation or Et₂O vapor diffusion over about 16 h (or longer) produces a mixture of crystalline forms indicating that the complexes undergo isomerization in solution. When violet crystals of *trans-1*·2CH₃CN are dissolved in CH₃CN at room temperature, the resulting solution is colorless and paramagnetic ($\mu_{\text{eff}} = 5.0 \mu_{\text{B}}$), indicating that the LS nature of this complex is due to crystal packing effects (vide infra, [DFT Calculations](#) section). The ¹H NMR spectrum of *C*_{2h} symmetric *trans-1*·2CH₃CN (or of *trans-1*·4CH₃CN) immediately after dissolution consists of six resonances: five for the hydrogens of the complex and one for CH₃CN. The resonance near 20 ppm consists of three overlapping signals, which is evident from integration and VT NMR experiments ([Figure S8](#)). Over time, new resonances characteristic of a *C*₂ symmetric *cis* isomer (notably near 51, 48, 45, and 21 ppm, [Figure 13](#) and [Figure S9](#)) grow in intensity at the expense of those for *trans-1* until an equilibrium mixture of *trans* and *cis* isomers is reached. By monitoring the *trans* to *cis* isomerization at 22, 50, 60, and 70 °C, full kinetic and thermodynamic parameters for the equilibrium ([eq 1](#)) were obtained (see [Supporting Information](#) for full details).

(1) The *trans* to *cis* isomerization reaction (forward reaction [eq 1](#)) is first order in *trans-1* with a half-life of 36.5 h at 295 K and only 19.4 min at 343 K. The activation barrier for this conversion is only 83 kJ/mol, which is much smaller than typical metal–nitrogen bond dissociation enthalpies (ca. 300–400 kJ/mol).^[80] Thus, the isomerization likely occurs via bond stretching and torsional modes of vibration rather than by dissociation. An observation supporting this assertion is that when solutions of **1** are spiked with excess ligand, the spectrum consists of two separate sets of resonances, one set for **1** (as a mixture of *cis* and *trans*) and one set for the ligand; the ligand exchange is slow on the time scale of the experiment. At room temperature (295 K), the isomerization proceeds until an equilibrium *cis/trans* ratio ($K_{\text{eq},295}$) of 0.66 is achieved. At 343 K, the equilibrium favors the *cis* isomer, $K_{\text{eq},343} = 2.2$. The van't Hoff plot at four different temperatures ([Figure S13](#)) gives $\Delta H = +22$ kJ/mol and $\Delta S = +69$ J/K mol. The small positive value of ΔS is expected due to the lower symmetry of the *cis* versus *trans* isomer. However, the endothermic nature of the *trans* to *cis* transformation was not expected (nor was it predicted by DFT, vide infra) given the otherwise identical HS FeN₆ kernels. The enthalpic contribution must originate from discrepancies in ion pairing between each isomer, or less likely in solvation, due to the different disposition of N–H bond donors. Perhaps the smaller electron repulsion of hydrogen-bonded triflate anions in the *trans* versus *cis* isomer may be responsible for the difference in enthalpy. We will further examine this line of query in future studies that probe anion effects on SCO of this complex cation. The

difference in the apparent composition of the as-formed powders depending on whether the solution is heated or not during evaporation (Figure S7) originates from the values of ΔH and ΔS which indicate that the *cis* isomer is favored above 311 K (38 °C). In a related manner, NMR monitoring of the formation of **1** in situ by dissolving the ligand and $\text{Fe}(\text{OTf})_2 \cdot 2\text{CH}_3\text{CN}$ in CD_3CN initially shows a mixture of isomers that slightly favors *trans*-**1** but that converts rapidly to the equilibrium mixture after heating (Figures S9b and S11). The ability to isolate pure *trans*-**1**·2 CH_3CN from solutions of as-formed powders of **1** in CH_3CN when stored in a freezer (253 K) is facilitated by $K_{\text{eq},253} = 0.15$ and solubility differences in isomers. Finally, the limited boiling temperature of CH_3CN (355 K), the equilibrium constant at that temperature, $K_{\text{eq},355} = 2.3$, and the larger rate constant of the reverse versus the forward reaction in eq 1 all have hampered the ability to isolate pure *cis*-**1** in the bulk from this solvent.

Figure 13. Overlay of the downfield portions of the 295 K ^1H NMR spectra of a 0.02 M solution of *trans*-**1**·2 CH_3CN in CD_3CN acquired at five time points after dissolution: 5 min (blue), 240 min (black), 480 min (black), 1380 min (black), and 1800 min (red). The green arrows highlight emergence of resonances for the *cis* isomer while the purple arrows indicate the receding resonances for the *trans* isomer.

DFT Calculations

To gain further insight into the nature of the electronic ground state and relative stability of isomeric dications in **1**, theoretical calculations were performed using a density functional method, (OPBE/def2-SV(P) (C,H,N), def2-QZVPP (Fe)/PCM (CH_2Cl_2), that has been successfully used for other iron complexes that undergo spin crossover.^[70] First, for both isomers DFT calculations predict the quintet state to be lowest in energy at 298 K. This is in line with the experimental observation that, in solution, both isomers are paramagnetic HS species. The singlet state was higher in energy by 21 and 22 kJ/mol for the *trans* and *cis* isomers, respectively. These small values of spin-state splitting are in the range where spin crossover is expected. Finally, the isomers are nearly degenerate, with the *trans* isomer being only 1–2 kJ more stable than the *cis* isomer in either the quintet or singlet states. This slight preference may be due to the lower interligand repulsions in the *trans* (two pz^* methyl/ pz^* methyl clashes) versus the *cis* (three pz^* methyl/ pz^* methyl clashes) isomer, Figure 14. If the isomers are degenerate, then one may expect a statistical 2:1 ratio of *cis*:*trans* isomers (the value achieved in the high temperature solution NMR studies). Thus, the DFT calculations are surprisingly in rather good qualitative agreement with the experimental solution isomerization equilibrium despite not accounting for potential electrostatic interactions with anions. As mentioned above, perhaps neglecting these latter interactions in the computations is responsible for the discrepancies between calculated and experimental ΔH and ΔS values.

Figure 14. DFT calculated geometries of the LS form of each isomer of **1** viewed down the H–C_{methine}...Fe vector, showing areas of interligand steric interactions as filled pink circles.

Conclusions

Complex **1**, [Fe(^HL*)]₂(OTf)₂, was initially prepared to compare electronic and magnetic properties with the parent complex [Fe(^HL)₂](OTf)₂, **2** (with a $T_{1/2}$ near 360 K). It was expected that the interligand steric interactions among methyl substituents on the pyrazolyl rings in **1** should lower $T_{1/2}$ (i.e., stabilize the HS state) versus the parent complex. Indeed, **1** was found to be HS in solution at room temperature in contrast to the LS complex **2**. A secondary benefit of adding methyls to the normal pyrazolyl rings is that **1** enjoyed much greater solubility in CH₃CN than **2** which greatly facilitated the solution NMR studies of the former. The fairly significant temperature dependence of the solution isomerization equilibrium (eq 1) observed for **1** by NMR was surprising since both the enthalpic and entropic contributions to the equilibrium were expected to be minimal on the basis of the consideration of only FeN₆ cores and, perhaps, the change in point group symmetry. It would seem that interactions with the triflate anions play an important role in governing the temperature dependence. Not only does the *trans* isomer have fewer interligand steric interactions than the *cis* isomer, but also if the triflate ions here hydrogen-bonded to the acidic N–H group in each isomer, then the triflate ions in the *trans* isomer would be further apart than in the *cis* isomer, minimizing anion–anion repulsions making the *trans* isomer more stable than the *cis* isomer. Regardless, the temperature dependence of the equilibria provided insight into conditions that would favor one isomer over another. Indeed, six different crystalline forms of **1** could be prepared: *cis*-**1**, *co*-**1**, and *trans*-**1**·*x*CH₃CN (*x* = 0, 1, 2, 4). It is worth comment that the rich structural chemistry, as observed for **1**, was not discovered in the parent complex, [Fe(^HL)₂](OTf)₂. Such behavior was missed due in part to the relatively high pseudosymmetry of the “confused” and “normal” pyrazolyl rings that results in crystallographically disordered dications which prevented definitive identification of isomers in the solid state and the low solubility in solution that stymied NMR characterization. It is also of interest that CH₃CN solvates of *cis*-**1** have neither been isolated nor identified by PXRD. Perhaps this is a fortuitous consequence of the solution equilibrium. It is also possible that the juxtaposition of the two N–H groups allows for chelation of one triflate anion in solution (the other anion being either outer sphere or associated with the acidic methine) that outcompetes solvent for hydrogen bonding. In the case of the *trans* isomer, only monodentate coordination to the anion or solvent is possible and gives rise to the observed mixture of solvate and solvate-free forms. Regardless, five of the six crystalline forms were HS in the solid state at room temperature with *trans*-**1**·2CH₃CN being the LS exception. The crystal packing of this latter derivative is remarkably efficient, being denser than *co*-**1** (and only slightly less dense than *trans*-**1** or *cis*-**1**) despite having two solvate CH₃CN molecules included in the lattice. Four of the derivatives (*cis*-**1**, *co*-**1**, and *trans*-**1**·*x*CH₃CN (*x* = 0, 1)) showed SCO by magnetometry, and only the structure of the latter remains unknown. It is now clear after examining the average pz twist angles of *cis*-**1** (6°), *co*-**1** (*cis* component 4°, *trans* component 6°), *trans*-**1**·4CH₃CN (10°), and [Fe(^TL)₂](BF₄)₂ (8°) reported earlier that the empirical “11° rule” needs to be amended, at least for N-confused scorpionates, to state the following: If pz twisting is above 11° then SCO will not be observed, but if pyrazolyl ring twisting is less than 11°, SCO is not guaranteed. Clearly other ligand distortions (pz-tilting <175°) or other crystal packing effects are

sufficient to prevent SCO of these iron(II) scorpionates. For three derivatives with known structures and that undergo SCO, the triflate anion plays an important role in their magnetic behavior. In all three cases, at least one of the triflate ions is disordered and the minor disorder component is responsible for SCO behavior. The ability for the triflate to adopt different geometries thereby giving more room for HS/LS interconversions in the dications may be promoted by the incompatibility of the C_{3v} point symmetry of the anion with 2-fold point symmetry of the dication in most (the observed) space groups, forcing the anion to occupy crystallographic general positions (and increasing probability for disordered structures). Finally, one of the unique design features of these N-confused C-scorpionates is the availability of an N–H moiety on the confused pyrazolyl ring that can be involved in hydrogen-bonding interactions with either anions or solvent. It remains unclear whether these weak hydrogen-bonding interactions have any effect on cooperativity, as both abrupt and gradual SCO transitions have been observed among the four reported examples. Future studies will be directed toward developing a better understanding of the relationships between symmetry and hydrogen-bonding capabilities of anions on the cooperativity of SCO in these systems by using judicious choices of hydrogen-bonding acceptors.

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](https://pubs.acs.org/doi/10.1021/acs.inorgchem.8b03454) at DOI: [10.1021/acs.inorgchem.8b03454](https://doi.org/10.1021/acs.inorgchem.8b03454).

Supramolecular structure description, PXRD and NMR data, and computational details ([PDF](#))

File of models ([XYZ](#))

[ic8b03454_si_002.xyz \(13.54 kb\)](#)

pdf

[ic8b03454_si_001.pdf \(2.51 MB\)](#)

Accession Codes

CCDC [1883589–1883594](#) and [1917600–1917601](#) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Author Contributions

All authors have approved the final version of this manuscript.

The authors declare no competing financial interest.

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>.

Acknowledgments

J.R.G. thanks Dr. Gregory Morrison (University of South Carolina) for magnetic measurements and discussions.
J.R.G. also thanks Marquette University for support.

References

- 1** Halcrow, M. A. *Spin Crossover Materials, Properties and Applications*; John Wiley & Sons, Ltd., **2013**.
- 2** Gutlich, P.; Goodwin, H. A. *Spin Crossover in Transition Metal Compounds I-III*; Topics in Current Chemistry; Springer-Verlag: Berlin, Germany, **2004**; Vol. 233–235.
- 3** Gütlich, P.; Hauser, A.; Spiering, H. Thermal and Optical Switching of Iron(II) Complexes. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024– 2054, DOI: 10.1002/anie.199420241
- 4** Gütlich, P.; Garcia, Y.; Goodwin, H. A. Spin crossover phenomena in Fe(II) complexes. *Chem. Soc. Rev.* **2000**, *29*, 419– 427, DOI: 10.1039/b003504l
- 5** Gütlich, P. Spin transition in iron(II) complexes induced by heat, pressure, light, and nuclear decay. *Hyperfine Interact.* **1987**, *33*, 105– 132, DOI: 10.1007/BF02394103
- 6** Levchenko, G. G.; Khristov, A. V.; Varyukhin, V. N. Spin crossover in iron(II)-containing complex compounds under a pressure. *Low Temp. Phys.* **2014**, *40*, 571– 585, DOI: 10.1063/1.4891445
- 7** Drickamer, H. G. Electronic transfer reactions in transition metal compounds at high pressure. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 39– 47, DOI: 10.1002/anie.197400391
- 8** Renz, F. Physical and chemical induced spin crossover. *J. Phys.: Conf. Ser.* **2010**, *217*, 012022, DOI: 10.1088/1742-6596/217/1/012022
- 9** Nègre, N.; Conséjo, C.; Goiran, M.; Bousseksou, A.; Varret, F.; Tuchagues, J. P.; Barbaste, R.; Askénazy, S.; Haasnoot, J. G. Spin transitions in a series of FeII molecular complexes induced by a strong-pulsed magnetic field. *Physica B* **2001**, *91*, 294– 311, DOI: 10.1016/S0921-4526(00)00616-5
- 10** Unruh, D.; Homenya, P.; Kumar, M.; Sindelar, R.; Garcia, Y.; Renz, F. Spin state switching of metal complexes by visible light or hard X-rays. *Dalton Trans.* **2016**, *45*, 14008– 14018, DOI: 10.1039/C6DT01745B
- 11** Létard, J.-F. Photomagnetism of iron(II) spin crossover complexes—the T(LIESST) approach. *J. Mater. Chem.* **2006**, *16*, 2550– 2559, DOI: 10.1039/B603473J
- 12** Lefter, C.; Tan, R.; Dugay, J.; Tricard, S.; Molnár, G.; Salmon, L.; Carrey, J.; Nicolazzi, W.; Rotaru, A.; Bousseksou, A. Unidirectional electric field-induced spin-state switching in spin crossover based microelectronic devices. *Chem. Phys. Lett.* **2016**, *644*, 138– 141, DOI: 10.1016/j.cplett.2015.11.036
- 13** Kumar, K. S.; Ruben, M. Emerging trends in spin crossover (SCO) based functional materials and devices. *Coord. Chem. Rev.* **2017**, *346*, 176– 205, DOI: 10.1016/j.ccr.2017.03.024
- 14** Lefter, C.; Davesne, V.; Salmon, L.; Molnar, G.; Demont, P.; Rotaru, A.; Bousseksou, A. Charge transport and electrical properties of spin crossover materials: towards nanoelectronic and spintronic devices. *Magnetochemistry* **2016**, *2*, 18, DOI: 10.3390/magnetochemistry2010018
- 15** Holovchenko, A.; Dugay, J.; Gimenez-Marques, M.; Torres-Cavanillas, R.; Coronado, E.; van der Zant, H. S. J. Near room-temperature memory devices based on hybrid spin crossover@SiO₂ nanoparticles coupled to single-layer graphene nanoelectrodes. *Adv. Mater.* **2016**, *28*, 7228– 7233, DOI: 10.1002/adma.201600890
- 16** Manrique-Juarez, M. D.; Mathieu, F.; Shalabaeva, V.; Cacheux, J.; Rat, S.; Nicu, L.; Leichle, T.; Salmon, L.; Molnar, G.; Bousseksou, A. A Bistable Microelectromechanical System Actuated by Spin crossover Molecules. *Angew. Chem., Int. Ed.* **2017**, *56*, 8074– 8078, DOI: 10.1002/anie.201702739
- 17** von Ranke, P. J. A microscopic refrigeration process triggered through spin crossover mechanism. *Appl. Phys. Lett.* **2017**, *110*, 181909, DOI: 10.1063/1.4982792
- 18** Kucheriv, O. I.; Oliynyk, V. V.; Zagorodnii, V. V.; Launets, V. L.; Gural'skiy, I. A. Spin crossover Materials towards Microwave Radiation Switches. *Sci. Rep.* **2016**, *6*, 38334, DOI: 10.1038/srep38334

- 19** Thorarinsdottir, A. E.; Gaudette, A. I.; Harris, T. D. Spin crossover and high-spin iron(II) complexes as chemical shift ^{19}F magnetic resonance thermometers. *Chem. Sci.* **2017**, *8*, 2448–2456, DOI: 10.1039/C6SC04287B
- 20** Jeon, I.-R.; Park, J. G.; Haney, C. R.; Harris, T. D. Spin crossover iron(II) complexes as PARACEST MRI thermometers. *Chem. Sci.* **2014**, *5*, 2461–2465, DOI: 10.1039/C4SC00396A
- 21** Brooker, S. Spin crossover with thermal hysteresis: practicalities and lessons learnt. *Chem. Soc. Rev.* **2015**, *44*, 2880–2892, DOI: 10.1039/C4CS00376D
- 22** Polymorphs:
 - (a) Shatruk, M.; Phan, H.; Chrisostomo, B. A.; Suleimenova, A. Symmetry-Breaking Structural Phase Transitions in Spin crossover Complexes. *Coord. Chem. Rev.* **2015**, *289–290*, 62–73, DOI: 10.1016/j.ccr.2014.09.018 .
 - (b) Tao, J.; Wei, R.-J.; Huang, R.-B.; Zheng, L.-S. Polymorphism in Spin crossover Systems. *Chem. Soc. Rev.* **2012**, *41*, 703–737, DOI: 10.1039/C1CS15136C
- 23** (a) Vela, S.; Paulsen, H. Deciphering Crystal Packing Effects in the Spin Crossover of six $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2$ Solvatomorphs. *Dalton Trans* **2019**, *48*, 1237–1245, DOI: 10.1039/C8DT04394A .
- (b) Bartual-Murgui, C.; Codina, C.; Roubeau, O.; Aromí, G. A Sequential Method to Prepare Polymorphs and Solvatomorphs of $[\text{Fe}(\text{1,3-bpp})_2](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 2$) with Varying Spin-Crossover Behaviour. *Chem. - Eur. J.* **2016**, *22*, 12767–12777, DOI: 10.1002/chem.201601843
- 24** (a) Berdiell, I. C.; Kulmaczewski, R.; Cespedes, O.; Halcrow, M. A. An Incomplete Spin Transition Associated with a $Z' = 1$ to $Z' = 24$ Crystallographic Symmetry Breaking. *Chem. Eur. J.* **2018**, *24*, 5055–5059, DOI: 10.1002/chem.201704896 .
- (b) Craig, G. A.; Roubeau, O.; Aromí, G. Spin state switching in 2,6-bis(pyrazol-3-yl)pyridine (3-bpp) based Fe(II) complexes. *Coord. Chem. Rev.* **2014**, *269*, 13–31, DOI: 10.1016/j.ccr.2014.02.002
- 25** Roubeau, O. Triazole-Based One-Dimensional Spin crossover Coordination Polymers. *Chem. - Eur. J.* **2012**, *18*, 15230–15244, DOI: 10.1002/chem.201201647
- 26** Olguin, J.; Brooker, S. Spin crossover active iron(II) complexes of selected pyrazole-pyridine/pyrazine ligands. *Coord. Chem. Rev.* **2011**, *255*, 203–240, DOI: 10.1016/j.ccr.2010.08.002
- 27** Munoz, M. C.; Real, J. A. Thermo-, piezo-, photo- and chemo-switchable spin crossover iron(II)-metallocyanate based coordination polymers. *Coord. Chem. Rev.* **2011**, *255*, 2068–2093, DOI: 10.1016/j.ccr.2011.02.004
- 28** Goodwin, H. A. Spin crossover in iron(II) tris(diimine) and bis(terimine) systems. *Top. Curr. Chem.* **2004**, *233*, 59–90, DOI: 10.1007/b13529
- 29** Phan, H.; Hrudka, J. J.; Igimbayeva, D.; Lawson Daku, L. M.; Shatruk, M. A Simple Approach for Predicting the Spin State of Homoleptic Fe(II) Tris-diimine Complexes. *J. Am. Chem. Soc.* **2017**, *139*, 6437–6447, DOI: 10.1021/jacs.7b02098
- 30** Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial Press: London, **1999**.
- 31** Pettinari, C. *Scorpionates II: Chelating Borate Ligands*; Imperial Press: London, **2008**.
- 32** Long, G. J.; Grandjean, F.; Reger, D. L. Spin Crossover in Pyrazolylborate and Pyrazolylmethane Complexes. *Top. Curr. Chem.* **2004**, *233*, 91–122, DOI: 10.1007/b13530
- 33** Lavrenova, L. G.; Shakirova, O. G. Spin Crossover and Thermochromism of Iron(II) Coordination Compounds with 1,2,4-Triazoles and Tris(pyrazol-1-yl)methanes. *Eur. J. Inorg. Chem.* **2013**, *2013*, 670–682, DOI: 10.1002/ejic.201200980
- 34** Real, J. A.; Muñoz, M. C.; Faus, J.; Solans, X. Spin Crossover in Novel Dihydrobis(1-pyrazolyl)borate $[\text{H}_2\text{B}(\text{pz})_2]$ -Containing Iron(II) Complexes. Synthesis, X-ray Structure, and Magnetic Properties of $[\text{FeL}\{\text{H}_2\text{B}(\text{pz})_2\}_2]$ ($\text{L} = 1,10\text{-Phenanthroline}$ and $2,2'\text{-Bipyridine}$). *Inorg. Chem.* **1997**, *36*, 3008–3013, DOI: 10.1021/ic960965c
- 35** (a) Moliner, N.; Salmon, L.; Capes, L.; Muñoz, M. C.; Létard, J.-F.; Bousseksou, A.; Tuchagues, J.-P.; McGarvey, J. J.; Dennis, A. C.; Castro, M.; Burriel, R.; Real, J. A. Thermal and Optical Switching of Molecular Spin

States in the $\{[\text{FeL}(\text{H}_2\text{B}(\text{pz})_2)_2]\}$ Spin crossover System (L = bpy, phen). *J. Phys. Chem. B* **2002**, *106*, 4276– 4283, DOI: 10.1021/jp013872b .

- (b) Galet, A.; Gaspar, A. B.; Agusti, G.; Muñoz, M. C.; Levchenko, G.; Real, J. A. Pressure Effect Investigations on the Spin Crossover Systems $\{\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{bipy})\}$ and $\{\text{Fe}[\text{H}_2\text{B}(\text{pz})_2]_2(\text{phen})\}$. *Eur. J. Inorg. Chem.* **2006**, *2006*, 3571– 3573, DOI: 10.1002/ejic.200600517
- 36** Xue, S.; Guo, Y.; Rotaru, A.; Müller-Bunz, H.; Morgan, G. G.; Trzop, E.; Collet, E.; Oláh, J.; Garcia, Y. Spin Crossover Behavior in a Homologous Series of Iron(II) Complexes based on Functionalized Bipyridyl Ligands. *Inorg. Chem.* **2018**, *57*, 9880– 9891, DOI: 10.1021/acs.inorgchem.8b00850
- 37** Moertel, M.; Witt, A.; Heinemann, F. W.; Bochmann, S.; Bachmann, J.; Khusniyarov, M. M. Synthesis, Characterization, and Properties of Iron(II) Spin- Crossover Molecular Photoswitches Functioning at Room Temperature. *Inorg. Chem.* **2017**, *56*, 13174– 13186, DOI: 10.1021/acs.inorgchem.7b01952
- 38** Ru, J.; Yu, F.; Shi, P.-P.; Jiao, C.-Q.; Li, C.-H.; Xiong, R.-G.; Liu, T.; Kurmoo, M.; Zuo, J.-L. Three Properties in One Coordination Complex: Chirality, Spin Crossover, and Dielectric Switching. *Eur. J. Inorg. Chem.* **2017**, *2017*, 3144– 3149, DOI: 10.1002/ejic.201700609
- 39** Luo, Y.-H.; Nihei, M.; Wen, G.-J.; Sun, B.-W.; Oshio, H. Ambient-Temperature Spin-State Switching Achieved by Protonation of the Amino Group in $[\text{Fe}(\text{H}_2\text{Bpz}_2)_2(\text{bipy-NH}_2)]$. *Inorg. Chem.* **2016**, *55*, 8147– 8152, DOI: 10.1021/acs.inorgchem.6b01193
- 40** Mahfoud, T.; Molnár, G.; Cobo, S.; Salmon, L.; Thibault, C.; Vieu, C.; Demont, P.; Bousseksou, A. Electrical properties and non-volatile memory effect of the $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$ spin crossover complex integrated in a microelectrode device. *Appl. Phys. Lett.* **2011**, *99*, 053307, DOI: 10.1063/1.3616147
- 41** Davesne, V.; Gruber, M.; Studniarek, M.; Doh, W. H.; Zafeiratos, S.; Joly, L.; Sirotti, F.; Silly, M. G.; Gaspar, A. B.; Real, J. A.; Schmerber, G.; Bowen, M.; Weber, W.; Boukari, S.; Da Costa, V.; Arabski, J.; Wulfhekel, W.; Beaurepaire, E. Hysteresis and change of transition temperature in thin films of $\text{Fe}\{[\text{Me}_2\text{Pyrz}]_3\text{BH}\}_2$, a new sublimable spin crossover molecule. *J. Chem. Phys.* **2015**, *142*, 194702, DOI: 10.1063/1.4921309
- 42** Iasco, O.; Boillot, M.-L.; Bellec, A.; Guillot, R.; Rivière, E.; Mazerat, S.; Nowak, S.; Morineau, D.; Brosseau, A.; Miserque, F.; Repain, V.; Mallah, T. The disentangling of hysteretic spin transition, polymorphism and metastability in bistable thin films formed by sublimation of bis(scorpionate) Fe(II) molecules. *J. Mater. Chem. C* **2017**, *5*, 11067– 11075, DOI: 10.1039/C7TC03276E
- 43** Ossinger, S.; Naggert, H.; Kipgen, L.; Jasper-Toennies, T.; Rai, A.; Rudnik, J.; Nickel, F.; Arruda, L. M.; Bernien, M.; Kuch, W.; Berndt, R.; Tuczek, F. Vacuum-Evaporable Spin crossover Complexes in Direct Contact with a Solid Surface: Bismuth versus Gold. *J. Phys. Chem. C* **2017**, *121*, 1210– 1219, DOI: 10.1021/acs.jpcc.6b10888
- 44** Beniwal, S.; Zhang, X.; Mu, S.; Naim, A.; Rosa, P.; Chastanet, G.; Letard, J.-F.; Liu, J.; Sterbinsky, G. E.; Arena, D. A.; Dowben, P. A.; Enders, A. Surface-induced spin state locking of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ spin crossover complex. *J. Phys. (Paris)* **2016**, *28*, 206002, DOI: 10.1088/0953-8984/28/20/206002
- 45** Naggert, H.; Rudnik, J.; Kipgen, L.; Bernien, M.; Nickel, F.; Arruda, L. M.; Kuch, W.; Naether, C.; Tuczek, F. Vacuum-evaporable spin crossover complexes: physicochemical properties in the crystalline bulk and in thin films deposited from the gas phase. *J. Mater. Chem. C* **2015**, *3*, 7870– 7877, DOI: 10.1039/C5TC00930H
- 46** Bernien, M.; Naggert, H.; Arruda, L. M.; Kipgen, L.; Nickel, F.; Miguel, J.; Hermanns, C. F.; Krüger, A.; Krüger, D.; Schierle, E.; Weschke, E.; Tuczek, F.; Kuch, W. Highly Efficient Thermal and Light-Induced Spin-State Switching of an Fe(II) Complex in Direct Contact with a Solid Surface. *ACS Nano* **2015**, *9*, 8960– 8966, DOI: 10.1021/acs.nano.5b02840
- 47** Milek, M.; Heinemann, F. W.; Khusniyarov, M. M. Spin Crossover Meets Diarylethenes: Efficient Photoswitching of Magnetic Properties in Solution at Room Temperature. *Inorg. Chem.* **2013**, *52*, 11585– 11592, DOI: 10.1021/ic401960x

- 48** Goodman, M. A.; Nazarenko, A. Y.; Casavant, B. J.; Li, Z.; Brennessel, W. W.; DeMarco, M. J.; Long, G.; Goodman, M. S. Tris(5-methylpyrazolyl)methane: Synthesis and Properties of Its Iron(II) Complex. *Inorg. Chem.* **2012**, *51*, 1084– 1093, DOI: 10.1021/ic2022038
- 49** Goodman, M. A.; DeMarco, M. J.; Tarasek, S. E.; Nazarenko, A. Y.; Brennessel, W.; Goodman, M. S. Iron complexes of tris(pyrazolyl)ethane ligands methylated in the 3-, 4-, and 5-positions. *Inorg. Chim. Acta* **2014**, *423*, 358– 368, DOI: 10.1016/j.ica.2014.08.046
- 50** Sohrin, Y.; Kokusen, H.; Matsui, M. Control of Ligand Field Strength through Intra- and Interligand Contact. Octahedral Iron(II) Poly(pyrazolyl)borate Complexes. *Inorg. Chem.* **1995**, *34*, 3928– 3934, DOI: 10.1021/ic00119a014
- 51** Hamon, P.; Thépot, J.-Y.; Le Floch, M.; Boulon, M.-E.; Cador, O.; Golhen, S.; Ouahab, L.; Fadel, L.; Saillard, J.-Y.; Hamon, J.-R. Dramatic Remote Substituent Effects on the Electronic Spin State of Bis(scorpionate) Iron(II) Complexes. *Angew. Chem., Int. Ed.* **2008**, *47*, 8687– 8691, DOI: 10.1002/anie.200802567
- 52** Reger, D. L.; Gardinier, J. R.; Elgin, J. D.; Smith, M. D.; Hautot, D.; Long, G. J.; Grandjean, F. Structure-Function Correlations in Iron(II) Tris(pyrazolyl)borate Spin-State Crossover Complexes. *Inorg. Chem.* **2006**, *45*, 8862– 8875, DOI: 10.1021/ic0607437
- 53** Gardinier, J. R.; Meise, K. J.; Jahan, F.; Lindeman, S. V. Reaction Chemistry of Silver(I) Trifluoromethanesulfonate Complexes of Nitrogen-Confused C-Scorpionates. *Inorg. Chem.* **2018**, *57*, 1572– 1589, DOI: 10.1021/acs.inorgchem.7b02927
- 54** Gardinier, J. R.; Treleven, A. R.; Meise, K. J.; Lindeman, S. V. Accessing Spin crossover Behaviour in Iron(II) complexes of N-Confused Scorpionate Ligands. *Dalton Trans.* **2016**, *45*, 12639– 12643, DOI: 10.1039/C6DT01898J
- 55** (a) Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Concolino, T.; Mohan, A.; Long, G. J. Structural, Electronic, and Magnetic Properties of $\{\text{Fe}[\text{HC}(3,5\text{-Me}_2\text{ pz})_3]_2\}(\text{BF}_4)_2$ (pz = Pyrazolyl): Observation of Unusual Spin crossover Behavior. *Inorg. Chem.* **2000**, *39*, 4674– 4675, DOI: 10.1021/ic000721z .
- (b) Reger, D. L.; Little, C. A.; Young, V. G., Jr.; Pink, M. Variable-Temperature X-ray Structural Investigation of $\{\text{Fe}[\text{HC}(3,5\text{-Me}_2\text{ pz})_3]_2\}(\text{BF}_4)_2$ (pz = Pyrazolyl Ring): Observation of a Thermally Induced Spin State Change from All High Spin to an Equal High Spin-Low Spin Mixture, Concomitant with the Onset of Nonmerohedral Twinning. *Inorg. Chem.* **2001**, *40*, 2870– 2874, DOI: 10.1021/ic010056+ .
- (c) Reger, D. L.; Little, C. A.; Smith, M. D.; Long, G. J. Solid-State Structural and Magnetic Investigations of $\{\text{M}[\text{HC}(3,5\text{-Me}_2\text{ pz})_3]_2\}(\text{BF}_4)_2$ (M = Fe, Co, Ni, Cu): Observation of a Thermally Induced Solid-State Phase Change Controlling an Iron(II) Spin-State Crossover. *Inorg. Chem.* **2002**, *41*, 4453– 4460, DOI: 10.1021/ic0112645
- 56** Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Liable-Sands, L. M.; Rhagitan, B.; Concolino, T.; Mohan, A.; Long, G. J.; Briois, V.; Grandjean, F. A Synthetic, Structural, Magnetic, and Spectral Study of Several $\{\text{Fe}[\text{tris}(\text{pyrazolyl})\text{methane}]_2\}(\text{BF}_4)_2$ Complexes: Observation of an Unusual Spin-State Crossover. *Inorg. Chem.* **2001**, *40*, 1508– 1520, DOI: 10.1021/ic001102t.
- Briois, V.; Saintavit, P.; Long, G. J.; Grandjean, F. Importance of Photoelectron Multiple Scattering in the Iron K-Edge X-ray Absorption Spectra of Spin crossover Complexes: Full Multiple Scattering Calculations for Several Iron(II) Trispyrazolylborate and Trispyrazolylmethane Complexes. *Inorg. Chem.* **2001**, *40*, 912– 918, DOI: 10.1021/ic0007153
- 57** Reger, D. L.; Elgin, J. D.; Foley, E. A.; Smith, M. D.; Grandjean, F.; Long, G. J. Structural, Magnetic, and Mössbauer Spectral Study of the Electronic Spin-State Transition in $[\text{Fe}\{\text{HC}(3\text{-Mepz})_2\}_2]_2(\text{BF}_4)_2$. *Inorg. Chem.* **2009**, *48*, 9393– 9401, DOI: 10.1021/ic901259e
- 58** Moubaraki, B.; Leita, B. A.; Halder, G. J.; Batten, S. R.; Jensen, P.; Smith, J. P.; Cashion, J. D.; Kepert, C. J.; Létard, J.-F.; Murray, K. S. Structure, magnetism and photomagnetism of mixed-ligand tris(pyrazolyl)methane iron(II) spin crossover compounds. *Dalton Trans* **2007**, 4413– 4426, DOI: 10.1039/b708773j

- 59**(a) Moertel, M.; Witt, A.; Heinemann, F. W.; Bochmann, S.; Bachmann, J.; Khusniyarov, M. M. Synthesis, Characterization, and Properties of Iron(II) Spin crossover Molecular Photoswitches Functioning at Room Temperature. *Inorg. Chem.* **2017**, *56*, 13174– 13186, DOI: 10.1021/acs.inorgchem.7b01952 .
- (b) Rösner, B.; Milek, M.; Witt, A.; Gobaut, B.; Torelli, P.; Fink, R. H.; Khusniyarov, M. M. Reversible Photo-switching of a Spin crossover Molecular Complex in the Solid State at Room Temperature. *Angew. Chem., Int. Ed.* **2015**, *54*, 12976– 12980, DOI: 10.1002/anie.201504192
- 60** Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176– 2179, DOI: 10.1021/om100106e
- 61**(a) Evans, D. F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.* **1959**, 2003– 2005, DOI: 10.1039/jr9590002003 .
- (b) Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. Organometallic compounds of bivalent europium, ytterbium, and samarium. *J. Chem. Soc. A* **1971**, 1931– 1934, DOI: 10.1039/j19710001931 .
- (c) Piguet, C. Paramagnetic Susceptibility by NMR: The “Solvent Correction” Removed for Large Paramagnetic Molecules. *J. Chem. Educ.* **1997**, *74*, 815– 816, DOI: 10.1021/ed074p815
- 62** Morrison, G.; zur Loye, H.-C. Simple correction for the sample shape and radial offset effects on SQUID magnetometers: Magnetic measurements on Ln_2O_3 ($Ln=Gd, Dy, Er$) standards. *J. Solid State Chem.* **2015**, *221*, 334– 337, DOI: 10.1016/j.jssc.2014.10.026
- 63** Bain, G. A.; Berry, J. F. Diamagnetic Corrections and Pascal’s Constants. *J. Chem. Educ.* **2008**, *85*, 532– 536, DOI: 10.1021/ed085p532
- 64** Agilent Technologies. *CrysAlisProVersion 1.171.34.46 (release 25-11-2010 CrysAlis171.NET)*; (compiled Nov 25 **2010**, 17:55:46).
- 65** Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339– 341, DOI: 10.1107/S0021889808042726
- 66** Sheldrick, G. M. *SHELXTL*, Version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI, **2001**.
- 67**(a) Swart, M.; Groenhof, A. R.; Ehlers, A. W.; Lammertsma, K. Validation of Exchange-Correlation Functionals for Spin States of Iron Complexes. *J. Phys. Chem. A* **2004**, *108*, 5479– 5483, DOI: 10.1021/jp049043i .
- (b) Swart, M.; Ehlers, A. W.; Lammertsma, K. Performance of the OPBE exchange-correlation functional. *Mol. Phys.* **2004**, *102*, 2467– 2474, DOI: 10.1080/0026897042000275017
- 68** Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297– 3305, DOI: 10.1039/b508541a
- 69**(a) Liddle, B. J.; Wanniarachchi, S.; Hewage, J. S.; Lindeman, S. V.; Bennett, B.; Gardinier, J. R. Electronic Communication Across Diamagnetic Metal Bridges: A Homoleptic Gallium(III) Complex of a Redox-Active Diarylamido-Based Ligand and Its Oxidized Derivatives. *Inorg. Chem.* **2012**, *51*, 12720– 12728, DOI: 10.1021/ic301437f .
- (b) Wanniarachchi, S.; Liddle, B. J.; Kizer, B.; Hewage, J. S.; Lindeman, S. V.; Gardinier, J. R. Syntheses and Electronic Properties of Rhodium(III) Complexes Bearing a Redox-Active Ligand. *Inorg. Chem.* **2012**, *51*, 10572– 10580, DOI: 10.1021/ic300772h .
- (c) Wanniarachchi, S.; Liddle, B. J.; Toussaint, J.; Lindeman, S. V.; Bennett, B.; Gardinier, J. R. Using sterics to promote reactivity in *fac*-Re(CO)₃ complexes of some ‘non-innocent’ NNN-pincer ligands. *Dalton Trans.* **2011**, *40*, 8776– 8787, DOI: 10.1039/c1dt10030k
- 70**(a) Güell, M.; Solà, M.; Swart, M. Spin-state splittings of iron(II) complexes with trispyrazolyl ligands. *Polyhedron* **2010**, *29*, 84– 93, DOI: 10.1016/j.poly.2009.06.006 .

- (b) Gruden-Pavlović, M.; Stepanović, S.; Perić, M.; Güell, M.; Swart, M. A density functional study of the spin state energetics of polypyrazolylborato complexes of first-row transition metals. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14514– 14522, DOI: 10.1039/c3cp55488k .
- (c) Swart, M.; Gruden, M. Spinning Around in Transition-Metal Chemistry. *Acc. Chem. Res.* **2016**, *49*, 2690– 2697, DOI: 10.1021/acs.accounts.6b00271 .
- (d) Sirirak, J.; Sertphon, D.; Phonsri, W.; Harding, P.; Harding, D. J. Comparison of density functionals for the study of the high spin low spin gap in Fe(III) spin crossover complexes. *Int. J. Quantum Chem.* **2017**, *117*, e25362 DOI: 10.1002/qua.25362
- 71** Scalmani, G.; Frisch, M. J. Continuous surface charge polarizable continuum models of solvation. I. General formalism. *J. Chem. Phys.* **2010**, *132*, 114110– 114124, DOI: 10.1063/1.3359469
- 72** Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, Revision B.01; Gaussian, Inc.: Wallingford, CT, **2016**.
- 73**(a) Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. Defining the hydrogen bond: An account (IUPAC Technical Report). *Pure Appl. Chem.* **2011**, *83*, 1619– 1636, DOI: 10.1351/PAC-REP-10-01-01 .
- (b) Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. Definition of the hydrogen bond (IUPAC Recommendations 2011). *Pure Appl. Chem.* **2011**, *83*, 1637– 1641, DOI: 10.1351/PAC-REC-10-01-02 .
- (c) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bonding in Structural Chemistry and Biology*; Oxford University Press: New York, **1999**.
- (d) Taylor, R.; Kennard, O. Hydrogen Bond Geometry in Organic Crystals. *Acc. Chem. Res.* **1984**, *17*, 320– 326, DOI: 10.1021/ar00105a004
- 74**(a) Bernstein, J. It Isn't. *Cryst. Growth Des.* **2013**, *13*, 961– 964, DOI: 10.1021/cg301519k .
- (b) Gu, Y.; Kar, T.; Scheiner, S. Fundamental Properties of the CH $\cdots$ O Interaction: Is It a True Hydrogen Bond?. *J. Am. Chem. Soc.* **1999**, *121*, 9411– 9422, DOI: 10.1021/ja991795g .
- (c) Desiraju, G. J. The C-H $\cdots$ O Hydrogen Bond: Structural Implications and Supramolecular Design. *Acc. Chem. Res.* **1996**, *29*, 441– 449, DOI: 10.1021/ar950135n .
- (d) Steiner, T.; Saenger, F. *J. Am. Chem. Soc.* **1992**, *114*, 10146– 10154, DOI: 10.1021/ja00052a009 .
- (e) Desiraju, G. J. The CH $\cdots$ O hydrogen bond in crystals: what is it?. *Acc. Chem. Res.* **1991**, *24*, 290– 296, DOI: 10.1021/ar00010a002 .
- (f) Taylor, R.; Kennard, O. Crystallographic evidence for the existence of CH $\cdots$ O, CH $\cdots$ N and CH $\cdots$ Cl hydrogen bonds. *J. Am. Chem. Soc.* **1982**, *104*, 5063– 5070, DOI: 10.1021/ja00383a012 .
- (g) Gardinier, J. R.; Tatlock, H. M.; Hewage, J. S.; Lindeman, S. V. Cyclic versus Polymeric Supramolecular Architectures in Metal Complexes of Dinucleating Ligands: Silver(I) Trifluoromethanesulfonate Complexes of the Isomers of Bis(di(1H-pyrazolyl)methyl)-1,1'-biphenyl. *Cryst. Growth Des.* **2013**, *13*, 3864– 3877, DOI: 10.1021/cg400466k

- 75** (a) Takahashi, H.; Tsuboyama, S.; Umezawa, Y.; Honda, K.; Nishio, M. CH/ π Interactions as Demonstrated in the Crystal Structure of Host/Guest Compounds. A Database Study. *Tetrahedron* **2000**, *56*, 6185– 6191, DOI: 10.1016/S0040-4020(00)00575-5 .
- (b) Tsuzuki, S.; Honda, K.; Uchimar, T.; Mikami, M.; Tanabe, K. Origin of the Attraction and Directionality of the NH/ π Interaction: Comparison with OH/ π and CH/ π Interactions. *J. Am. Chem. Soc.* **2000**, *122*, 11450– 11458, DOI: 10.1021/ja001901a .
- (c) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH-T Interaction: Evidence, Nature, and Consequences*; Wiley-VCH, Inc.: New York, **1998**.
- (d) Umezawa, Y.; Tsuboyama, S.; Honda, K.; Uzawa, J.; Nishio, M. CH/ π Interaction in the Crystal Structure of Organic Compounds. A Database Study. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1207– 1213, DOI: 10.1246/bcsj.71.1207 .
- (e) Braga, D.; Grepioni, F.; Tedesco, E. X-H--- π (X = O, N, C) Hydrogen Bonds in Organometallic Crystals. *Organometallics* **1998**, *17*, 2669– 2672, DOI: 10.1021/om971096h
- 76** (a) Choudhury, A. R.; Row, T. N. G. *Cryst. Growth Des.* **2004**, *4*, 47– 52, DOI: 10.1021/cg034137n .
- (b) van den Berg, J. A.; Seddon, K. R. Critical Evaluation of C-H...X Hydrogen Bonding in the Crystalline State. *Cryst. Growth Des.* **2003**, *3*, 643– 661, DOI: 10.1021/cg034083h.
- (c) Brammer, L.; Bruton, E. A.; Sherwood, P. Fluoride ligands exhibit marked departures from the hydrogen bond acceptor behavior of their heavier halogen congeners. *New J. Chem.* **1999**, *23*, 965– 968, DOI: 10.1039/a906512a .
- (d) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. Crystal Forms of Hexafluorophosphate Organometallic Salts and the Importance of Charge-Assisted C-H...F Hydrogen Bonds. *Organometallics* **1998**, *17*, 296– 307, DOI: 10.1021/om9706626 .
- (e) Thalladi, V. R.; Weiss, H.-C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. C-H...F Interactions in the Crystal Structures of Some Fluorobenzenes. *J. Am. Chem. Soc.* **1998**, *120*, 8702– 8710, DOI: 10.1021/ja981198e
- 77** Coronado, E.; Giménez-López, M. C.; Giménez-Saiz, C.; Romero, F. M. Spin crossover complexes as building units of hydrogen-bonded nanoporous Structures. *Cryst. Eng. Comm* **2009**, *11*, 2198– 2203, DOI: 10.1039/b911137a
- 78** Roberts, T. D.; Little, M. A.; Tuna, F.; Kilner, C. A.; Halcrow, M. A. Isostructural salts of the same complex showing contrasting thermal spin-crossover mediated by multiple phase changes. *Chem. Commun.* **2013**, *49*, 6280– 6282, DOI: 10.1039/c3cc43613f
- 79** Bartual-Murgui, C.; Codina, C.; Roubeau, O.; Aromí, G. A Sequential Method to Prepare Polymorphs and Solvatomorphs of [Fe(1,3-bpp)₂](ClO₄)₂·nH₂O (n = 0, 1, 2) with Varying Spin-Crossover Behaviour. *Chem. - Eur. J.* **2016**, *22*, 12767– 12776, DOI: 10.1002/chem.201601843
- 80** *CRC Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, **1996**; Section 9, Table 1.