



Article Spin-Crossover in Iron(II) Complexes of N,N'-Disubstituted 2,6-Bis(Pyrazol-3-yl)Pyridines: An Effect of a Distal Substituent in the 2,6-Dibromophenyl Group

Igor A. Nikovskiy¹, Alexander V. Polezhaev^{1,2}, Valentin V. Novikov^{1,3}, Dmitry Yu. Aleshin¹, Rinat R. Aysin^{1,3}, Elizaveta K. Melnikova^{1,4}, Luca M. Carrella⁵, Eva Rentschler⁵ and Yulia V. Nelyubina^{1,2,3,*}

- ¹ Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova Str., 28, 119991 Moscow, Russia; igornikovskiy@mail.ru (I.A.N.); aleksandr.polejaev@gmail.com (A.V.P.); novikov84@gmail.com (V.V.N.); dima.aleshin26@gmail.com (D.Y.A.); aysin.rinat@gmail.com (R.R.A.); elizaveta2198@gmail.com (E.K.M.)
- ² Bauman Moscow State Technical University, 2nd Baumanskaya Str., 5, 105005 Moscow, Russia
- ³ Moscow Institute of Physics and Technology, Institutskiy per., 9, 141700 Dolgoprudny, Russia
- ⁴ Lomonosov Moscow State University, Leninskiye Gory, 1–3, 119991 Moscow, Russia
- ⁵ Johannes Gutenberg-Universität Mainz, Duesbergweg 10–14, 55128 Mainz, Germany; carrella@uni-mainz.de (L.M.C.); rentschl@uni-mainz.de (E.R.)
- Correspondence: unelya@ineos.ac.ru

Abstract: A series of new bis(pyrazol-3-yl)pyridines (L^R) N,N'-disubstituted by 4-functionalized 2,6-dibromophenyl groups have been synthesized to study the effect of a distal substituent on the spin-crossover (SCO) behaviour of the iron(II) complexes [Fe(L^R)₂](ClO₄)₂ by variable-temperature magnetometry, NMR spectroscopy, and X-ray diffraction. The SCO-assisting tendency of the substituents with different electronic and steric properties (i.e., the bromine atom and the methyl group) in the para-position of the 2,6-dibromophenyl group is discussed. Together with earlier reported SCO-active iron(II) complexes with N,N'-disubstituted bis(pyrazol-3-yl)pyridines, these new complexes open the way for this family of SCO compounds to emerge as an effective 'tool' in revealing structure–function relations, a prerequisite for successful molecular design of switchable materials for future breakthrough applications in sensing, switching, and memory devices.

Keywords: distal substituent; iron(II) complexes; molecular design; paramagnetic NMR spectroscopy; spin-crossover; X-ray diffraction

1. Introduction

Metal complexes or frameworks [1] with the transition metal ions able to reversibly switch between low-spin (LS) and high-spin (HS) electronic configurations as a response to an applied stimulus (such as temperature, pressure, light irradiation, or electric or magnetic field [1]) are promising candidates to be incorporated into various materials and devices [2,3]. This ability for a spin-crossover (SCO) between the two configurations with different optical, magnetic, electrical and mechanical properties is exploited in displays [4], switches [5], sensors [6], memory devices [7], thermometers [8], and contrast agents [9] in magnetic resonance imaging [2,3]. The required SCO behavior, which is most often observed in N6-coordinated complexes of iron(II) [10,11], is tailored for the listed applications [12] by chemical modifications to the heterocyclic N-donor ligands [13–22]. Recognizing them for the 'truly molecular' design [12] of SCO compounds (free from crystal packing [23,24] or substate [25,26] effects) relies on structure–function relations [12–16,18] identified for selected series of metal complexes in their systematic studies by an available solution-state technique such as NMR spectroscopy [12]. The results of these studies agree on a rather [27] general tendency of bulky groups close to the donor nitrogen atoms to



Citation: Nikovskiy, I.A.; Polezhaev, A.V.; Novikov, V.V.; Aleshin, D.Y.; Aysin, R.R.; Melnikova, E.K.; Carrella, L.M.; Rentschler, E.; Nelyubina, Y.V. Spin-Crossover in Iron(II) Complexes of N,N'-Disubstituted 2,6-Bis (Pyrazol-3-yl)Pyridines: An Effect of a Distal Substituent in the 2,6-Dibromophenyl Group. *Crystals* 2021, *11*, 922. https://doi.org/ 10.3390/cryst11080922

Academic Editors: Neil Champness and Younes Hanifehpour

Received: 20 July 2021 Accepted: 5 August 2021 Published: 8 August 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). stabilize the HS state of the metal ion through the steric demand that makes its LS state more unlikely, with a less straightforward role for other, more remote substituents [12].

Among many different ligands found in SCO complexes, such as a popular family of bis(pyrazol-1-yl)pyridines (1-bpp) [12], isomeric bis(pyrazol-3-yl)pyridines (3-bpp) [28] induce a SCO tuned by counterions or solvents via hydrogen bonds with the unsubstituted NH groups [29–33]. The latter, however, render the spin state of the metal ion environment-dependent [34,35] in the resulting complexes that are otherwise HS [12,24,36–39], thus precluding their further evolution as SCO compounds [12] until very recently [27].

We have proposed [27] a ligand design to obtain the first SCO-active iron(II) (and cobalt(II) [40]) complexes of N,N'-disubstituted 3-bpp by introducing bulky ortho-groups into N-phenyl substituents. Following this research, here we report a series of 3-bpp ligands with 2,6-dibromophenyl groups functionalized in its para-position by another bromine atom and a methyl group with different electronic and steric properties (Scheme 1). The latter allowed us to study the effect of a distal substituent on the spin-state behavior of the iron(II) complexes in an attempt to make new SCO compounds from a 3-bpp family that are amenable to molecular design.



Scheme 1. Ligands in this study: L^H, 3,3'-(pyridine-2,6-diyl)bis(1-(2,6-dibromophenyl)-1H-pyrazol-5-ol); L^{Br}, 3,3'-(pyridine-2,6-diyl)bis(1-(2,4,6-tribromophenyl)-1H-pyrazol-5-ol); and L^{Me}, 3,3'-(pyridine-2,6-diyl)bis(1-(2,6-dibromo-4-methylphenyl)-1H-pyrazol-5-ol).

2. Materials and Methods

Synthesis. All synthetic manipulations were carried out in air. Solvents were purchased and purified by distilling from conventional drying agents under an argon atmosphere prior to use. 2,6-Bis(1,3-dioxo-3-ethoxypropyl)pyridine was synthesized as reported previously [41]. 2,6-dibromo- and 2,4,6-tribromophenylhydrazines were synthesize from commercially available anilines using a standard diazotization protocol with a subsequent reduction with SnCl₂ [42]. 2,6-dibromo-4-methyl-phenylhydrazine was also synthesized from the corresponding aniline using a standard diazotization protocol described above. 2,6-dibromo-4-methyl-aniline was synthesized by bromination of p-toluidine with Br₂ in glacial acetic acid [43]. Analytical data (C, H and N contents) were obtained with a Carlo Erba model 1106 microanalyzer.

Synthesis of 2,6-bis(1,3-dioxo-3-ethoxypropyl)pyridine. To a mixture of 2,6-pyridine dicarboxylic ethyl ester (2.23 g, 10 mmol) and ethyl acetate (2.44 mL, 25 mmol) in dry THF (25 mL), sodium hydride was added (1.8 g, 50% in mineral oil). The reaction mixture was refluxed for 4 h and then allowed to cool. The volatiles were evaporated, and the residual solid was washed with diethyl ether (2×30 mL), filtered, and dried. The crude product was dispersed in water (30 mL), and the resulting alkaline solution was treated with 1 M hydrochloric acid until it became slightly acidic (pH 5). The precipitated solid product was filtered, washed with water, dried, and finally recrystallized from a mixture of diethyl ether

and hexane. The yield was 78% (2.4 g) ¹H NMR (CDCl₃, 400 MHz; a mixture of diketo and keto-enol forms): (ppm) = 1.21-1.33 (t + t + t, 6H, CH2CH3), 4.15-4.28 (q + q, 4H, CH₂CH₃), 4.14 (s, CH2 of the diketo form), 6.36 (s, CH of the keto-enol form), 7.35 (t, p-CH of the diketo form), 8.03 (t, p-CH of the keto-enol form), 8.08 (d, m-CH of the diketo form), 8.24 (d, m-CH of the keto-enol form), and 12.40 (s, OH of the keto-enol form), lit. [41].

Synthesis of 2,6-dibromo-4-methylaniline. p-Toluidine (8 g, 74.66 mmol) was dissolved in 100 mL of glacial acetic acid. A solution of liquid bromine (7.7 mL, 149.32 mmol) in 25 mL of acetic acid was added dropwise to the resulting toluidine solution at 0–5 °C. The mixture was stirred for 1 h at room temperature, and then 100 mL of water was added. The precipitate was filtered and washed with 1 M aqueous solution of sodium hydroxide. The wet product was recrystallized from aqueous ethanol to give pale red crystals. The yield was 16.22 g (82%) ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 2.21 (s, 3H, CH₃), 4.38 (br. s., 2H, NH₂), 7.20 (s., 2H, m-Ph-H), lit. [43].

General procedure for synthesis of 4-substituted-2,6-dibromoarylhydrazine. A suspension of an appropriate aniline (30.0 mmol) in 25 mL of HCl (38%, aqueous) was cooled to -10 °C. A solution of sodium nitrite (2.17 g, 31.5 mmol) in 5 mL of water was then added dropwise while keeping the temperature below -5 °C. After stirring the reaction mixture for 1 h, SnCl₂ (75 mmol) in 30 mL of concentrated HCl was added dropwise at -5 °C. The resulting suspension was heated to r.t. and then stirred at this temperature for 1 h. A yellowish precipitate was filtered, washed with 100 mL of methylene chloride and HCl, and dried under vacuum. The obtained product was sensitive to light, so it was stored as a hydrochloride salt in a dark vial and converted into a freebase form with a 1 M aqueous solution of sodium hydroxide right before use.

2,4,6-tribromophenylhydrazine [44]. Yield: 3.30 g (61%). ¹H NMR (DMSO-d6, 400 MHz): δ (ppm) = 4.33 (s, 2H), 5.78 (s, 1H), 7.74 (s, 2H).

2,6-dibromophenylhydrazine [45]. Yield: 4.38 g (55%). ¹H NMR (DMSO-d6, 300 MHz): δ (ppm) = 7.6 (d, ³*J*_{*H*,*H*} = *8.1 Hz*, 2H, m-Ph-H), 6.92 (t, ³*J*_{*H*,*H*} = *8.1 Hz*, 1H, p-Ph-H), 4.91 (br.s, 3H, NH).

(2,6-dibromo-4-methylphenyl)hydrazine. Yield: 5.79 g (69%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) = 7.25 (s, 2H, m-Ph-H), 5.34 (br.s, 1H, NH), 3.88 (br.s, 2H, NH₂), 2.21 (s, 3H, CH₃).

General procedure for synthesis of ligands L^H, L^{Br} and L^{Me} (Scheme 2). A mixture of diethyl 3,3'-(pyridine-2,6-diyl)bis(3-oxopropanoate) (0.307 g, 1 mmol) and an appropriate phenylhydrazine (2.3 mmol) was dissolved in 10 mL of acetic acid to produce an orange solution. After its heating under reflux for 8 h, a light-yellow precipitate was formed, which was then filtered, washed with acetic acid and water, and dried under vacuum. The product was used without further purification.

L^H.Yield: 0.576 g (81%). ¹H NMR (DMSO-d6, 400 MHz): δ (ppm) = 6.19 (s, 2H, Pz-CH), 7.43 (t, ³*J*_{*H*,*H*} = 8,1 *Hz*, 2H, p-Ph-H), 7.81 (br. s, 3H, Py), 7.87 (d, ³*J*_{*H*,*H*} = 8,1, 4H, m-Ph-H). ¹³C NMR (DMSO-d6, 101 MHz): δ (ppm) = 84.93 (s, 4-Pz), 118.50 (s, 3-Py), 124.9 (s, 4-Ph), 132.91 (s,1-Ph), 133.08 (s, 2-Ph), 136.74 (s, 3-Ph), 137.75 (s, 4-Py), 151.77 (s, 3-Pz), 151.70 (s, 2-Py), 154.61 (s, 5-Pz). Calc. for (C23H13Br4N5O2): C, 38.85; H, 1.84; N, 9.85; Found: C, 38.91, H, 1.92, N, 9.59.

 L^{Br} .Yield: 0.764 g (88%). ¹H NMR (DMSO-d6, 400 MHz): δ (ppm) = 6.19 (s, 2H, Pz-CH), 7.81 (s, 4H, m-Ph-H), 8.18 (br. s, 3H, Py). ¹³C NMR (DMSO-d6, 101 MHz): δ (ppm) = 84.64 (s, 4-Pz), 118.22 (s, 3-Py), 124.15 (s, 4-Ph), 125.41 (s,1-Ph), 134.72 (s, 2-Ph), 136.0 (s, 3-Ph), 137.42 (s, 4-Py), 151.22 (s, 3-pyraz), 151.69 (s, 2-Py), 154.27 (s, 5-Pz). Calc. for (C23H11Br6N5O2): C, 31.80; H, 1.28; N, 8.06; Found: C, 39.01, H, 1.37, N, 8.29.

 L^{Me} .Yield: 0.569 g (77 %). ¹H NMR (DMSO-d6, 400 MHz): δ (ppm) = 2.40 (s, 6H, CH₃), 6.15 (s, 2H, Pz-CH), 7.70 (s, 4H, p-Ph-H), 7.78 (br. s, 3H, Py), 11.61 (br.s, 2H, OH, D2O-exchangeable). ¹³C NMR (DMSO-d6, 101 MHz): δ (ppm) = 20.13 (s, CH₃), 84.33 (s, 4-Pz), 117.89 (s, 3-Py), 123.88 (s, 4-Ph), 132.76 (s,1-Ph), 133.79 (s, 2-Ph), 137.08 (s, 3-Ph), 143.30 (s, 4-Py), 151.47 (s, 3-Pz), 151.57 (s, 2-Py), 154.13 (s, 5-Pz). Calc. for (C25H17Br4N5O2): C, 40.63; H, 2.32; N, 9.48; Found: C, 40.55, H, 2.37, N, 9.61.



Scheme 2. Synthesis of the ligands L^R with R = H, Br and Me.

General procedure for synthesis of complexes $[Fe(L)_2](ClO_4)_2$, $L = L^H$, L^{Br} and L^{Me} . Perchlorate salts are potential explosives and must be handled with care. One should avoid producing large quantities of these materials.

In a 10 mL scintillation vial, iron perchlorate hexahydrate (0.072 g, 0.2 mmol) and an appropriate ligand (0.4 mmol) were mixed in 3 mL of THF and stirred for 1 h. As these manipulations were carried out in air and the iron(II) perchlorate hexahydrate contained an excess of water, the synthesis of the complexes was not a stoichiometric reaction so that a small amount of the ligands remained in the reaction mixture. To obtain them as high-purity samples for further magnetic measurements, they were purified by keeping the reaction mixture at -78 °C to produce crystalline products that were filtered and dried under high vacuum; the ligands can be recovered by evaporation of the remaining solution and by washing the residue with acetonitrile. No side reactions occurred in the reaction mixture as identified by NMR spectroscopy. The obtained complexes are stable on air for approximately 24 h. For longer storage, they should be kept in nitrogen atmosphere to prevent oxidation.

[*Fe*(*L*^{*H*})₂](*ClO*₄)₂. Yield: 221 mg (66%). ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = 9.68 (br.s, 8H, m-Ph-H), 11.26 (br.s, 4H, p-Ph-H), 17.20 (br.s, 4H, OH), 21.52 (br.s, 2H, p-Py-H), 45.92 (br.s, 4H, Pz-CH), 61.17 (br.s, 4H, m-Py-H). Calc. for (C₄₆H₂₆Br₈Cl₂FeN₁₀O₁₂): C, 32.95, H, 1.56, N, 8.35; Found: C, 33.22, H, 1.71, N, 8.64.

[*Fe*(L^{Br})₂](*ClO*₄)₂. Yield: 198 mg (58%). ¹H NMR (CD₃CN, 400 MHz): δ(ppm) = 5.58 (br.s, 12H, CH₃), 9.37 (br.s, 8H, m-Ph-H), 17.44 (br.s, 4H, OH), 21.60 (br.s, 2H, p-Py-H), 44.44 (br.s, 4H, Pz-CH), 59,10 (br.s, 4H, m-Py-H). Calc. for (C₅₀H₃₄Br₈Cl₂FeN₁₀O₁₂): C, 34.66, H, 1.98, N, 8.08; Found: C, 34.87, H, 2.14, N, 8.35.

[$Fe(L^{Me})_2$](ClO_4)₂. Yield: 179 mg (45%). ¹H NMR (CD₃CN, 400 MHz): δ (ppm) = 9.95 (br.s, 8H, m-Ph-H), 16.98 (br.s, 4H, OH), 22.00 (br.s, 2H, p-Py-H), 45.09 (br.s, 4H, Pz-CH), 60.01 (br.s, 4H, m-Py-H). Anal. Calc. for ($C_{46}H_{22}Br_{12}Cl_2FeN_{10}O_{12}$): C, 27.73, H, 1.11, N, 7.03; Found: C, 27.92, H, 1.29, N, 7.24.

X-ray crystallography. Single crystals of $[Fe(L^H)_2](ClO_4)_2$ and $[Fe(L^{Br})_2](ClO_4)_2$ were grown from concentrated THF solutions kept in a Dewar flask with dry ice for 2 days, those of $[Fe(L^{Me})_2](ClO_4)_2$, from a mixture of acetonitrile and diethyl ether on air. X-ray diffraction data were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using the graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) for $[Fe(L^H)_2](ClO_4)_2$ and $[Fe(L^{Br})_2](ClO_4)_2$, and Cu-Kα radiation ($\lambda = 1.54178$ Å) for $[Fe(L^{Me})_2](ClO_4)_2$. Using Olex2 [46], the structures were solved with the ShelXT structure solution program [47] using intrinsic phasing and refined using least-squares minimization. Hydrogen atoms of OH groups were located in difference Fourier synthesis. Positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation in the riding model. Crystal data and structure refinement parameters for these complexes are given in Table 1. CCDC 1959676, 1959677, and 1959678 contain the supplementary crystallographic data for $[Fe(L^H)_2](ClO_4)_2$, $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, respectively.

Parameter	[Fe(L ^H) ₂](ClO ₄) ₂	[Fe(L ^{Br}) ₂](ClO ₄) ₂	$[Fe(L^{Me})_2](ClO_4)_2$
Formula unit	2C ₄₆ H ₂₆ Br ₈ FeN ₁₀ O ₄ , 4ClO ₄ , 11C ₄ H ₈ O	2C ₄₆ H ₂₂ Br ₁₂ FeN ₁₀ O ₄ , 4ClO ₄ , 11C ₄ H ₈ O, 4H ₂ O	C ₅₀ H ₃₄ Br ₈ FeN ₁₀ O ₄ , 4ClO ₄ , 2C ₄ H ₁₀ O, 2CH ₃ CN
Formula weight	4146.70	4850.01	1963.25
Т, К	120	120	120
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$	P2 ₁ /c
Z	2	2	4
a, Å	34.797(3)	15.914(2)	15.4750(3)
b, Å	12.9466(10)	17.779(2)	18.6741(4)
c, Å	23.6896(18)	30.696(4)	24.7555(5)
β, °	131.9720(10)	102.245(2)	90.3160(10)
V, Å ³	7934.5(11)	8487.4(18)	7153.8(3)
$D_{\rm calc}~({\rm g~cm^{-1}})$	1.736	1.898	1.823
Linear absorption, μ (cm ⁻¹)	43.57	59.62	82.10
F(000)	4108	4736	3872
$2\Theta_{ m max}$, $^{\circ}$	58	54	135
Reflections measured	89,248	89,299	100,303
Independent reflections	10,553	18,529	12,778
Observed reflections $[I > 2\sigma(I)]$	8445	8377	11,985
Parameters	504	1026	952
R1	0.0749	0.1152	0.0437
wR2	0.1667	0.3278	0.1086
GOF	1.044	1.083	1.055
$\Delta ho_{ m max}/\Delta ho_{ m min}$ (e Å $^{-3}$)	1.760/-1.551	1.822/-1.055	0.868 / -0.673

Table 1. Crystal data and structure refinement parameters for [Fe(L^H)₂](ClO₄)₂, [Fe(L^{Br})₂](BF₄)₂ and [Fe(L^{Me})₂](ClO₄)₂.

Magnetic measurements. Magnetic susceptibility of the iron(II) complexes was measured with a Quantum Design MPMS-XL-7 SQUID magnetometer under the dc magnetic field of 0.1 T in the temperature range 2–300 K. Finely ground microcrystalline powders were immobilized in eicosane matrix inside a polycarbonate capsule. The data obtained were corrected for the eicosane, the capsule, the sample holder, and the diamagnetic contribution. The latter was done by using the Pascal constants [48]. Smoothing was performed by the Savitzky–Golay method with five points of window and polynomial order of two. The observed variable-temperature *dc* magnetic susceptibility data for $[Fe(L^H)]_2(ClO_4)_2$ were fitted in PHI software [49] using the spin Hamiltonian:

$$\hat{H} = D\left(\hat{S}_z^2 - \frac{\hat{S}^2}{3}\right) + \beta H \cdot g_{iso} \cdot \hat{S}$$

NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded from the solutions of the iron(II) complexes in CD₃CN and CD₃OD with Bruker Avance 300 and 600 FT-spectrometers (300.15 and 600.22 MHz ¹H frequency), respectively. The measurements were conducted using the residual signals of CD₃CN (¹H 1.94 ppm, ¹³C 118.26 ppm) or CD₃OD (¹H 3.31, 4.87 ppm, ¹³C 49.00 ppm).

Evans method. Magnetic susceptibility of the iron(II) complexes in acetonitrile- d_3 was evaluated by the Evans method [50,51] in the temperature range 235–325 K. For $[Fe(L^H)_2](ClO_4)_2$, the data were also collected in methanol- d_4 in the temperature range 190–330 K. In all cases, a Wilmad NMR tube with a coaxial insert was used. The inner (reference) tube was filled with acetonitrile- d_3 with approximately 1% of Me₄Si, and the outer tube, with the solution of the complex (~1–5 mg/cm³) in the same solvent with the same concentration of Me₄Si. The sample was kept at each temperature for 15 min before collecting the spectra to reach the thermal equilibrium. Molar magnetic susceptibility was calculated from the difference between the chemical shift of Me₄Si in

pure acetonitrile-d₃ and its shift in a solution of the complex ($\Delta\delta$ in Hz) in this solvent using the following equation:

$$\chi_M = \frac{\Delta \delta M}{\nu_0 S_f c} - \chi_M^{dia}$$

where *M*—molar weight of the complex, g/mol; ν_0 —frequency of the spectrometer, Hz; S_f —shape factor of the magnet (4 π /3); *c*—concentration of the complex, g/cm³; and χ_M^{dia} —molar diamagnetic contribution to the paramagnetic susceptibility calculated using the Pascal's constant [48]. The concentration *c* was recalculated for each temperature in concert with the change in the solvent's density ρ : $c_T = m_s \rho / m_{sol}$, where m_s is the mass of the complex and m_{sol} is the mass of the solution.

Temperature-dependence of chemical shifts. Chemical shifts in ¹H NMR spectra of the iron(II) complexes in acetonitrile-d₃ were analyzed in the temperature range 235–345 K. For a compound that may exist in two spin states, the observed chemical shift of a given nucleus in the ¹H NMR spectrum is a weighted average of those for LS and HS species (η_{LS} and η_{HS} are their populations):

$$\delta_{obs} = \eta_{LS} \delta_{LS} + \eta_{HS} \delta_{HS}$$

For the iron(II) complexes with the diamagnetic LS state, this chemical shift (in ppm) can be approximated as:

$$\delta_{obs} = \eta_{LS} \delta_{dia}^{LS} + \eta_{HS} \left(\delta_{dia}^{HS} + \delta_{par}^{HS} \right) \approx \delta_{dia} + \eta_{HS} \delta_{par}^{HS}$$

Diamagnetic contribution δ_{dia} to the observed chemical shift, which is virtually the same for the LS and HS states, was taken as a chemical shift of the same nucleus in the NMR spectrum of a free ligand [52]. Therefore, paramagnetic contribution δ_{par}^{HS} was measured as a difference between the chemical shifts of the iron(II) complexes and those of the corresponding ligands. For systems in a pure spin state with low magnetic anisotropy [53,54] at high T (>200 K), the paramagnetic chemical shifts that are different for each nucleus in a complex follow the linear dependence on the inverse temperature: $\delta_{par}^{HS} = A + BT^{-1}$. As small paramagnetic shifts are measured less accurately, the hydrogen atoms that featured the largest chemical shifts (those of the pyrazolyl and meta-pyridine moiety; Scheme 1) were used in the fit by a regular solution model [53] to produce average thermodynamic parameters for the SCO-active iron(II) complexes.

The population of the HS state for these complexes was calculated based on the average deviations of the paramagnetic shifts of these hydrogen atoms from the values observed for the HS complex $[Fe(L^H)_2](ClO_4)_2$ at each temperature:

$$\eta_{HS} = \frac{\delta_{par}}{\delta_{par}^F}$$

Quantum chemistry. Geometry optimization of the ligands L^R and model arylpyrazole pyridines was performed using the ORCA package, v. 4.2 [55,56], with a TPSSh functional [57–59] and a basis set def2-TZVP [60]. For the iron(II) complexes [Fe(L^R)₂]²⁺, X-ray diffraction geometries were chosen as a starting point for geometry optimization with the TPSSh functional, which provides a satisfactory estimate for the energy difference between the HS and LS states in (pseudo)octahedral iron(II) complexes [61], and a basis set def2-TZVP [60]. To speed up the calculations, the RIJCOSX approximation [62] with a def2/J fitting basis [63] set was used. Extra tight thresholds for forces and displacements were used.

3. Results and Discussion

The corresponding N,N'-disubstituted 3-bpp ligands L^R were obtained with high yields from 2,6-bis(1,3-dioxo-3-ethoxypropyl)pyridine [41] and 2,6-dibromo-4-R-phenylhy

drazines (R = H, Br, Me) through a previously reported [27] one-step cyclization process. They were filtered from the reaction mixture after precipitation due to low solubility in glacial acetic acid and were used without further purification. The subsequent reaction with $Fe(ClO_4)_2 \bullet 6H_2O$ in THF produced the iron(II) complexes $[Fe(L^{\mathbf{k}})_2](ClO_4)_2$ as finecrystalline powders. Their yellow color hinted on the HS state of the iron(II) ion [1], which was confirmed by variable-temperature magnetic measurements between 2 and 300 K (Figure 1). Note that perchlorate salts are potential explosives and have to be handled with care. At room temperature, the observed χT values for $[Fe(L^R)_2](ClO_4)_2$ are 3.04–3.51 cm³ K mol⁻¹ and close to the expected one for one iron(II) ion in the pure HS state with S = 2 (3.00 cm³ K mol⁻¹) and to those reported for HS iron(II) complexes of 3-bpp [27,37,64]. The χ T values remain nearly constant on cooling the samples down to 30–50 K, with a drop to 1.40–1.74 cm³ K mol⁻¹ below these temperatures as a result of zero-field splitting effects, intermolecular antiferromagnetic interactions, and/or the saturation of magnetization rather than a spin-state switching [65]. Satisfactorily simulation of the data was obtained with isotropic values for the g-tensor g_{iso} and zero-field splitting energies |D| equal to 2.00–2.13 and 5.64–8.2 cm⁻¹, respectively; those are quite expected for N,N'-disubstituted 3-bpp [27,37].



Figure 1. Variable-temperature magnetic susceptibility data for a fine-crystalline sample of $[Fe(L^{H})_{2}](ClO_{4})_{2}$ according to the *dc*-magnetometry. The red line represents the fit. For $[Fe(L^{Br})_{2}]$ (ClO₄)₂ and $[Fe(L^{Me})_{2}](ClO_{4})_{2}$, see Figure S1 of ESI.

Although typical of N,N'-disubstituted 3-bpp ligands [27], the observed 'locking' [37] of the complexes $[Fe(L^R)_2](ClO_4)_2$ in the HS state is, however, in a stark contrast with their behavior in solutions as probed by variable-temperature NMR spectroscopy. Two separate techniques were used for this purpose: the popular [12] Evans technique [50,51] and the less popular but more powerful [40] analysis of a temperature dependence of chemical shifts in the NMR spectra [40,66] that are collected with the same experimental setup (see experimental section). The former allows for measuring the magnetic susceptibility of a solution as an alternative to a more cumbersome magnetometry [12], while the latter allows for screening of paramagnetic complexes that may exist in mixtures of unknown concentrations [40]. The two approaches rooted in the widely available NMR spectroscopy are helpful tools in molecular design of SCO compounds [12,40] exploiting the spin state behaviour decoupled from crystal packing [23,24] or substrate [25,26] effects that sometimes block a SCO [23,24].

For $[Fe(L^R)_2](ClO_4)_2$, both methods show the complexes with the para-substituted 2,6-dibromophenyl groups to undergo a temperature-induced SCO between 235 and 325 K in acetonitrile solutions, while $[Fe(L^H)_2](ClO_4)_2$ remains HS even in methanol, which provides access to lower temperatures down to 190 K. The latter follows from the χT values being constant at ~3.3 cm³ K mol⁻¹ (Figure 2), which is close to the theoretical value for the

HS iron(II) ion (3.00 cm³ K mol⁻¹), and from the linear dependence of the chemical shifts on the inverse temperature (Figure 3, left), which is a typical Curie behavior of a paramagnetic complex in one spin state [53,54]. For $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, however, the χ T values decrease from 3.03 and 3.54 cm³ K mol⁻¹ at room temperature to 2.40 and 2.99 cm³ K mol⁻¹ at 235 K (Figure 2), thus indicating a gradual depopulation of the paramagnetic HS state and the population of the diamagnetic LS state upon cooling. This is further supported by the chemical shifts in the corresponding NMR spectra that feature a significant deviation from the above linear dependence at temperatures below 285 K (Figure 3, right).



Figure 2. Variable-temperature magnetic susceptibility data for the solutions of $[Fe(L^R)_2](ClO_4)_2$ in acetonitrile-d₃ according to the Evans method. For $[Fe(L^H)_2](ClO_4)_2$ in methanol-d₄, see Figure S2 of ESI.



Figure 3. Chemical shifts in ¹H NMR spectra for $[Fe(L^{H})_{2}](ClO_{4})_{2}$ (**left**) and $[Fe(L^{Br})_{2}](ClO_{4})_{2}$ (**right**) in an acetonitriled₃ solution plotted versus *1/T*. Solid lines represent the linear fit over the entire temperature range (**left**) and over the temperature range 285–325 K (**right**); each color indicates a specific type of the protons that are the same between the complexes. For the corresponding variable-temperature ¹H NMR spectra, see Figure S3. For $[Fe(L^{Me})_{2}](ClO_{4})_{2}$ and $[Fe(L^{H})_{2}](ClO_{4})_{2}$ in a methanol-d₄ solution, see Figure S4 and S5 of ESI, respectively.

Fitting these sets of NMR-derived data separately (Figures 2 and 3) by a regular solution model [53] resulted in midpoint temperatures $T_{1/2}$ of this SCO equal to 195–198 and 205 K for $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, respectively, and the thermodynamic parameters (Table 2) typical for such measurements [16,67]. The similar midpoint temperatures of the two complexes, which agree nicely between the two different approaches, mirror similar steric effects of the para-substituents in the 2,6-dibromophenyl groups, as gauged by the volumes [68] of the bromine atom and the methyl group (34.3 and 32.2 Å³),

with the larger bromine atom predictably [12] favoring the HS state (Figure 4). In contrast, their opposite electronic effects cannot explain the SCO-assisting tendency (or the lack thereof) in $[Fe(L^R)_2](ClO_4)_2$.





Table 2. SCO parameters ¹ from the NMR data for $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$ in acetonitrile-d₃.

Parameter	[Fe(L ^{Br}) ₂](ClO ₄) ₂	[Fe(L ^{Me}) ₂](ClO ₄) ₂
Т _{1/2} , К	198	205
ΔH , kJ/mol	18.7	21.1
ΔS , J/mol	94.3	103.8

¹ Thermodynamic parameters are obtained by fitting the deviations of the chemical shifts in the NMR spectra of $[Fe(L^{Br})_2](ClO_4)_2$ (R = Br, Me) from the same values for $[Fe(L^{H})_2](ClO_4)_2$ by a regular solution model. For those obtained by fitting the Evans data, see Table S1 of ESI.

For SCO-active iron(II) complexes of other N,N'-disubstituted 3-bpp ligands with the ortho-substituents in the N-phenyl groups (Scheme 1) that are generally smaller than the bromine atom in $[Fe(L^R)_2](ClO_4)_2$ [27], the midpoint temperatures $T_{1/2}$ in acetonitrile are between 240 and 270 K [27], the smaller substituent favoring the LS state. The smallest fluorine and hydrogen atoms, however, counterintuitively [27] produced HS complexes only, which was attributed [27,69] to the energy penalty associated with the loss of planarity between the 2,6-substituted N-phenyl group and the pyrazolyl moiety that are almost perpendicular to each other in the LS state.

To shed light on the appropriate geometry features that may be behind the SCOactivity of $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, we resorted to X-ray diffraction data (Figure 5) for their single crystals collected from THF solutions or mixtures of acetonitrile and diethyl ether as solvates $[Fe(L^H)_2](ClO_4)_2 \bullet 5.5THF$, $[Fe(L^{Br})_2](ClO_4)_2 \bullet 5.5THF \bullet 2H_2O$ and $[Fe(L^{Me})_2](ClO_4)_2 \bullet 2Et_2O \bullet 2CH_3CN$ with the lattice solvents 'trapped' by hydrogen bonds with the hydroxyl groups of the 3-bpp ligands L^R (O ... O 2.534(12)–2.663(5) Å, OHO 153.8(9)–177.8(12)°). At the low temperature (120 K) of the X-ray diffraction experiments (Table 3), the Fe-N bond lengths are typical for HS (pseudo)octahedral complexes of iron(II) in a N6-coordination environment [23] distorted towards an edge-bicapped tetrahedron [70], as judged by 'twist' θ and 'rotatioN' φ angles and continuous symmetry measures [70] relative to the two reference shapes, an ideal octahedron and an edgebicapped tetrahedron. Of the three, $Fe(L^H)_2](ClO_4)_2$ matches the former better than the two other complexes, while $[Fe(L^{Me})_2](ClO_4)_2$, matches the latter better than the two other



complexes. In all cases, however, the observed differences are not conclusive enough to rationalize the different spin-state behavior of $[Fe(L^R)_2](ClO_4)_2$ in solutions.

Figure 5. General view of the cation in $[Fe(L^H)]_2(ClO_4)_2$ as obtained from X-ray diffraction at 120 K. Non-hydrogen atoms are shown as thermal ellipsoids (p = 30%), hydrogen atoms except those of OH groups are omitted for clarity, and only labels of the heteroatoms in an asymmetric part of the unit cell are given. For $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, see Figure S7 of ESI.

Table 3. Main geometric parameters and continuous symmetry measures ¹ as obtained from X-ray diffraction at 120 K for HS $[Fe(L^{H})_2](ClO_4)_2$, HS $[Fe(L^{Br})_2](BF_4)_2$ and HS $[Fe(L^{Me})_2](ClO_4)_2$.

Parameter	[Fe(L ^H) ₂](ClO ₄) ₂	[Fe(L ^{Br}) ₂](ClO ₄) ₂	$[Fe(L^{Me})_2](ClO_4)_2$
Fe-N _{Pv} , Å	2.098(5)	2.071(13)-2.123(12)	2.105(5)-2.109(5)
Fe-N _{Pz} , Å	2.242(5), 2.262(5)	2.208(12)-2.277(13)	2.225(5)-2.266(5)
N _{pz} N _{pz} , Å	4.340(9)	4.303(18), 4.38(2)	4.311(6), 4.417(7)
$\dot{N_{pz}}N_{py}N_{pz}$, °	110.6(3)	109.4(6), 112.5(6)	110.5(2), 111.9(2)
θ,°	82.43(10)	81.64(13)	81.58(10)
φ,°	166.5(3)	167.0(5)	166.31(18)
° °	82.9(3), 83.4(4)	82.8(6), 82.2(7), 78.0(7), 81.8(7)	79.8(2), 81.2(2), 77.1(2), 77.2(2)
Υ,	av. 83.1	av. 81.2	av. 78.8
β,°	15.0(3), 2.3(3)	11.8(6), 2.4(7), 12.8(6), 3.1(6)	14.7(2), 3.2(2), 8.5(2), 4.3(2)
S(O _h)	5.473	5.534	5.840
S(ebcT)	10.379	10.264	10.192
Br Br, Å	3.615(2), 3.690(4), 3.904(19),	3.808(3), 3.579(3), 3.804(3),	3.5644(9), 3.8028(10),
	3.7094(13)	3.630(3)	3.6351(11), 3.7500(11)

¹ N_{pz} and N_{py} are the coordinating nitrogen atoms from the pyrazol-3-yl and pyridine moieties; θ is the 'twist' angle between the least-squares planes of the two 3-bpp ligands; φ is the 'rotatioN' angle N_{Py} -M- N_{Py} ; γ is the rotation angle of the N-phenyl group relative to the pyrazol-3-yl plane; β is the rotation angle of the pyrazol-3-yl moiety relative to the pyridine plane; $S(O_h)$ and S(ebcT) are octahedral and edge-bicapped tetrahedral symmetry measures, respectively; Br ... Br are the distances between the bromine atoms from possible intramolecular Br ... Br interactions.

This behavior cannot be also explained by the rotation of the 2,6-dibromophenyl group from the pyrazolyl plane (Figure 5) to adapt to bulky ortho-substituents proposed [27] as the reason for the SCO-assisting tendency of the N,N'-disubstituted 3-bpp ligands. Indeed, the rotation angles in $[Fe(L^R)_2](ClO_4)_2$ are between 77.1(2) and 83.4(4)° (Table 3), with the largest values unexpectedly adopted by the fully HS complex $[Fe(L^H)]_2(ClO_4)_2$, and the smallest by the SCO-active complex $[Fe(L^{Me})]_2(ClO_4)_2$. Those fall nicely between the corresponding ranges for the earlier reported LS ($67.6(5)-75.4(5)^{\circ}$) and HS ($83.85(18)-89.6(2)^{\circ}$) iron(II) complexes of 3-bpp with ortho-substituted N-phenyl groups [27]. The rotation results in a severe distortion of the bis(pyrazol-3-yl)pyridine cores. The angles between the pyrazolyl and pyridine planes vary in a wide range of $2.3(3)-15.0(3)^{\circ}$, with the ligands in $[Fe(L^{Br})_2](ClO_4)_2$ being slightly flatter in terms of an average and the largest value of this angle (Table 3). It also enables the 2,6-dibromophenyl groups to form intramolecular 'parallel-displaced' [71] stacking interactions with the pyridine moieties of the second 3-bpp ligand, which may [37] (or may not [17]) contribute to highly distorted molecular geometries of $[Fe(L^R)_2](ClO_4)_2$ often associated with SCO-inactive complexes [23,72]. As a result, there is no 'terpyridine embrace' packing motif [73] in the crystals of the solvates $[Fe(L^H)_2](ClO_4)_2 \bullet 5.5THF$, $[Fe(L^{Br})_2](ClO_4)_2 \bullet 5.5THF \bullet 2H_2O$ and [Fe(L^{Me})₂](ClO₄)₂•2Et₂O•2CH₃CN (Figure 6) that is behind a cooperative SCO in some SCO-active metal complexes [74]. The geometrical parameters of these intramolecular stacking interactions, i.e., angles between the planes $(1.0(4)-5.4(2)^{\circ})$, centroid-centroid and shift distances (3.577(5)-3.730(5) and 1.008(6)-1.214(5) Å), again reveal no correlation with the SCO-activity of $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, as they are generally smaller in the former and are larger in the latter.

Other intramolecular interactions identified in the above solvates by the X-ray diffraction are similarly inconclusive, including those between the bromine ortho-substituents in the N-phenyl groups (Table 3) tentatively assigned to halogen bonds [75]. Based on interatomic distances Br ... Br that should be smaller and angles C-Br ... Br that should be closer to 180° for stronger halogen bonds, they seem to be slightly weaker in the less distorted complex [Fe(L^H)₂](ClO₄)₂; the appropriate average values are 3.74 Å and 104.0° as compared to 3.56-3.69 Å and $110.7-111.1^{\circ}$ in the two others. The bromine atoms also form Br ... pi interactions with the pi-systems of the pyrazolyl moieties, although the distances to these planes are almost the same at 3.3-3.4 Å in [Fe(L^H)₂](ClO₄)₂•5.5THF, [Fe(L^{Br})₂](ClO₄)₂•5.5THF•2H₂O and [Fe(L^{Me})₂](ClO₄)₂•2Et₂O•2CH₃CN.

As the above geometrical parameters of $[Fe(L^R)_2](ClO_4)_2$ were measured in a crystalline state, any correlations between them (or other parameters from Table 3) and the ability of the complexes $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$ to undergo a SCO in solutions may be hidden by crystal packing effects [23,24]. From the Hirshfeld surface analysis [76,77] that maps different types of intermolecular interactions on a 'molecular' surface of the cation $[Fe(L^R)_2]^{2+}$ and from 2D fingerprint plots [78] that quantify their occurrence (Figure 7), the major contribution in the solvates [Fe(L^H)₂](ClO₄)₂•5.5THF and $[Fe(L^{Me})_2](ClO_4)_2 \bullet 2Et_2 O \bullet 2CH_3 CN$ (39.4% and 36.4%, respectively) comes from numerous H... H contacts. In $[Fe(L^{Br})_2](ClO_4)_2$, however, Br... H contacts contribute the most (36.8% vs. 16.2 and 21.1% in the above solvates) while the H ... H contacts account for 22.6%. Similar values are found for O ... H interactions, the strongest of them being hydrogen bonds between the hydroxyl groups of the 3-bpp ligands and the perchlorate anions or solvent molecules that appear as bright red areas on the Hirshfeld surfaces and as most intense areas on the 2D fingerprint plots. Combined with the O ... H contacts produced by hydrogen atoms of 2,6-dibromophenyl, pyrazolyl or pyridine groups, they result in significant and rather similar contributions (23.7, 20.0 and 22.5%) to the overall crystal packing in [Fe(L^H)₂](ClO₄)₂•5.5THF, [Fe(L^{Br})₂](ClO₄)₂•5.5THF•2H₂O and $[Fe(L^{Me})_2](ClO_4)_2 \bullet 2Et_2O \bullet 2CH_3CN$. For comparison, C ... H contacts account for 9.3, 8.8 and 9.7% only.



Figure 6. Spiral-like packing of the cations $[Fe(L)_2]^{2+}$ in $[Fe(L^H)_2](ClO_4)_2$. For $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, see Figure S8 of ESI.



Figure 7. Hirshfeld surface (**left**) of the cation in $[Fe(L^H)_2](ClO_4)_2$ and its 2D fingerprint plot (**right**) as generated by Crystal Explorer [79]. On the Hirshfeld surfaces (**left**), intermolecular interactions with interatomic distances below, equal, or above a sum of van-der-Waals radii are shown by red, white, and blue areas, respectively. Green and blue areas on 2D fingerprint plots (**right**) stand for higher and lower concentration of points corresponding to (di, de) pairs. For $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, see Figure S9 of ESI.

To decouple the inherent structural features of $[Fe(L^R)_2](ClO_4)_2$ from these intermolecular interactions in $[Fe(L^H)_2](ClO_4)_2 \bullet 5.5$ THF, $[Fe(L^{Br})_2](ClO_4)_2 \bullet 5.5$ THF $\bullet 2H_2O$, and $[Fe(L^{Me})_2](ClO_4)_2 \bullet 2Et_2O \bullet 2CH_3CN$, we performed quantum chemical calculations of the isolated cations $[Fe(L^R)_2]^{2+}$, as crystal packing effects often prohibit a SCO [23,24] by, for example, inducing an additional distortion to the coordination geometry [23,24]. Indeed, a SCO does not generally [80] occur [81] in iron(II) complexes of 1-bpp [72] with the 'rotatioN' angle $\varphi < 172^{\circ}$ and/or the 'twist' angle $\theta < 76^{\circ}$, which is the case of $[Fe(L^R)_2](ClO_4)_2$ (Table 3). In the absence of X-ray diffraction data at higher temperatures due to low crystal quality, no conventional (or inverse [82]) SCO in any of the obtained solvates follows from their yellow color common for HS iron(II) complexes [1].

In the HS state, the isolated cations $[Fe(L^{\bar{R}})_2]^{2+}$ feature less distorted and more consistent coordination geometries than those measured experimentally (Tables 3 and S2), with weaker intramolecular interactions resulted from an expected overestimation of the Fe-N bond lengths. Indeed, the appropriate distances for the above stacking interactions, halogen bonds and Br ... pi contacts increase by 0.2–0.5 Å while remaining almost the same between the cations. Upon switching to the LS state, the Fe-N bonds in $[Fe(L^{R})_2]^{2+}$ shorten to values typical [1] for LS complexes of iron(II) in an octahedron-like coordination environment with a minor distortion towards an edge-bicapped tetrahedron induced by the rigid 3-bpp ligands [24]. For $[Fe(L^{H})_2]^{2+}$, however, this distortion is more pronounced, as highlighted by continuous symmetry measures [70] and the 'rotatioN' φ and 'twist' θ angles. The latter parameter even becomes smaller in the LS state (Table S2). Its bis(pyrazol-3-yl)pyridine cores also remain significantly distorted, with an average angle between the heterocyclic planes of 8.5° as compared to 5.2 and 4.5° in $[Fe(L^{Br})_2]^{2+}$ and $[Fe(L^{Me})_2]^{2+}$, respectively.

On the other hand, the rotation angle of the 2,6-dibromophenyl group from the pyrazolyl plane is nearly the same, with the values larger by 6° than in the HS state, mirroring a more 'perpendicular' molecular geometry of LS iron(II) complexes with N,N'-disubstituted 1-bpp, 3-bpp, or similar ligands [27] favored by intramolecular 'parallel-displaced' [71] stacking interactions. The latter, however, does not straightforwardly follow from the appropriate angles between the two planes, the centroid-centroid, and

shift distances that go from average values of $9.1-9.4^{\circ}$, 3.977-3.986, and 1.174-1.244 Å, respectively, to $10.0-13.6^{\circ}$, 3.837-3.893, and 1.013-1.518 Å, respectively, upon switching to the LS state. The cation $[Fe(L^H)_2]^{2+}$ again stands out, as it features a decrease in the shift distances in contrast to the other two cations. A similar behavior is observed for the other two types of intramolecular interactions, the halogen bonds Br ... Br and the interactions Br ... pi. In $[Fe(L^H)_2]^{2+}$, the average distance between the bromine ortho-substituents and to the pyrazolyl planes decreases by ~0.1 and 0.2 Å, respectively. In the cations $[Fe(L^{Br})_2]^{2+}$ and $[Fe(L^{Me})_2]^{2+}$, however, the former decreases by ~0.4 Å while the latter remains virtually the same at 3.6 Å.

Although none of the above geometric parameters clearly correlates with the SCOassisting tendency (or the lack thereof) of the complexes $[Fe(L^R)_2](ClO_4)_2$, an overall more distorted [23,24] molecular geometry of the LS cation $[Fe(L^H)_2]^{2+}$ that distinguishes it from the two others may be the reason for its LS state not being accessed in the entire temperature range of 190–325 K probed in solutions of $[Fe(L^H)_2](ClO_4)_2$. Indeed, the calculated energy difference between the two spin states of $[Fe(L^H)_2]^{2+}$ strongly favors the HS state, which is preferred by 7.7 kcal/mol. The same values of 4.2 and 1.2 kcal/mol for the cations $[Fe(L^{Br})_2]^{2+}$ and $[Fe(L^{Me})_2]^{2+}$ agree nicely with the complexes $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$ undergoing a SCO with the midpoint temperatures of 195–198 and 205 K, indicative of a HS state stabilization [12] by the larger bromine atom.

To trace the observed differences in the solution behaviour of the complexes $[Fe(L^R)_2]$ (ClO₄)₂ to the ligand design, the electronic and steric effects of the para-substituents in the N-phenyl groups were probed by charges of coordinating nitrogen atoms [15] and distances between them [13] in the free ligands L^R and by energy profiles to the rotation of the N-phenyl groups [27]. The calculated charges [15] are virtually the same in the three ligands (Table 4) but their geometries are not. While the distances between the pyrazolyl and pyridine nitrogen atoms in L^{Br} and L^{Me} fall into the ranges for SCO-active iron(II) complexes, the ligand L^H features smaller values associated with the LS state [13], as opposed to the entirely HS complex $[Fe(L^H)_2](ClO_4)_2$. Large separations between the pyrazolyl nitrogen atoms result from the rotation of one of the pyrazol-3-yl moieties relative to the pyridine plane, which is less pronounced in L^H . Note, however, a typical configuration of the free 3-bpp ligands from the available X-rays diffraction data [41,83–85], with these nitrogen atoms pointing towards the para-position of the pyridine moiety which undermines the validity of the distance-based correlation proposed for the bidentate ligands [13].

Parameter	LH	L ^{Br}	L ^{Me}
Fe-N _{Pv} , Å	4.794	5.085	5.002
Fe-N _{Pz} , Å	2.795/2.771	2.811/2.902	2.763/2.893
N _{pz} N _{pz} , Å	118.9	125.7	124.4
$N_{py} \dots N_{pz}$, Å	-0.22	-0.22	-0.22
NpzNpyNpz, °	-0.37	-0.38	-0.37
q(N _{Pz}), e	81.1/88.9	84.7/75.7	80.8/81.2
q(N _{Py}), e	4.5/19.2	15.5/36.0	12.2/39.8
γ, \circ	4.794	5.085	5.002
β,°	2.795/2.771	2.811/2.902	2.763/2.893

Table 4. Selected geometric parameters ¹ and NBO charges of coordinating nitrogen atoms in the ligands L^{R} as obtained from TPSSh/def2-TZVP calculations.

 $\frac{1}{\gamma}$ is the rotation angle of the N-phenyl group relative to the pyrazol-3-yl plane; β is the rotation angle of the pyrazol-3-yl moiety relative to the pyridine plane.

As should be common for a distal substituent, the energy profiles for the rotation of the para-substituted 2,6-dibromophenyl groups are identical for the three model compounds (Figure 8), with a monotonical increase up to ca. 21.0 kcal/mol at 0° expected [27] for the large bromine atoms in the ortho-positions [27]. For the para-substituents, however, the size cannot explain the SCO-assisting tendency or the lack thereof by the energy penalty to



rotation (although they have the same effect as the bulky ortho-substituents in the N-phenyl groups of the 3-bpp ligands on the spin-state behavior of their iron(II) complexes [27]).

Figure 8. Energy variation upon the rotation of 2,6-disubstituted N-phenyl group relative to the pyrazol-3-yl plane as quantified by an angle between their least-square planes in model arylpyrazole pyridines according to TPSSh/def2-TZVP calculations.

4. Conclusions

A combined study of new iron(II) complexes $[Fe(L^R)_2](ClO_4)_2$ with 3-bpp ligands N,N'-disubstituted by 4-functionalized 2,6-dibromophenyl groups allowed for probing the effect of a distal para-substituent on the spin-state behavior of these complexes and determining the reasons behind it using X-ray diffraction, variable-temperature magnetic measurements, and NMR spectroscopy (the latter being the method of choice for 'truly molecular' design [12] of SCO compounds). An absence of a thermally-induced SCO in the case of the unsubstituted 2,6-dibromophenyl group in L^H agrees with an accepted [12] tendency for the HS state stabilization of bulky [27] substituents close to the metal ion. It, however, cannot explain the SCO-assisting tendency of the substituents in its para-position unambiguously identified by two separate approaches in NMR spectroscopy (i.e., the popular Evans method [50,51] and the analysis of chemical shifts in variable-temperature NMR spectra [40]).

The chosen para-substituents, i.e. the bromine atom and the methyl group, have different electronic characteristics, although they hardly affect the spin state of the iron(II) ion, as expected for such distal substituents and supported by the charges of the coordinating nitrogen atoms [15] in the free ligands. In contrast to previously discarded [27,69] electronic reasons behind the LS state stabilization by mesityl-substituted 1-bpp, a possible explanation by intramolecular stacking interactions [37] tuned by the electronic effects [86] does not seem viable. Indeed, the bromine atom and the methyl group should have opposite electronic effects. However, the resulting SCO-assisting tendency of the 3-bpp ligands L^{Br} and L^{Me} is almost the same as judged by similar midpoint temperatures $T_{1/2}$ of the SCO in solutions of $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$. The latter also mirrors similar steric demands of these substituents (as gauged by their sizes), with the larger bromine atom [12] favoring the HS state in compliance with the common wisdom in SCO research [12]. However, their effect on the spin state through the rotation of an appropriately substituted 2,6-dibromophenyl group [27,69] is expectedly negligible, as follows from the calculated energy variation in the corresponding phenylpyrazole molecules.

Other possible reasons could be intramolecular dispersion interactions between the bromine atom or the methyl group and the pyridine moiety of the second ligand in the complex $[Fe(L^R)_2](ClO_4)_2$ favoring the LS state [87] or, as an alternative, steric clashes between them. The latter, counterintuitive finding is, however, in an agreement with a

previously stated idea that the LS state of the iron(II) complex of a mesityl-substituted 1-bpp is a result of the mesityl groups avoiding steric clashes [69].

Either way, the para-substituents introduced at the 2,6-dibromophenyl groups induce a SCO, as do bulky (but not too bulky [27]) substituents in the ortho-positions of the N-phenyl groups. Although the exact reason behind their SCO-assisting tendency in the N,N'-disubstituted 3-bpp ligands is still unknown, it is probably an intricate combination of the above aspects of the ligand and the complex design and is clearly rooted in the planar shape of the N-phenyl group [27].

With an observed SCO in solution of $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$, a series of SCO-active complexes of N,N'-disubstituted 3-bpp contains seven representatives [27,40], thus paving the way for this family of SCO compounds amenable to functionalization at other positions of the ligand and screening [40] by NMR spectroscopy to become as instructive as the most populated [12] 1-bpp family in revealing structure–function relations for the successful molecular design of SCO compounds.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/cryst11080922/s1. Figure S1: Variable-temperature magnetic susceptibility data for finecrystalline samples of $[Fe(L^{Br})_2](ClO_4)_2$ (left) and $[Fe(L^{Me})_2](ClO_4)_2$ (right) according to the dcmagnetometry (the red lines represent the fits); Figure S2: Variable-temperature magnetic susceptibility data for the solution of $[Fe(L^{H})_{2}](ClO_{4})_{2}$ in methanol-d₄ according to the Evans method; Figure S3: Variable-temperature ¹H NMR spectra for [Fe(L^H)₂](ClO₄)₂ (top) and [Fe(L^{Br})₂](ClO₄)₂ (bottom) in an acetonitrile-d₃ solution; Figure S4: Variable-temperature ¹H NMR spectra for $[Fe(L^{Me})_2](ClO_4)_2$ in an acetonitrile- d_3 solution (top) and its chemical shifts plotted versus 1/T (bottom). Solid lines represent the linear fit over the temperature range 285–325 K, and each color indicates a specific type of the protons that are the same between the complexes; Figure S5: Variable-temperature ¹H NMR spectra for [Fe(L^H)₂](ClO₄)₂ in a methanol-d₄ solution (top) and its chemical shifts plotted versus 1/T (bottom)./ Solid lines represent the linear fit over the entire temperature range, and each color indicates a specific type of the protons that are the same between the complexes; Figure S6: HS state population of $[Fe(L^{Br})_2](ClO_4)_2$ and $[Fe(L^{Me})_2](ClO_4)_2$ in acetonitrile-d₃ from the Evans method. The lines correspond to the best fit by a regular solution model; Figure S7: General view of the cations in $[Fe(L^{Br})]_2(ClO_4)_2$ (left) and $[Fe(L^{Me})]_2(ClO_4)_2$ (right) as obtained from X-ray diffraction at 120 K. Non-hydrogen atoms are shown as thermal ellipsoids (p = 30%), hydrogen atoms except those of OH groups are omitted for clarity, and only labels of the heteroatoms in an asymmetric part of the unit cell are given; Figure S8: Spiral-like packing of the cations in $[Fe(L^{Br})]_2(ClO_4)_2$ (left) and [Fe(L^{Me})]₂(ClO₄)₂ (right); Figure S9: Hirshfeld surfaces (left) of the cations and their 2D fingerprint plots (right) as generated by Crystal Explorer in [Fe(L^{Br})₂](ClO₄)₂ (top) and [Fe(L^{Me})₂](ClO₄)₂ (bottom). On the Hirshfeld surfaces (left), intermolecular interactions with interatomic distances below, equal or above a sum of van-der-Waals radii are shown by red, white and blue areas, respectively. Green and blue areas on fingerprint plots (right) stand for higher and lower concentration of points corresponding to (di, de) pairs; Table S1: SCO parameters from the NMR data for acetonitrile-d₃ solutions; Table S2: Main geometric parameters and continuous symmetry measures¹ as obtained from TPSSh/def2-TZVP calculations of the cations $[Fe(L^R)_2]^{2+}$ in the LS and the HS states.

Author Contributions: Conceptualization, Y.V.N.; methodology, E.K.M., D.Y.A., R.R.A., L.M.C. and I.A.N.; software, E.K.M. and D.Y.A.; validation, Y.V.N., A.V.P., E.R. and V.V.N.; formal analysis, E.K.M. and D.Y.A.; investigation, E.K.M., D.Y.A., R.R.A. and I.A.N.; resources, Y.V.N.; data curation, Y.V.N.; writing—original draft preparation, E.K.M. and I.A.N.; writing—review and editing, Y.V.N.; visualization, E.K.M., I.A.N., R.R.A. and D.Y.A.; supervision, Y.V.N.; project administration, Y.V.N.; funding acquisition, Y.V.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Russian Science Foundation (Project 17-13-01456). Elemental analysis was performed using the equipment of the Center for Molecular Composition Studies of INEOS RAS with the financial support from the Ministry of Science and Higher Education of the Russian Federation.

Data Availability Statement: Data is contained within the article or Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Halcrow, M.A. Spin-Crossover Materials: Properties and Applications; John Wiley & Sons, Ltd.: Chichester, UK, 2013. [CrossRef]
- Molnár, G.; Rat, S.; Salmon, L.; Nicolazzi, W.; Bousseksou, A. Spin Crossover Nanomaterials: From Fundamental Concepts to Devices. Adv. Mater. 2017, 30, 1703862. [CrossRef]
- Senthil Kumar, K.; Ruben, M. Emerging trends in spin crossover (SCO) based functional materials and devices. *Coord. Chem. Rev.* 2017, 346, 176–205. [CrossRef]
- 4. Kahn, O.; Kröber, J.; Jay, C. Spin Transition Molecular Materials for displays and data recording. *Adv. Mater.* **1992**, *4*, 718–728. [CrossRef]
- Resines-Urien, E.; Burzurí, E.; Fernandez-Bartolome, E.; García García-Tuñón, M.Á.; de la Presa, P.; Poloni, R.; Teat, S.J.; Costa, J.S. A switchable iron-based coordination polymer toward reversible acetonitrile electro-optical readout. *Chem. Sci.* 2019, 10, 6612–6616. [CrossRef]
- 6. Linares, J.; Codjovi, E.; Garcia, Y. Pressure and Temperature Spin Crossover Sensors with Optical Detection. *Sensors* **2012**, *12*, 4479–4492. [CrossRef]
- Villalva, J.; Develioglu, A.; Montenegro-Pohlhammer, N.; Sánchez-de-Armas, R.; Gamonal, A.; Rial, E.; García-Hernández, M.; Ruiz-Gonzalez, L.; Costa, J.S.; Calzado, C.J.; et al. Spin-state-dependent electrical conductivity in single-walled carbon nanotubes encapsulating spin-crossover molecules. *Nat. Commun.* 2021, *12*, 1578. [CrossRef]
- 8. 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. [CrossRef] [PubMed]
- 9. Tsukiashi, A.; Min, K.S.; Kitayama, H.; Terasawa, H.; Yoshinaga, S.; Takeda, M.; Lindoy, L.F.; Hayami, S. Application of spin-crossover water soluble nanoparticles for use as MRI contrast agents. *Sci. Rep.* **2018**, *8*, 14911. [CrossRef]
- 10. Guionneau, P.; Le Gac, F.; Kaiba, A.; Costa, J.S.; Chasseau, D.; Létard, J.-F. A reversible metal–ligand bond break associated to a spin-crossover. *Chem. Commun.* 2007, *36*, 3723–3725. [CrossRef] [PubMed]
- 11. Guionneau, P.; Costa, J.S.; Létard, J.F. Revisited crystal symmetry of the high-spin form of the iron(II) spin-crossover complex dicyano[2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene]iron(II) monohydrate. *Acta Cryst. C* 2004, *60*, m587–m589. [CrossRef] [PubMed]
- Halcrow, M.A. The Effect of Ligand Design on Metal Ion Spin State—Lessons from Spin Crossover Complexes. *Crystals* 2016, 6, 58. [CrossRef]
- 13. 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. [CrossRef] [PubMed]
- 14. Rodríguez-Jiménez, S.; Yang, M.; Stewart, I.; Garden, A.L.; Brooker, S. A Simple Method of Predicting Spin State in Solution. *J. Am. Chem. Soc.* 2017, 139, 18392–18396. [CrossRef] [PubMed]
- 15. Kimura, A.; Ishida, T. Spin-Crossover Temperature Predictable from DFT Calculation for Iron(II) Complexes with 4-Substituted Pybox and Related Heteroaromatic Ligands. *ACS Omega* **2018**, *3*, 6737–6747. [CrossRef] [PubMed]
- 16. Kershaw Cook, L.J.; Kulmaczewski, R.; Mohammed, R.; Dudley, S.; Barrett, S.A.; Little, M.A.; Deeth, R.; Halcrow, M.A. A Unified Treatment of the Relationship Between Ligand Substituents and Spin State in a Family of Iron(II) Complexes. *Angew. Chem. Int. Ed.* **2016**, *55*, 4327–4331. [CrossRef]
- 17. Elhaïk, J.; Evans, D.J.; Kilner, C.A.; Halcrow, M.A. A structural, magnetic and Mössbauer spectroscopic study of an unusual angular Jahn–Teller distortion in a series of high-spin iron(ii) complexes. *Dalton Trans.* **2005**, 1693–1700. [CrossRef]
- 18. McPherson, J.N.; Elton, T.E.; Colbran, S.B. A Strain-Deformation Nexus within Pincer Ligands: Application to the Spin States of Iron(II) Complexes. *Inorg. Chem.* 2018, 57, 12312–12322. [CrossRef]
- Santoro, A.; Kershaw Cook, L.J.; Kulmaczewski, R.; Barrett, S.A.; Cespedes, O.; Halcrow, M.A. Iron(II) Complexes of Tridentate Indazolylpyridine Ligands: Enhanced Spin-Crossover Hysteresis and Ligand-Based Fluorescence. *Inorg. Chem.* 2015, 54, 682–693. [CrossRef]
- 20. Nakano, K.; Suemura, N.; Yoneda, K.; Kawata, S.; Kaizaki, S. Substituent effect of the coordinated pyridine in a series of pyrazolato bridged dinuclear diiron(ii) complexes on the spin-crossover behavior. *Dalton Trans.* 2005, 740–743. [CrossRef]
- Kitchen, J.A.; Olguín, J.; Kulmaczewski, R.; White, N.G.; Milway, V.A.; Jameson, G.N.L.; Tallon, J.L.; Brooker, S. Effect of N4-Substituent Choice on Spin Crossover in Dinuclear Iron(II) Complexes of Bis-Terdentate 1,2,4-Triazole-Based Ligands. *Inorg. Chem.* 2013, 52, 11185–11199. [CrossRef]
- 22. Hoselton, M.A.; Wilson, L.J.; Drago, R.S. Substituent effects on the spin equilibrium observed with hexadentate ligands on iron(II). *J. Am. Chem. Soc.* **1975**, *97*, 1722–1729. [CrossRef]
- Kershaw Cook, L.; Mohammed, R.; Sherborne, G.; Roberts, T.D.; Alvarez, S.; Halcrow, M.A. Spin state behavior of iron(II)/dipyrazolylpyridine complexes. New insights from crystallographic and solution measurements. *Coord. Chem. Rev.* 2015, 289, 2–12. [CrossRef]
- Craig, G.A.; Costa, J.S.; Roubeau, O.; Teat, S.J.; Aromí, G. Local Coordination Geometry and Spin State in Novel Fe^{II} Complexes with 2,6-Bis(pyrazol-3-yl)pyridine-Type Ligands as Controlled by Packing Forces: Structural Correlations. *Chem. Eur. J.* 2012, 18, 11703–11715. [CrossRef]
- Beniwal, S.; Zhang, X.; Mu, S.; Naim, A.; Rosa, P.; Chastanet, G.; Létard, J.F.; Liu, J.; Sterbinsky, G.E.; Arena, D.A.; et al. Surface-induced spin state locking of the [Fe(H2B(pz)2)2(bipy)] spin crossover complex. *J. Phys. Condensed Mat.* 2016, 28, 206002. [CrossRef]

- Gentili, D.; Liscio, F.; Demitri, N.; Schäfer, B.; Borgatti, F.; Torelli, P.; Gobaut, B.; Panaccione, G.; Rossi, G.; Degli Esposti, A.; et al. Surface induces different crystal structures in a room temperature switchable spin crossover compound. *Dalton Trans.* 2016, 45, 134–143. [CrossRef]
- Nikovskiy, I.; Polezhaev, A.V.; Novikov, V.V.; Aleshin, D.; Pavlov, A.A.; Saffiulina, E.; Aysin, R.R.; Dorovatovskii, P.; Nodaraki, L.; Tuna, F.; et al. Towards molecular design of spin-crossover complexes of 2,6-bis(pyrazol-3-yl)pyridines. *Chem. Eur. J.* 2020, 26, 5629–5638. [CrossRef]
- 28. 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. [CrossRef]
- Scudder, M.L.; Craig, D.C.; Goodwin, H.A. Hydrogen bonding influences on the properties of heavily hydrated chloride salts of iron(ii) and ruthenium(ii) complexes of 2,6-bis(pyrazol-3-yl)pyridine, 2,6-bis(1,2,4-triazol-3-yl)pyridine and 2,2':6',2"-terpyridine. *CrystEngComm* 2005, 7, 642–649. [CrossRef]
- 30. Clemente-León, M.; Coronado, E.; Giménez-López, M.C.; Romero, F.M. Structural, Thermal, and Magnetic Study of Solvation Processes in Spin-Crossover [Fe(bpp)2][Cr(L)(ox)2]2·nH2O Complexes. *Inorg. Chem.* 2007, 46, 11266–11276. [CrossRef]
- Coronado, E.; Gimenez-Lopez, M.C.; Gimenez-Saiz, C.; Romero, F.M. Spin crossover complexes as building units of hydrogenbonded nanoporous structures. *CrystEngComm* 2009, 11, 2198–2203. [CrossRef]
- 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. [CrossRef]
- 33. Jornet-Molla, V.; Gimenez-Saiz, C.; Romero, F.M. Synthesis, Structure, and Photomagnetic Properties of a Hydrogen-Bonded Lattice of [Fe(bpp)2]2+ Spin-Crossover Complexes and Nicotinate Anions. *Crystals* **2018**, *8*, 439. [CrossRef]
- 34. Barrett, S.A.; Halcrow, M.A. Anion-dependent spin crossover in solution for an iron(ii) complex of a 1H-pyrazolyl ligand. *RSC Adv.* **2014**, *4*, 11240–11243. [CrossRef]
- 35. Barrett, S.A.; Kilner, C.A.; Halcrow, M.A. Spin-crossover in [Fe(3-bpp)2][BF4]2 in different solvents—A dramatic stabilisation of the low-spin state in water. *Dalton Trans.* 2011, 40, 12021–12024. [CrossRef]
- Roberts, T.D.; Little, M.A.; Kershaw Cook, L.J.; Barrett, S.A.; Tuna, F.; Halcrow, M.A. Iron(II) complexes of 2,6-di(1-alkylpyrazol-3-yl)pyridine derivatives—The influence of distal substituents on the spin state of the iron centre. *Polyhedron* 2013, 64, 4–12. [CrossRef]
- Nelyubina, Y.V.; Polezhaev, A.V.; Pavlov, A.A.; Aleshin, D.; Savkina, S.A.; Efimov, N.N.; Aliev, T.; Novikov, V.V. Intramolecular Spin State Locking in Iron(II) 2,6-Di(pyrazol-3-yl)pyridine Complexes by Phenyl Groups: An Experimental Study. *Magnetochemistry* 2018, 4, 46. [CrossRef]
- 38. Argent, S.P.; Adams, H.; Harding, L.P.; Riis-Johannessen, T.; Jeffery, J.C.; Ward, M.D. Homo- and heteropolynuclear helicates with a '2 + 3 + 2'-dentate compartmental ligand. *New J. Chem.* **2005**, *29*, 904–911. [CrossRef]
- Barrios, L.A.; Bartual-Murgui, C.; Peyrecave-Lleixa, E.; Le Guennic, B.; Teat, S.J.; Roubeau, O.; Aromi, G. Homoleptic versus Heteroleptic Formation of Mononuclear Fe(II) Complexes with Tris-Imine Ligands. *Inorg. Chem.* 2016, 55, 4110–4116. [CrossRef] [PubMed]
- 40. Pankratova, Y.; Aleshin, D.; Nikovskiy, I.; Novikov, V.; Nelyubina, Y. In Situ NMR Search for Spin-Crossover in Heteroleptic Cobalt(II) Complexes. *Inorg. Chem.* 2020, *59*, 7700–7709. [CrossRef]
- Polezhaev, A.V.; Chen, C.-H.; Kinne, A.S.; Cabelof, A.C.; Lord, R.L.; Caulton, K.G. Ligand Design toward Multifunctional Substrate Reductive Transformations. *Inorg. Chem.* 2017, *56*, 9505–9514. [CrossRef] [PubMed]
- 42. Wang, X.; Chen, Y.-F.; Yan, W.; Cao, L.-L.; Ye, Y.-H. Synthesis and Biological Evaluation of Benzimidazole Phenylhydrazone Derivatives as Antifungal Agents against Phytopathogenic Fungi. *Molecules* **2016**, *21*, 1574. [CrossRef]
- Chan, J.H.; Hong, J.S.; Hunter, R.N.; Orr, G.F.; Cowan, J.R.; Sherman, D.B.; Sparks, S.M.; Reitter, B.E.; Andrews, C.W.; Hazen, R.J.; et al. 2-Amino-6-arylsulfonylbenzonitriles as Non-nucleoside Reverse Transcriptase Inhibitors of HIV-1. *J. Med. Chem.* 2001, 44, 1866–1882. [CrossRef] [PubMed]
- 44. Delany, E.G.; Connon, S.J. Highly chemoselective intermolecular cross-benzoin reactions using an ad hoc designed novel N-heterocyclic carbene catalyst. *Org. Biomol. Chem.* **2018**, *16*, 780–786. [CrossRef]
- 45. Fairhead, M.; Shen, D.; Chan, L.K.M.; Lowe, E.D.; Donohoe, T.J.; Howarth, M. Love–Hate ligands for high resolution analysis of strain in ultra-stable protein/small molecule interaction. *Bioorg. Med. Chem.* **2014**, 22, 5476–5486. [CrossRef]
- 46. 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. Cryst. 2009, 42, 339–341. [CrossRef]
- 47. Sheldrick, G.M. SHELXT-Integrated space-group and crystal-structure determination. Acta Cryst. A 2015, 71, 3–8. [CrossRef]
- 48. Bain, G.A.; Berry, J.F. Diamagnetic Corrections and Pascal's Constants. J. Chem. Educ. 2008, 85, 532. [CrossRef]
- 49. Chilton, N.F.; Anderson, R.P.; Turner, L.D.; Soncini, A.; Murray, K.S. Phi: A Powerful New Program for the Analysis of Anisotropic Monomeric and Exchange-Coupled Polynuclear D- and F-Block Complexes. *J. Comp. Chem.* **2013**, *34*, 1164–1175. [CrossRef]
- 50. Evans, D.F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.* **1959**, 2003–2005. [CrossRef]
- 51. Piguet, C. Paramagnetic Susceptibility by NMR: The "Solvent Correction" Removed for Large Paramagnetic Molecules. *J. Chem. Educ.* **1997**, *74*, 815. [CrossRef]

- 52. Pavlov, A.A.; Nehrkorn, J.; Pankratova, Y.A.; Ozerov, M.; Mikhalyova, E.A.; Polezhaev, A.V.; Nelyubina, Y.V.; Novikov, V.V. Detailed electronic structure of a high-spin cobalt(ii) complex determined from NMR and THz-EPR spectroscopy. *Phys. Chem. Chem. Phys.* **2019**, *21*, 8201–8204. [CrossRef] [PubMed]
- 53. Weber, B.; Walker, F.A. Solution NMR studies of iron(II) spin-crossover complexes. *Inorg. Chem.* 2007, *46*, 6794–6803. [CrossRef] [PubMed]
- 54. Creutz, S.E.; Peters, J.C. Spin-State Tuning at Pseudo-tetrahedral d6 Ions: Spin Crossover in [BP3]FeII–X Complexes. *Inorg. Chem.* **2016**, *55*, 3894–3906. [CrossRef]
- 55. Neese, F. The ORCA program system. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 73–78. [CrossRef]
- 56. Neese, F. Software update: The ORCA program system, version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2018, *8*, e1327. [CrossRef]
- 57. Tao, J.; Perdew, J.P.; Staroverov, V.N.; Scuseria, G.E. Climbing the Density Functional Ladder: Nonempirical Meta–Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401. [CrossRef] [PubMed]
- 58. Staroverov, V.N.; Scuseria, G.E.; Tao, J.; Perdew, J.P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys.* **2003**, *119*, 12129–12137. [CrossRef]
- 59. Staroverov, V.N.; Scuseria, G.E.; Tao, J.; Perdew, J.P. Erratum: "Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes" [J. Chem. Phys. 119, 12129 (2003)]. J. Chem. Phys. 2004, 121, 11507. [CrossRef]
- 60. 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. [CrossRef]
- 61. Cirera, J.; Via-Nadal, M.; Ruiz, E. Benchmarking Density Functional Methods for Calculation of State Energies of First Row Spin-Crossover Molecules. *Inorg. Chem.* 2018, *57*, 14097–14105. [CrossRef]
- 62. Neese, F. An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix. *J. Comput. Chem.* **2003**, *24*, 1740–1747. [CrossRef]
- 63. Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. Phys. Chem. Chem. Phys. 2006, 8, 1057–1065. [CrossRef]
- 64. Pavlov, A.A.; Aleshin, D.Y.; Nikovskiy, I.A.; Polezhaev, A.V.; Efimov, N.N.; Korlyukov, A.A.; Novikov, V.V.; Nelyubina, Y.V. New Spin-Crossover Complexes of Substituted 2,6-Bis(pyrazol-3-yl)pyridines. *Eur. J. Inorg. Chem.* **2019**, 2019, 2819–2829. [CrossRef]
- 65. Petzold, H.; Djomgoue, P.; Hörner, G.; Lochenie, C.; Weber, B.; Rüffer, T. Bis-meridional Fe2+ spincrossover complexes of phenyl and pyridyl substituted 2-(pyridin-2-yl)-1,10-phenanthrolines. *Dalton Trans.* **2018**, *47*, 491–506. [CrossRef]
- Pavlov, A.A.; Denisov, G.L.; Kiskin, M.A.; Nelyubina, Y.V.; Novikov, V.V. Probing Spin Crossover in a Solution by Paramagnetic NMR Spectroscopy. *Inorg. Chem.* 2017, 56, 14759–14762. [CrossRef]
- Galadzhun, I.; Kulmaczewski, R.; Cespedes, O.; Yamada, M.; Yoshinari, N.; Konno, T.; Halcrow, M.A. 2,6-Bis(pyrazol-1yl)pyridine-4-carboxylate Esters with Alkyl Chain Substituents and Their Iron(II) Complexes. *Inorg. Chem.* 2018, 57, 13761–13771. [CrossRef]
- 68. Ammon, H.L. New Atom/Functional Group Volume Additivity Data Bases for the Calculation of the Crystal Densities of C-, H-, N-, O-, F-, S-, P-, Cl-, and Br-Containing Compounds. *Struct. Chem.* **2001**, *12*, 205–212. [CrossRef]
- 69. Bartual-Murgui, C.; Vela, S.; Roubeau, O.; Aromi, G. Designed intramolecular blocking of the spin crossover of an Fe(ii) complex. *Dalton Trans.* **2016**, *45*, 14058–14062. [CrossRef]
- 70. Alvarez, S. Distortion Pathways of Transition Metal Coordination Polyhedra Induced by Chelating Topology. *Chem. Rev.* 2015, 115, 13447–13483. [CrossRef]
- 71. Wheeler, S.E. Understanding Substituent Effects in Noncovalent Interactions Involving Aromatic Rings. *Acc. Chem. Res.* 2013, *46*, 1029–1038. [CrossRef] [PubMed]
- 72. Halcrow, M.A. Iron(II) complexes of 2,6-di(pyrazol-1-yl)pyridines—A versatile system for spin-crossover research. *Coord. Chem. Rev.* 2009, 253, 2493–2514. [CrossRef]
- 73. Scudder, M.L.; Goodwin, H.A.; Dance, I.G. Crystal supramolecular motifs: Two-dimensional grids of terpy embraces in [ML2] complexes (L = terpy or aromatic N3-tridentate ligand). *New J. Chem.* **1999**, *23*, 695–705. [CrossRef]
- 74. Pritchard, R.; Kilner, C.A.; Halcrow, M.A. Iron(ii) complexes with a terpyridine embrace packing motif show remarkably consistent cooperative spin-transitions. *Chem. Commun.* 2007, 577–579. [CrossRef]
- 75. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* 2016, 116, 2478–2601. [CrossRef]
- McKinnon, J.J.; Mitchell, A.S.; Spackman, M.A. Hirshfeld Surfaces: A New Tool for Visualising and Exploring Molecular Crystals. *Chem. Eur. J.* 1998, 4, 2136–2141. [CrossRef]
- 77. Spackman, M.A.; Jayatilaka, D. Hirshfeld surface analysis. CrystEngComm 2009, 11, 19–32. [CrossRef]
- 78. Spackman, M.A.; McKinnon, J.J. Fingerprinting intermolecular interactions in molecular crystals. *CrystEngComm* **2002**, *4*, 378–392. [CrossRef]
- 79. Wolff, S.K.; Grimwood, D.J.; McKinnon, J.J.; Turner, M.J.; Jayatilaka, D.; Spackman, M.A. *CrystalExplorer (Version 3.1)*; University of Western Australia: Perth, Australia, 2012.
- Berdiell, I.C.; Kulmaczewski, R.; Shahid, N.; Cespedes, O.; Halcrow, M.A. The number and shape of lattice solvent molecules controls spin-crossover in an isomorphous series of crystalline solvate salts. *Chem. Commun.* 2021, 57, 6566–6569. [CrossRef] [PubMed]

- Kershaw Cook, L.J.; Thorp-Greenwood, F.L.; Comyn, T.P.; Cespedes, O.; Chastanet, G.; Halcrow, M.A. Unexpected Spin-Crossover and a Low-Pressure Phase Change in an Iron(II)/Dipyrazolylpyridine Complex Exhibiting a High-Spin Jahn–Teller Distortion. *Inorg. Chem.* 2015, 54, 6319–6330. [CrossRef] [PubMed]
- 82. Hayami, S.; Komatsu, Y.; Shimizu, T.; Kamihata, H.; Lee, Y.H. Spin-crossover in cobalt(II) compounds containing terpyridine and its derivatives. *Coord. Chem. Rev.* 2011, 255, 1981–1990. [CrossRef]
- 83. Sherbow, T.J.; Fettinger, J.C.; Berben, L.A. Control of Ligand pKa Values Tunes the Electrocatalytic Dihydrogen Evolution Mechanism in a Redox-Active Aluminum(III) Complex. *Inorg. Chem.* **2017**, *56*, 8651–8660. [CrossRef] [PubMed]
- Zabel, D.; Schubert, A.; Wolmershäuser, G.; Jones Jr, R.L.; Thiel, W.R. Iron and Cobalt Complexes of Tridentate N-Donor Ligands in Ethylene Polymerization: Efficient Shielding of the Active Sites by Simple Phenyl Groups. *Eur. J. Inorg. Chem.* 2008, 2008, 3648–3654. [CrossRef]
- 85. Cook, B.J.; Chen, C.-H.; Pink, M.; Lord, R.L.; Caulton, K.G. Coordination and electronic characteristics of a nitrogen heterocycle pincer ligand. *Inorg. Chim. Acta* 2016, 451, 82–91. [CrossRef]
- Holland, J.M.; Barrett, S.A.; Kilner, C.A.; Halcrow, M.A. Control of the spin state of Fe(II) 2,6-di(pyrazol-1-yl)pyridine complexes by distal ligand substitution. *Inorg. Chem. Comm.* 2002, *5*, 328–332. [CrossRef]
- Deeth, R.J.; Halcrow, M.A.; Kershaw Cook, L.J.; Raithby, P.R. Ab Initio Ligand Field Molecular Mechanics and the Nature of Metal-Ligand π-Bonding in Fe(II) 2,6-di(pyrazol-1-yl)pyridine Spin Crossover Complexes. *Chem. Eur. J.* 2018, 24, 5204–5212. [CrossRef] [PubMed]