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Room-Temperature Spin Crossover in a Solution of Iron(II) Complexes with *N*,*N*'-Disubstituted Bis(pyrazol-3-yl)pyridines

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ABSTRACT: Here, we report a combined study of the effects of two chemical modifications to an N,N'-disubstituted bis(pyrazol-3-yl)pyridine (3-bpp) and of different solvents on the spin-crossover (SCO) behavior in otherwise high-spin iron(II) complexes by solution NMR spectroscopy. The observed stabilization of the low-spin state by electron-withdrawing substituents in the two positions of the ligand that induce opposite electronic effects in SCO–active iron(II) complexes of isomeric bis(pyrazol-1-yl)pyridines (1-bpp) was previously hidden by NH functionalities in 3-bpp precluding the molecular design of SCO compounds with this family of ligands. With the recent SCO-assisting substituent design, the uncovered trends converged toward the first iron(II) complex of N,N'-disubstituted 3-bpp to undergo an almost complete SCO centered at room temperature in a less polar solvent of a high hydrogen-bond acceptor ability.



■ INTRODUCTION

Spin-crossover (SCO) complexes¹ have been actively sought in the last few decades to create new materials with switchable magnetic, optical, mechanical, and polyfunctional properties.^{2,3} They use the ability of a transition-metal ion to reversibly switch between two spin states—low spin (LS) and high spin (HS) under an applied physical or chemical stimulus.¹ Changes in temperature or pressure,¹ light irradiation,⁴ chemical transformations, or noncovalent interactions⁵ may cause an abrupt hysteretic^{6,7} SCO in solids, mostly of iron(II) complexes with a (pseudo)octahedral coordination by *N*-heterocyclic donor ligands,^{8,9} or a gradual incomplete SCO in solutions. Both behaviors are exploited in displays,¹⁰ switches,¹¹ memory devices,¹² sensors^{13–16} for detection of various stimuli and analytes, thermometers^{17,18} and contrast agents¹⁹ in magnetic resonance imaging, etc.^{2,3}

For these applications, an SCO centered around room temperature⁵ is often preferred that can be induced at the single-molecule level by molecular design. The latter relies on a good control of SCO temperatures by chemical modifications to the ligands achieved in solutions of SCO compounds²⁰ with no contribution from crystal packing or other crystal-related effects, such as polymorphism. Of various techniques suited for the purpose,^{21,22} the method of choice²³ is often NMR spectros-copy²⁰ that probes an SCO by the Evans method.²⁴ As a solution-state alternative to magnetometry, the Evans method²⁴ measures magnetic susceptibility of a compound by comparing chemical shifts of an inert substance in NMR spectra collected simultaneously from the solution that contains the compound in an appropriate solvent and the one that contains only the

solvent. It, however, requires pure solutions of known concentration with no side-products or chemical transformations occurring during the measurement to provide results within a claimed error of 5-10%.²⁵ Instead of or in combination with the Evans method, various approaches²⁶⁻²⁹ to the analysis of NMR chemical shifts³⁰ are sometimes used to quantify the spin state evolution in the presence of diamagnetic²³ or even paramagnetic^{31,32} compounds. Such studies allowed identifying a thermally induced SCO centered at^{14,29,33-38} or slightly above^{39,40} room temperature in solutions of few coordination compounds. There are, however, fewer examples of an SCO that is almost complete^{31,34,37,38} in the accessible temperature range (such as accessed in a large series of different solvents³⁸ or followed by UV–vis spectroscopy^{41,42} and SQUID-magnetometry⁴³).

In our search for SCO complexes of N,N'-disubstituted bis(pyrazol-3-yl)pyridines (3-bpp)^{32,44-46} devoid of NH groups close to the coordinating nitrogen atoms that preclude^{47–51} their "truly molecular" design,²⁰ a family of SCO-active complexes was obtained^{45,46} by a counterintuitive²⁰ SCO-assisting ligand design with ortho-functionalized *N*-phenyl groups (Scheme 1).⁴⁴ Of them, ligand L with dichlorophenyl *N*-substituents and hydroxyl groups in the fifth position of the

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pyrazol-3-yl moiety produced the thermally induced SCO with the highest midpoint temperature of 270 K in a solution.⁴⁴

To bring this SCO closer to room temperature, an electronwithdrawing substituent such as a *p*-cyanophenyl group introduced into the para-position of the pyridyl moiety of the same ligand may help. Based on "structure—property" relations for iron(II) complexes of isomeric bis(pyrazol-1-yl)pyridines $(1-bpp)^{52}$ and other pyridine-based ligands,⁴³ it should strengthen the ligand field and thereby stabilize the LS state of the iron(II) ion, shifting the SCO to higher temperatures. The proposed modification to *N*,*N'*-disubstituted 3-bpp (Chart 1) allowed designing an almost complete SCO centered at room temperature that can be followed by NMR spectroscopy using two different solvents;³⁸ an additional motivation was to probe the solvent effect on the SCO behavior of otherwise HS^{20,53–57} complexes.

Another option for SCO tuning through molecular design,²⁰ which was mastered for iron(II) complexes of 1-bpp,⁵² is functionalization at the fifth position of the pyrazol-3-yl moiety. It is also explored here by substituting the above electron-withdrawing hydroxyl groups in \mathbf{L}^{OH} (as gauged by Hammet⁵⁸ constant $\sigma_{\rm m}$)⁵² for substituents with an opposite electronic effect and no hydrogen-bonding ability, the t-butyl groups (Chart 1). We expected the resulting trends in the SCO behavior to reconcile contradictory results²⁰ of such a modification to the 3-bpp ligands in iron(II)^{20,45,59} (and cobalt(II)³²) complexes.

Chart 1. Ligands in This Study: L^{OH}, 4-(2,6-Bis(1-(2,6-dichlorophenyl)-5-hydroxy-1*H*-pyrazol-3-yl)pyridin-4yl)benzonitrile, and L^{t-Bu}, 4-(2,6-Bis(5-*tert*-butyl-1-(2,6dichlorophenyl)-1*H*-pyrazol-3-yl)pyridin-4-yl)benzonitrile; L, 3,3'-(Pyridine-2,6-diyl)bis(1-(2,6-dichlorophenyl)-1*H*pyrazol-5-ol), Was Reported Earlier⁴⁴



RESULTS AND DISCUSSION

The target N,N'-disubstituted 3-bpp (L^R) were synthesized by a previously reported⁴⁴ one-step cyclization of 2,6-dichlorophenylhydrazine⁴⁴ with diethyl 3,3'-(4-(4-cyanophenyl)pyridine-2,6-diyl)bis(3-oxopropanoate) or 4-(2,6-bis(4,4-dimethyl-3oxopentanoyl)pyridin-4-yl)benzonitrile, both resulted from Claisen condensation of diethyl 4-(4-cyanophenyl)pyridine-2,6-dicarboxylate⁶⁰ with ethyl acetate or pinacolone (Scheme 1). Mixing any of them with iron(II) tetrafluoroborate in methanol produced inseparable mixtures of paramagnetic compounds as Scheme 2. Synthesis of the Complexes $[Fe(L^R)_2](BF_4)_2$





Figure 1. General view of the cations in (a) $[Fe(L^{OH})_2](BF_4)_2$ and (b) $[Fe(L^{t-Bu})_2](BF_4)_2$ as obtained from X-ray diffraction at 120 K. Minor component of the disordered p-cyanophenyl groups, second symmetry-independent cation in $[Fe(L^{t-Bu})_2](BF_4)_2$, and hydrogen atoms except those of OH groups in $[Fe(L^{OH})_2](BF_4)_2$ are omitted for clarity. Atoms are shown as anisotropic displacement ellipsoids (p = 30%), and only the labels of heteroatoms are given.

identified by NMR spectroscopy of the appropriate solutions. This implies the coordination of both the tridentate heterocyclic core and of the *p*-cyanophenyl group, as the coordination by only the *p*-cyanophenyl group would stabilize the diamagnetic LS state of the iron(II) ion.

To obtain the target complexes $[Fe(L^R)_2](BF_4)_2$, an alternative synthetic pathway was used that included the formation of an intermediate product $[Fe(L^R)_2]Cl_2$ by the reaction of L^R with anhydrous iron(II) chloride in methanol and

a subsequent addition of solid $NaBF_4$ to this solution (Scheme 2).

The resulting violet crystals were confirmed by X-ray diffraction to belong to the complexes $[Fe(L^R)_2](BF_4)_2$ (Figure 1). The Fe–N bond lengths⁶¹ and the shape of the coordination polyhedra⁶² at 120 K (Table 1) were typical of the iron(II) ion in a N6-coordination environment of 3-bpp ligands⁵⁷ that adopts the LS state. The latter was also hinted by the distinct red color of the crystals¹ retained upon warming to room temperature, as they should turn yellow in an event of an SCO to the HS state of

Tabl	e 1. Sel	ected (Geometric	Paramet	ters"	as (Obtained	from
X-ray	y Diffra	ction a	t 120 K fo	r [Fe(L ^F	$(1)_{2}](H)$	$3F_4$	2	

parameter	$[Fe(L^{OH})_2](BF_4)_2$	$[\operatorname{Fe}(\mathbf{L}^{t-\operatorname{Bu}})_2](\operatorname{BF}_4)_2^{b}$
$Fe-N_{Py}(A)$	1.915(8)-1.917(8)	1.891(11)-1.935(10)
$Fe-N_{Pz}$ (Å)	1.975(7) - 2.012(8)	2.011(11)-2.049(11)
θ (deg)	89.99(7)	89.65(11) [89.93(10)]
ϕ (deg)	179.1(3)	179.1(4) [179.6(4)]
S(O _h)	2.425	2.351 [2.461]
S(ebcT)	12.897	13.142 [13.464]

^{*a*} θ is the "twist" angle between the two least-squares planes of 3-bpp ligands; ϕ is the "rotation" angle N_{Py}–Fe–N_{Py}; S(O_h) and S(ebcT) are octahedral and edge-bicapped tetrahedral⁶² continuous shape measures, respectively. ^{*b*}In brackets, the values for the second symmetry-independent cation in [Fe(L^{*t*-Bu})₂](BF₄)₂ are given.

an iron(II) complex of 3-bpp.^{32,44–46} However, the quality of the crystals was too low to perform an X-ray diffraction study for $[Fe(L^R)_2](BF_4)_2$ at this temperature. Given a general tendency of *N*,*N'*-disubstituted 3-bpp to produce HS complexes,^{20,53–57} it may be a sign of a thermally induced SCO that is "blocked" by crystal packing effects.^{45,46}

To confirm that there is indeed an SCO tunable by the proposed modifications to the 3-bpp ligand, the spin state of the complexes $[Fe(L^R)_2](BF_4)_2$ was probed in a solution by the Evans technique.²⁴ This approach in variable-temperature NMR spectroscopy is a method of choice²⁰ in molecular design of SCO compounds. The ¹H NMR spectra were collected from DMF- d_7 solutions, as both complexes are readily soluble in this solvent and do not decompose upon heating/cooling (Figure S1). The latter is a prerequisite for accurately measuring the magnetic susceptibility with the Evans method.²⁴

At room temperature (Figure S1), the ¹H NMR spectra show sets of seven paramagnetically shifted signals expected for $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t-Bu})_2](BF_4)_2$. Upon heating to 365 K, the highest temperature accessible due to the solvent evaporation from the NMR tube and a limitation of the spectrometer, the observed signals of $[Fe(L^{OH})_2](BF_4)_2$ broaden and shift further toward the paramagnetic region. This behavior is in contrast to a linear (Curie) dependence of the paramagnetic chemical shifts on the inverse temperature expected for the compounds in a pure spin state,^{30,63⁺} such as one observed for $[Fe(L^{t-Bu})_2](BF_4)_2$ above room temperature. However, cooling the DMF- d_7 solutions of both complexes to 230 K causes the chemical shifts to converge rapidly ([Fe- $(L^{OH})_2](BF_4)_2)$ or sluggishly $([Fe(L^{t-Bu})_2](BF_4)_2)$ toward the diamagnetic region (Figure S1), implying²⁶ the thermal population of the diamagnetic LS state.

The magnetic susceptibility measured by the Evans method²⁴ provides another piece of evidence for a sluggish and a more abrupt SCO in these solutions (Figure 2). In the temperature range 230–365 K, the χT value gradually decreases by 1 cm³/ mol K in the case of $[Fe(L^{f-Bu})_2](BF_4)_2$ and drops from 2.9 to 0.4 cm³/mol K in the case of $[Fe(L^{OH})_2](BF_4)_2$. An unexpectedly high magnetic susceptibility of the former complex above room temperature, which exceeds the typical value for the HS iron(II) ion (3.5 cm³/mol K)^{33,38,64} beyond the 5–10% error of the Evans method,²⁵ may arise from the presence of a paramagnetic side product that has a fast relaxation in the NMR timescale or is an inorganic species and thus does not appear in the NMR spectrum.

As a result, thermodynamic parameters of the SCO in $[Fe(L^{OH})_2](BF_4)_2\,(Table\ 2)$ are typical of iron(II) complexes of



Figure 2. Variable-temperature magnetic susceptibility data for the solutions of $[Fe(L^{OH})_2](BF_4)_2$ (black squares) and $[Fe(L^{t-Bu})_2](BF_4)_2$ (black circles) in DMF- d_7 according to the Evans method. The lines correspond to the best fit by a regular solution model.³⁰

 $N_{1}N'$ -disubstituted 3-bpp,^{44,46} while those in [Fe(L^{t-Bu})₂](BF₄)₂ seem underestimated. They, however, still fall into the ranges expected for SCO-active iron(II) compounds in solutions (ΔH = 4-41 kJ/mol, ΔS = 22-146 J/mol K).³³ The corresponding midpoint temperatures for the two complexes are 299 and 201 K (Table 2). A decrease by almost 100 K following the substitution of the hydroxyl groups in $[Fe(L^{OH})_2](BF_4)_2^{\circ}$ by the *t*-butyl groups in $[Fe(L^{t-Bu})_2](BF_4)_2$ agrees with the stabilization of the HS state by an electron-donating substituent in this position of the 3-bpp ligand, as suggested in previous studies of iron(II) complexes with N,N'-disubstituted 3-bpp.^{32,45} With no interference from NH groups,²⁰ this effect may have the same origin as does the stabilization of the HS state by an electrondonating substituent in the para-position of the pyridyl moiety. The latter lowers the midpoint temperature by stabilizing the e_{α} level of the metal d-orbitals and leading to a narrower $t_{2g}-e_g$ energy gap.^{20,43,52} For $[Fe(L^{OH})_2](BF_4)_2$, an opposite electronic effect of the *p*-cyanophenyl group shifts the SCO observed in a solution of the complex $[Fe(L)_2](ClO_4)_2^{44}$ (Table 2) to higher temperatures and thereby produces the SCO perfectly centered at room temperature (22 °C).

The latter allowed us to follow this, almost complete SCO by NMR spectroscopy in dimethylformamide (DMF) (Figure 2). To widen the accessible temperature range of the NMR experiment, another solvent (methanol- d_4) was used, which is a typical strategy in SCO research.³⁸ Of many different solvents other than DMF, only methanol provides good solubility of $[Fe(L^{OH})_2](BF_4)_2$ needed to obtain accurate Evans data.²⁵ For the same reason, acetonitrile was chosen for $[Fe(L^{t-Bu})_2](BF_4)_2$ to resolve the above issue with DMF (Figure 2). The stability of the complexes in these solvents was confirmed by electrospray ionization-mass spectrometry (ESI-MS) spectra that contained intense signals of $[Fe(L)_2]^{2+}$ ions and minor signals of $[Fe(L^{t-Bu})_2BF_4]^+$ or $[Fe(L^{OH})_2-H]^+$ ions (Figure S2 of the Supporting Information) and were the same for freshly prepared samples and those kept for a long time. An additional motivation for using different solvents was to probe the solvent effect on the SCO behavior of $[Fe(L^R)_2](BF_4)_2$. This was not attempted before for complexes of N,N'-disubstituted 3-bpp, as none of them were SCO-active^{20,53-57} until very recently.⁴⁴

The ¹H NMR spectra collected from $[Fe(L^{OH})_2](BF_4)_2$ in methanol- d_4 and $[Fe(L^{t-Bu})_2](BF_4)_2$ in acetonitrile- d_3 show sets of 5 and 7 paramagnetically shifted signals (Figure S3 of the Supporting Information). Two signals of $[Fe(L^{OH})_2](BF_4)_2$ disappear in the solution owing to the fast exchange of the proton of the OH group of the ligand L^{OH} with the hydroxyl

'able 2. SCO Parameters for $[Fe(L^{\kappa})_2](BF_4)_2^{\mu}$ and $[Fe(L^{\kappa})_2](BF_4)_2^{\mu}$](ClO ₄) ₂ ^{<i>b</i>} from Variable-Temperature	e NMR Spectroscopy
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complex	$[Fe(L^{OH})_2](BF_4)_2$		$[\operatorname{Fe}(\mathbf{L}^{t-\operatorname{Bu}})_2](\mathrm{BF}_4)_2$		$[Fe(L)_2](ClO_4)_2^{44}$
solvent	methanol- d_4	DMF-d ₇	ccetonitrile-d ₃	$DMF-d_7$	ccetonitrile-d ₃
$T_{1/2}$ (K)	307 [318]	299 [292]	214 [213]	201 [209]	269
$\Delta H (kJ/mol)$	20.2 [29.5]	19.4 [24.8]	23.6 [15.6]	10.9 [21.5]	24.2
ΔS (J/mol K)	65.9 [92.5]	64.8 [85.1]	110.4 [73.0]	54.6 [102.5]	89.9

^{*a*}Thermodynamic parameters are obtained by fitting the Evans data by the regular solution model (Table S1 of the Supporting Information);³⁰ those obtained by fitting the chemical shifts with the first-order temperature-dependent Curie constants³⁷ (Tables S2–S5 of the Supporting Information) are given in brackets. ^{*b*}The values were obtained by fitting the chemical shifts by the regular solution model.⁴⁴



Figure 3. Variable-temperature magnetic susceptibility data for the solution of $[Fe(L^{OH})_2](BF_4)_2$ in methanol- d_4 (red squares) and DMF- d_7 (black squares) and for the solution of $[Fe(L^{t-Bu})_2](BF_4)_2$ in acetonitrile- d_3 (blue circles) and DMF- d_7 (black circles) according to the Evans method. The lines correspond to the best fit by a regular solution model.³⁰ For HS state populations, see Figure S6 of the Supporting Information.

deuterium atom of methanol- d_4 and a tautomeric transfer of the latter to the pyrazolyl moiety of L^{OH}.⁶⁵

The changes in these spectra with temperature are very similar to those occurring in DMF- d_7 . Cooling the methanol- d_4 solution of $[Fe(L^{OH})_2](BF_4)_2$ causes the chemical shifts to rapidly converge toward the diamagnetic region (Figure S3) in the violation of the Curie law. On the other hand, the same (anti-Curie) behavior for $[Fe(L^{t-Bu})_2](BF_4)_2$ in acetonitrile- d_3 is observed below 265 K. This is also true for the variabletemperature magnetic susceptibility measured by the Evans method (Figure 3). At the highest temperatures of 330 and 345 K accessible in methanol- d_4 and acetonitrile- d_3 , the complexes $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t-Bu})_2](BF_4)_2$ feature the χT values of 2.2 and 3.9 cm³/mol K, respectively. High magnetic susceptibility of $[Fe(L^{t-Bu})_2](BF_4)_2$ in acetonitrile- d_3 , however, arises from the presence of the free ligand identified by appropriate signals in ESI-MS spectra (Figure S2 of the Supporting Information) and signals in the NMR spectra (Figures S4 and S5 of the Supporting Information); those were absent in DMF- d_7 . Upon cooling these solutions to 200 and 235 K, the χT values decrease to 0.2 and 3.1 cm³/mol K, thus confirming an almost complete SCO occurring for $[Fe(L^{OH})_{2}]$ - $(BF_4)_2$ in the temperature range 200–360 K and an onset of the SCO at 265 K for $[Fe(L^{t-Bu})_2](BF_4)_2$.

The thermodynamic parameters of the SCO in these solvents are more consistent between the two complexes (Table 2) and with other complexes of N,N'-disubstituted 3-bpp.^{44,46} The resulting midpoint temperatures of 307 and 214 K for $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L'^{FBu})_2](BF_4)_2$ mirror the same electronic effect of the substituents in the pyridyl and pyrazol-3yl moieties on the SCO behavior as identified in DMF but also show its solvent dependence (Figure 3). For $[Fe(L^{OH})_2](BF_4)_2$, more polar methanol (if judged by Reichardt's parameters⁶⁶ of solvent polarity) shifts the SCO toward higher temperatures, although an inverse trend was previously observed³⁸ for an iron(II) complex of unsubstituted 3-bpp, $[Fe(3-bpp)_2](BF_4)_2$. Such a difference between the compounds with the same tetrafluoroborate anion and in the same solvents may arise from the OH functionalities in the ligand L^{OH} and/or NH functionalities in 3-bpp that tend to form hydrogen bonds known to affect the spin state of the iron(II) complexes.^{47–51}

The ligand $L^{t\text{-Bu}}$, however, has no hydrogen-bonding ability. The difference in the midpoint temperatures between DMF and acetonitrile solutions of $[Fe(L^{t\text{-Bu}})_2](BF_4)_2 (13 \text{ K})$ is the same as in the above iron(II) complex of unsubstituted 3-bpp (13 K)³⁸ but of the opposite sign, with more polar acetonitrile stabilizing the LS state and thus shifting the SCO toward higher temperatures. The gap of 13 K was the largest one among five different solvents excluding water³⁸ that were probed for $[Fe(3-bpp)_2](BF_4)_2$. Such a study resulted in a positive correlation of the midpoint temperature with their basicity and hydrogen bond acceptor ability gauged by the parameter of Kamlet and Taft.⁶⁷ For $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t\text{-Bu}})_2](BF_4)_2$, however, the SCO is consistently observed at higher temperatures in more polar solvents with a lower hydrogen-bond acceptor ability, such as methanol.

As the interpretation of these trends may be affected by the ambiguous Evans data for the complex $[Fe(L^{t-Bu})_2](BF_4)_2$ (Figure 3), an alternative approach in NMR spectroscopy was used that is known to produce accurate estimates of thermodynamic^{28–30,37,40,63,68,69} parameters of an SCO even in the presence of various admixtures in a solution.^{23,31,32} It is based on the analysis^{26–29} of the temperature behavior of chemical shifts³⁰ that only requires an assignment of at least some of the signals in the variable-temperature NMR spectra; those are routinely collected as a side-product of the Evans experiment.



Figure 4. ¹H NMR chemical shifts for (a) $[Fe(L^{OH})_2](BF_4)_2$ and (b) $[Fe(L^{t-Bu})_2](BF_4)_2$ in DMF- d_7 solution plotted vs 1/T. The lines correspond to the best fit of chemical shifts with the first-order temperature-dependent Curie constants;³⁷ each color indicates a specific type of proton. The proton of the OH group was excluded from the fit, as at high temperatures, it exchanges with the protons from traces of water in the hygroscopic DMF- d_7 . For other solvents, see Figure S7 of the Supporting Information.

In the ¹H NMR spectra, the chemical shifts of $[Fe(L^{OH})_2]$ - $(BF_4)_2$ and $[Fe(L^{t-Bu})_2](BF_4)_2$ do not follow a linear dependence with the inverse temperature dictated by the Curie law (Figure 4), as expected for the spin-state switching²⁶ experienced by the two complexes in the chosen solvents. The difference in the chemical shifts for $[Fe(L^{OH})_2](BF_4)_2$ in DMF- d_7 and methanol- d_4 at a temperature of 305 K is up to 10 ppm; those are larger in DMF- d_7 in an agreement with the Evans data (Figure 3) that show a higher HS population in this solvent (55 vs 49% at 305 K). For $[Fe(L^{t-Bu})_2](BF_4)_2$, however, the chemical shifts are virtually the same in DMF- d_7 and a different side-product (Figure 3). This observation illustrates the benefits of the analysis of chemical shifts for quantifying the SCO over the Evans method.

Fitting the chemical shifts with the temperature-invariant Curie constant^{29,39,70} produced unsatisfactory results (Tables S6-S9 of the Supporting Information). Indeed, the best fit for $[Fe(L^{t-Bu})_2](BF_4)_2$ in DMF- d_7 still had a mean square error of 0.85. This may be because the Curie law is applicable for ideal spin systems with no contributions from zero-field splitting effects, low-lying excited states, or molecular dynamics that may sometimes occur in iron(II) complexes.^{27,30,37,69,71,72} Therefore, the SCO curves (Figure S8 of the Supporting Information and Table 2) and appropriate thermodynamic parameters for $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t-Bu})_2](BF_4)_2$ were obtained from the fit with the first-order temperature-dependent Curie constants that account for the above effects.³⁷ Upon doing so, the mean square error in the best fit for $[Fe(L^{t-Bu})_2](BF_4)_2$ in DMF- d_7 dropped to 0.04 (Table S3 of the Supporting Information) and the thermodynamic parameters (Table 2) became more typical of iron(II) complexes with N,N'disubstituted 3-bpp ligands.44,46

The resulting midpoint temperatures for the two complexes differ from those obtained from the Evans data by 1–11 K. The largest and smallest differences between the two NMR-based methods are observed for $[Fe(L^{OH})_2](BF_4)_2$ in methanol- d_4 (318 vs 307 K) and $[Fe(L^{t-Bu})_2](BF_4)_2$ in acetonitrile- d_3 (213 vs 214 K), respectively. These values, however, agree on the SCO that is centered around room temperature for one complex and at a much lower temperature for the other (Table 2). They also show the same effect of the polarity and hydrogen bond acceptor ability of the solvent that is opposite to the one found for $[Fe(3-bpp)_2](BF_4)_2$.³⁸ The more polar and less associating methanol d_4 and acetonitrile- d_3 shift the SCO in solutions of $[Fe(L^{OH})_2]$. $(BF_4)_2$ and $[Fe(L^{\text{t-Bu}})_2](BF_4)_2$ toward higher temperatures by 26 and 4 K, respectively.

CONCLUSIONS

A solution study of the SCO-active iron(II) complexes $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t-Bu})_2](BF_4)_2$ with rationally functionalized 3-bpp ligands (Chart 1) revealed the first example of an almost complete SCO centered around room temperature in otherwise $HS^{20,53-57}$ complexes of *N*,*N*'-disubstituted 3-bpp. This SCO was unambiguously identified by two separate approaches in variable-temperature NMR spectroscopy, the Evans method²⁴ and the analysis of the NMR chemical shifts.³⁰ The two techniques produced qualitatively different but consistent results (Table 2) on the effect of the solvents on the observed SCO behaviors that is opposite to the one found in a previous study³⁸ of the iron(II) complex $[Fe(3-bpp)_2](BF_4)_2$ in various solvents. A plausible reason for this may be the NH functionalities in the unsubstituted 3-bpp ligands known to affect the spin state of the metal ion owing to their hydrogen bonding ability; 47-51 however, none of the complexes of N, N'disubstituted 3-bpp^{20,53-57} were SCO-active until very recently.⁴⁴ As such complexes, $[Fe(L^{OH})_2](BF_4)_2$ and [Fe- $(L^{t-Bu})_2$ (BF₄)₂ feature the thermally induced SCO at higher temperatures in more polar solvents with a lower hydrogenbond acceptor ability.

By comparison to the pioneering SCO–active complex $[Fe(L)_2](ClO_4)_2^{44}$ of the same SCO-assisting ligand design, introducing the p-cyanophenyl group into the para-position of the pyridyl moiety in the complex $[Fe(L^{OH})_2](BF_4)_2$ effectively shifts the SCO to room temperature. As a result, it can be largely followed by solution NMR spectroscopy. The observed stabilization of the LS state by an electron-withdrawing group in this position of *N*,*N*'-disubstituted 3-bpp mirrors the one occurring in iron(II) complexes with 1-bpp⁵² and other pyridine-based ligands.⁴³

In contrast, the midpoint temperatures of the SCO in the two complexes $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t-Bu})_2](BF_4)_2$ show the electron-donating t-butyl groups in the fifth position of the pyrazol-3-yl moiety to strongly (by up to 100 K) favor the HS state of the iron(II) ion. This result provides another piece of evidence^{20,32} for an opposite effect of such a modification to the 3-bpp ligand as compared to isomeric 1-bpp.⁵² To finally reconcile them, a systematic study of iron(II) complexes with N,N'-disubstituted 3-bpp of our SCO-assisting ligand design is in progress in our group.

EXPERIMENTAL SECTION

Synthesis. All synthetic manipulations were carried out in air unless stated otherwise. Solvents were purchased from commercial sources and purified by distilling from conventional drying agents under an argon atmosphere prior to use. 2,6-Dichlorophenylhydrazine (Scheme 1) was synthesized from commercially available 2,6-dichlroaniline using a standard diazotization protocol with a subsequent reduction with SnCl₂.⁴⁴

Diethyl 4-(4-Cyanophenyl)pyridine-2,6-dicarboxylate. Acetic acid (2.86 mL, 50 mmol) and pyrrolidine (1.64 mL, 20 mmol) were added to a solution of 4-cyano-benzaldehyde (6.55 g, 50 mmol) and ethyl pyruvate (11.6 mL, 150 mmol) in acetonitrile (50 mL), and the resulting mixture was stirred at r.t. for 12 h. Then, NH₄OAc (11.6 g, 150 mmol) and acetic acid (2.86 mL, 50 mmol) were added. After 24 h of additional stirring at the same temperature, the mixture was poured into a saturated aqueous NaHCO₃ solution (5.0 mL) and extracted with ethyl acetate. The organic layers were combined, dried over Na₂SO₄, filtered, concentrated, and purified by flash column chromatography with a mixture hexane-EtOAc (5/1) as an eluent to produce a white solid. Yield: 4.2 g (26%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 1.48 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 6H, CH₃), 4.53 (q, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, CH₂), 7.87–7.83 (m, 4H, 2-PhCN + 3-PhCN), 8.49 (s, 2H, 3-Py). Anal. calcd. for (C₁₈H₁₆N₂O₄): C, 66.66; H, 4.97; and N, 8.64. Found: C, 66.49; H, 4.81; and N, 8.58.

Diethyl 3,3'-(4-(4-Cyanophenyl)pyridine-2,6-diyl)bis(3-oxopropanoate). To a mixture of diethyl 4-(4-cyanophenyl)pyridine-2,6-dicarboxylate (1 g, 3.12 mmol) and ethyl acetate (0.760 mL, 7.8 mmol) in dry THF (25 mL), potassium tbutylate (0.873 g, 7.8 mmol) was added under argon. The reaction mixture was stirred for 6 h at r.t., and then the solvent was evaporated on a rotary evaporator. The product was dispersed in water (30 mL), and the resulting solution was treated with 1 M hydrochloric acid until it became acidic (pH 5) to produce a precipitate that was filtered off, washed with water, and dried in high vacuum. The resulting yellow solid was used without further purification. Yield: 0.942 g (74%). ¹H NMR (CDCl₃, 400 MHz; a mixture of diketo and keto–enol forms): δ (ppm) = 1.20-1.37 (t + t + t, 6H, CH₃), 4.13-4.32 (q + q + q + s, 6H, CH_2 + CH₂ diketo form), 6.45 (s, 2H, CH keto-enol form), 7.78-7.75 (m, 3-PhCN + 4-PhCN), 8.15 (s, 1H, 3-Py, keto-enol form), 8.29 (s, 1H, 3-Py, diketo form), 12.44 (s, OH keto-enol form). Anal. calcd. for $(C_{22}H_{20}N_2O_6)$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.85; H, 4.84; N, 6.98.

4-(2,6-Bis(4,4-dimethyl-3-oxopentanoyl)pyridin-4-yl)benzonitrile. To a mixture of diethyl 4-(4-cyanophenyl)pyridine-2,6-dicarboxylate (1 g, 3.12 mmol) and pinacolone (0.962 mL, 7.71 mmol) in dry THF (25 mL), potassium tbutylate (1.04 g, 9.24 mmol) was added under argon. The reaction mixture was stirred for 6 h at r.t., and then the solvent was evaporated on a rotary evaporator. The product was dispersed in water (30 mL), and the resulting solution was treated with 1 M hydrochloric acid until it became acidic (pH 5) to produce a precipitate that was filtered off, washed with water, and dried in high vacuum. The resulting yellow solid was used without further purification. Yield: 0.863 g (64%). ¹H NMR (CDCl₃, 400 MHz; a mixture of dienol and keto–enol forms): δ (ppm) = 1.06–1.10 (s + s + s, 18H, tBu), 4.42 (s, 2H, CH₂ keto-enol form), 6.80 (s, 2H, CH keto-enol form), 6.94 (s, 2H, CH dienol form), 7.78–7.75 (m, 2H, 2-PhCN), 7.89–7.95 (m, 2H, 3-PhCN), 8.24 (s, 1H, 3-Py, dienol form), 8.31 (s, 1H, 3-Py,

keto–enol form), 16.04 (c, OH dienol + keto–enol forms). Anal. calcd. for $(C_{26}H_{28}N_2O_4)$: C, 72.20; H, 6.53; N, 6.48. Found: C, 72.47; H, 6.61; N, 6.58.

 L^{OH} . A mixture of diethyl 3,3'-(4-(4-cyanophenyl)pyridine-2,6-diyl)bis(3-oxopropanate) (0.4 g, 0.98 mmol) and 2,6dichlorophenylhydrazine (0.398 g, 2.25 mmol) was dissolved in 10 mL of acetic acid to give a yellow solution that was heated to 70 °C for 8 h to produce a light-yellow precipitate. The precipitate was filtered off, washed with acetic acid and then with water, and dried in vacuum. The resulting white solid was used without further purification. Yield: 0.410 g (66%). ¹H NMR (DMSO-*d*₆, 400 MHz, Figure S9): δ (ppm) = 6.21 (s, 2H, Pz-CH), 7.58 (t, ³J_{H,H} = 8.0 Hz, 2H, 4-Ph), 7.69 (d, ³J_{H,H} = 8.0 Hz, 4H, 4-Ph), 7.90 (d, ³J_{H,H} = 7.8 Hz, 2H, 2-PhCN), 8.02–8.04 (m, 4H, 2-PhCN + 3-Py), 11.79 (s, 2H, OH). Anal. calcd. for (C₃₀H₁₆Cl₄N₆O₂): C, 56.81; H, 2.54; N, 13.25. Found: C, 56.88; H, 2.72; N, 13.27.

H, 2.72; N, 13.27. L^{t-Bu} . A mixture of 4-(2,6-bis(4,4-dimethyl-3-oxopentanoyl)pyridin-4-yl)benzonitrile (0.4 g, 0.925 mmol) and 2,6dichlorophenylhydrazine (0.377 g, 2.127 mmol) was dissolved in 10 mL of acetic acid to give a yellow solution that was heated to 70 °C for 8 h to produce a light-yellow precipitate. The precipitate was filtered off, washed with DMF and then with water, and dried in vacuum. The resulting white solid, which was poorly soluble even in DMSO or DMF, was used without further purification. Yield: 0.535 g (81%). ¹H NMR (DMSO-*d*₆, 400 MHz, Figure S10): δ (ppm) = 1.23 (s, 18H, *t*Bu) 7.14 (s, 2H, Pz-CH), 7.64 (t, ³J_{H,H} = 8.5 Hz, 2H, 4-Ph), 7.74 (d, ³J_{H,H} = 8,5 Hz, 4H, 4-Ph), 7.90 (d, ³J_{H,H} = 8.0 Hz 2H, 2-PhCN), 8.04 (d, 2H, 2-PhCN), 8.07 (s, 2H, 3-Py). Anal. calcd. for (C₃₈H₃₂Cl₄N₆): C, 63.88; H, 4.51; N, 11.76. Found: C, 63.99; H, 4.67; N, 11.93.

General Procedure for Synthesis of the Complexes $[Fe(L^R)_2](BF_4)_2$, $L^R = L^{OH}$ and $L^{t\cdot Bu}$. (Scheme 2) The ligand L^R (0.157 mmol) was suspended in methanol (15 mL) in a 50 mL Schlenk flask under argon. A solution of FeCl₂ (0.0099 g, 0.0785 mmol) in dry methanol (5 mL) was added dropwise to the resulting suspension and refluxed for 1 h. Solid NaBF₄ (0.017 g, 0.157 mmol) was added to the hot solution that was stirred for 15 min and then cooled to rt For $[Fe(L^{OH})_2](BF_4)_2$, the precipitate was filtered off, recrystallized from methanol at -10 °C, and dried in vacuum to produce a violet solid. For $[Fe(L^{t-Bu})_2](BF_4)_2$, the unreacted ligand was filtered off, and the methanol solution was evaporated to produce a violet solid that was dried under vacuum without further purification.

 $[Fe(L^{OH})_2](BF_4)_2$. Yield: 77 mg (68%). ¹H NMR (DMF- d_7 , 300 MHz, 305 K): δ (ppm) = 8.87 (br.s, 8H, 3-Ph), 9.96 (br.s, 4H, 3-PhCN), 10.5 (br.s, 4H, 4-Ph), 15.48 (br.s, 4H, 2-PhCN), 17.19 (br.s, OH), 34.69 (br.s, 4H, Pz-CH), 43.25 (br.s, 4H, m-Py-H). ¹H NMR (methanol- d_4 , 300 MHz, 305 K): δ (ppm) = 8.33 (br.s, 4H, 3-Ph), 9.43 (br.s, 4H, 3-PhCN), 9.51 (br.s, 4H, 4-Ph), 13.46 (br.s, 4H, 2-PhCN), 33.84 (br.s, 4H, m-Py-H). Anal. calcd. for ($C_{56}H_{32}B_2Cl_8F_8FeN_{12}O_4$): C, 46.39; H, 2.22; N, 11.59. Found: C, 46.56; H, 2.3; N, 11.54.

[*Fe*(*L*^{t-Bu})₂](*BF*₄)₂. Yield: 120 mg (92%). ¹H NMR (DMF-*d*₇, 300 MHz, 305 K): δ (ppm) = -0.63 (br.s, 36H, *t*-Bu), 10.07 (br.s, 8H, 3-Ph), 11.14 (br.s, 4H, 3-PhCN), 12.80 (br.s, 4H, 4-Ph), 18.54 (br.s, 4Hz, 2-PhCN), 50.15 (br.s, 4H, Pz-CH), 63.57 (br.s, 4H, 3-Py-H). ¹H NMR (acetonitrile-*d*₃, 300 MHz, 305 K): δ (ppm) = -0.79 (br.s, 36H, *t*Bu), 9.77 (br.s, 8H, 3-Ph), 10.93 (br.s, 4H, 3-PhCN), 12.49 (br.s, 4H, 4-Ph), 18.25 (br.s, 4H, 2-PhCN), 49.49 (br.s, 4H, Pz-CH), 63.51 (br.s, 4H, 3-Py-H). Anal. calcd. for ($C_{76}H_{64}B_2Cl_8F_8FeN_{12}$): *C*, 55.04; H, 3.89; N, 10.13. Found: *C*, 55.16; H, 3.96; N, 9.91.

X-ray Crystallography. X-ray diffraction data for single crystals of $[Fe(L^R)_2](BF_4)_2$ grown from methanol in air were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. Using Olex2,⁷³ the structures were solved with the ShelXT structure solution program⁷⁴ using Intrinsic Phasing and refined using least-squares minimization. Hydrogen atoms of OH groups in $[Fe(L^{OH})_2](BF_4)_2$ 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. Severely disordered water molecules in $[Fe(L^R)_2](BF_4)_2$, which probably resulted from keeping the solutions of these complexes in air, have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.⁷⁵ Crystal data and structure refinement parameters are given in Table 3. CCDC 2102395 and 2104368 contain the supplementary crystallographic data for $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{t-Bu})_2]$ - $(BF_4)_2$, respectively.

Table 3. Crystal Data and Structure Refinement Parameters for $[Fe(L^{OH})_2](BF_4)_2$ and $[Fe(L^{f-Bu})_2](BF_4)_2$

	$[Fe(L^{OH})_2](BF_4)_2$	$[\operatorname{Fe}(\mathbf{L}^{t\text{-}\mathbf{Bu}})_2](\mathrm{BF}_4)_2$
formula unit	$C_{60}H_{32}B_2Cl_8F_8FeN_{12}O_4\\$	$C_{76}H_{64}B_2Cl_8F_8FeN_{12}$
formula weight	1498.04	1658.46
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	P2 ₁ 2 ₁ 2
Ζ	4	8
a (Å)	13.206(3)	24.465(6)
b (Å)	37.665(8)	48.605(11)
c (Å)	17.218(4)	13.499(3)
α (deg)	90	90
β (deg)	107.433(4)	90
γ (deg)	90	90
$V(Å^3)$	8171(3)	16 052(6)
$D_{\rm calc} ({\rm g/cm})$	1.218	1.373
linear absorption μ (cm ⁻¹)	5.10	5.23
F(000)	3008	6784
$2\Theta_{\max}$ (deg)	52	56
reflections measured	77 396	183 700
independent reflections	16 055	38 727
observed reflections $[I > 2\sigma(I)]$	6036	13 633
parameters	890	2019
R1	0.0980	0.0954
wR2	0.3084	0.2580
GOOF	0.985	0.956
$\Delta ho_{ m max} / \Delta ho_{ m min} ~({ m e}/{ m \AA}^3)$	-0.570/0.697	-0.530/1.121

NMR Spectroscopy. ¹H NMR spectra for $[Fe(L^R)_2](BF_4)_2$ in DMF- d_7 , methanol- d_4 , and acetonitrile- d_3 were recorded with a Bruker Avance 300 FT-spectrometer (300.15 MHz ¹H frequency). The measurements were done using the residual signals of these solvents as reference. The temperature inside an NMR tube was adjusted using flow of cold nitrogen and hot air for low- and high-temperature experiments, respectively. To calibrate the temperature within the temperature range 200– 300 K, a Bruker standard temperature calibration sample (4% of MeOH in methanol- d_4) was used. Above 300 K, the temperature was calibrated using a known dependence of the chemical shifts of pure ethylene glycol. Evans Method. Magnetic susceptibility of $[Fe(L^R)_2](BF_4)_2$ in DMF- d_7 , methanol- d_4 , and acetonitrile- d_3 was measured by the Evans method^{24,76} in the temperature ranges 230–365, 200–330, and 235–345 K, respectively, using a Wilmad NMR tube with a coaxial insert. The inner (reference) tube was filled with the chosen solvent with approximately 1% of Me₄Si, and the outer tube contained the solution of the complex (~1 to 5 mg/ cm³) in this solvent with the same concentration of Me₄Si. Molar magnetic susceptibility was calculated from the difference between the chemical shift of Me₄Si in the pure solvent and its shift in a solution of the complex ($\Delta\delta$ in Hz) in the same solvent using the following equation

$$\chi_{\rm M} = \frac{\Delta \delta M}{\nu_0 S_{\rm f} c} - \chi_{\rm M}^{\rm dia}$$

(*M*—molar weight of the iron(II) complex, g/mol; ν_0 —frequency of the spectrometer, Hz; $S_{\rm f}$ —shape factor of the magnet (4 π /3); *c*—concentration of the complex, g/cm³; $\chi_{\rm M}^{\rm dia}$ —molar diamagnetic contribution to the paramagnetic susceptibility calculated using Pascal's constant⁷⁷). The concentration *c* was recalculated for each temperature in accordance with the density change of the solvent ρ : $c_{\rm T} = m_{\rm s}\rho/m_{\rm sol}$, where $m_{\rm s}$ is the mass of the complex and $m_{\rm sol}$ is the mass of the solution. Thermodynamic parameters of an SCO were obtained by fitting the observed temperature dependence of the magnetic susceptibility to the regular solution model⁴⁴ using the following equation⁷⁸ for an iron(II) complex with the diamagnetic LS state

$$\chi_{\rm M} T = \frac{(\chi_{\rm M} T)_{\rm HS}}{1 + \exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right)}$$

In our analysis, the magnetic susceptibility for a pure HS state $(\chi_{\rm M}T)_{\rm HS}$ (cm³/mol K) and the changes in enthalpy ΔH (kJ/mol) and entropy ΔS (J/mol K) are the fitting parameters.

Temperature-Dependence of Chemical Shifts. Chemical shifts in the ¹H NMR spectra for $[Fe(L^R)_2](BF_4)_2$ in DMF- d_7 , methanol- d_4 , and acetonitrile- d_3 were analyzed in the above temperature ranges. For a compound that may exist in two paramagnetic 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):

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

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

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

As the diamagnetic contribution δ_{dia} to the observed chemical shift is virtually the same for the LS and HS states, the paramagnetic contribution δ_{par}^{HS} was taken as a difference between the chemical shifts in the iron(II) complex and those in the free ligand.⁷⁹ Thermodynamic parameters of an SCO were calculated by fitting the observed temperature dependence of the paramagnetic chemical shifts in the NMR spectra with the first-order temperature-dependent Curie constants³⁷

$$\delta_{\text{obs}}(T) - \delta_{\text{dia}} = \frac{\frac{C^0}{T} + C^{1*}}{1 + \exp\left(\frac{\Delta H}{RT} - \frac{\Delta S}{R}\right)}$$

In this analysis, the Curie constants C^0 and C^{1*} that are specific for each proton and the changes in enthalpy ΔH (kJ/mol) and entropy ΔS (J/mol K) are the fitting parameters.

Liquid Chromatography–Mass Spectrometry (LC– MS). LC–MS analysis of $[Fe(L^R)_2](BF_4)_2$ in methanol- d_4 and acetonitrile- d_3 was performed with a Shimadzu LCMS-2020 high-performance liquid chromatograph mass spectrometer with an electrospray ionization (ESI) and single quadrupole detector (negative and positive ions) in the mass range between 500 and 2000. The desolvation line/heat block temperature was 250/400 °C. Nitrogen (99.5%) was used as a nebulizer and drying gas, and acetonitrile (>99.9% HPLC gradient grade, Chem-Lab), was used as the mobile phase with a flow rate 0.4 mL/min without any preliminary treatment. Injection volume of the solution was 5 μ L.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05463.

Variable-temperature ¹H NMR spectra; ESI-MS spectra; HS state populations; ¹H NMR chemical shifts plotted versus 1/T; results of the fits of the Evans data; and results of the fits of the chemical shifts in NMR spectra (PDF)

FeL^{OH} (CIF)

FeL^{tBu} (CIF)

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Notes

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ABBREVIATIONS

SCO, spin-crossover; LS, low-spin; HS, high-spin; NMR, nuclear magnetic resonance; 3-bpp, 2,6-bis(pirazol-3-yl)-pyridine; 1-bpp, 2,6-bis(pirazol-1-yl)pyridine

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