Spin-Crossover Temperature Predictable from DFT Calculation for Iron(II) Complexes with 4-Substituted Pybox and Related Heteroaromatic Ligands

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Supporting Information

ABSTRACT: Spin-crossover (SCO) is a reversible transition between low and high spin states by external stimuli such as heat. The SCO behavior and transition temperature (T_{1/2}) of a series of [Fe^{II}(X-pybox)_{2}](ClO_{4})_{2} were studied to establish a methodology for ligand-field engineering, where X-pybox stands for 2,6-bis(oxazolin-2-yl)pyridine substituted with X at the 4-position of the pyridine ring. We utilized X = MeO, Me, 3-thienyl, Ph, H, MeS, 2-thienyl, N_{3}, Cl, Br, 3-pyridyl, and 4-pyridyl. The solution susceptometry on five new derivatives with X = Me, 2-thienyl, N_{3}, Br, and 3-pyridyl was performed in acetone, giving the SCO temperatures of 220, 260, 215, 280, and 270 K, respectively. The density-functional-theory molecular orbital (MO) calculation was performed on the ligands with geometry optimization. The atomic charge on the pyridine nitrogen atom [\rho(N_{py})] was extracted from the natural orbital population analysis. Positive correlation appeared in the T_{1/2} versus \rho(N_{py}) plot with R^2 = 0.734, being consistent with the analysis using the Hammett substituent constants (\sigma_{p} and \sigma_{p}'). This finding well agrees with the mechanism proposed: the rich electron density lifts the t_{2g} energy level through the d_{z^2}–p_{x} interaction, resulting in a narrow t_{2g}–e_{g} energy gap and favoring the high-spin state and low T_{1/2}. The MO method was successfully applied to the known SCO-active iron(II) compounds involving 4-substituted 2,6-bis(pyrazol-1-yl)pyridines. A distinct positive correlation appeared in the T_{1/2} versus \rho(N_{py}) plot. The comparison of correlation coefficients indicates that \rho(N_{py}) is a more reliable parameter than \sigma_{p} or \sigma_{p}' to predict a shift of T_{1/2}. Furthermore, this method can be more generalized by application to another known SCO family having 3-azinyl-4-p-tolyl-5-phenyl-1,2,4-triazole ligand series, where azinyl stands for a 2-azaaromatic ring. A good linear correlation was found in the T_{1/2} versus \rho(N_{A}) plot (N_{A} is the ligating nitrogen atom in the azaaromatic ring). Finally, we will state a reason why the present treatment is competent to predict the SCO equilibrium position only by consideration on the electronic perturbation.

INTRODUCTION

Spin-crossover (SCO) is a reversible transition between low-spin (LS) and high-spin (HS) states associated with external stimuli such as heat, light, and pressure.\(^1\)\(^-\)\(^4\) Iron(II) (3d\(^6\)) coordination compounds are important SCO systems because SCO occurs between S = 0 dia- and S = 2 paramagnetic states, where a drastic magnetic change is expected. The six-nitrogen donor structures (i.e., Fe^{II}N_{6}) have been studied most extensively,\(^5\)\(^-\)\(^10\) and in particular, meridional trimine-type ligands are frequently applied for this purpose. The analogy between the well-established SCO ligands 2,6-bis(pyrazol-1-yl)pyridine (1-bpp),\(^11\) for the structural formula, see Scheme 1) and 2,6-bis(pyrazol-3-yl)pyridine (3-bpp)\(^12\) gives us a clue to the development of novel robust SCO ligands and furthermore a guide to the ligand-field engineering. We have developed the trimine ligand 2,6-bis(oxazolin-2-yl)pyridine (pybox) and its derivatives after the pioneering works by the Gao\(^13\)\(^,\)\(^14\) and Halcrow groups.\(^15\)

The physical properties should be predicted and controlled in a nonserendipitous manner. The SCO behavior and transition temperature of a series of [Fe^{II}(X-pybox)_{2}](ClO_{4})_{2} were studied in connection to the substituent effect, where pybox is substituted with X at the 4-position of the pyridine ring. The introduction of substituents will bring about drastic SCO tuning through the covalent bonds, in comparison with the effects through intermolecular interaction from counter ions and/or solvent molecules incorporated. A part of the experimental data has been communicated and clarified to undergo near-room-temperature SCO with X = H, Cl, Ph, CH_{3}O, CH_{3}S,\(^16\) 3-thienyl (3Th), and 4-pyridyl (4Py).\(^17\) The magnetic susceptibility measurements were performed in solution to purge intermolecular interactions and rigid crystal lattice effects, and discussion can be focused on the substituent effects.
effect. A plot of \( T_{1/2} \) against the Hammett substituent constant \( \sigma_p \) exhibited a strong correlation with a positive slope, indicating that electron-donating (-releasing) groups suppress \( T_{1/2} \) in this series. Here, the SCO temperature \( T_{1/2} \) is defined as the temperature at which equimolar fractions of the HS and LS species are present.

Five compounds with \( X = \text{Me}, 2\text{-thienyl (2Th)}, \text{N}_3, \text{Br}, \text{and 3-pyridyl (3Py)} \) are newly synthesized, and the SCO properties are investigated in the present work. Discussion will cover a wide range of the substituent \( e \) are investigated in the present work. Discussion will cover a wide range of the substituent effect. A plot of \( T_{1/2} \) against the Hammett substituent constant \( \sigma_p \) exhibited a strong correlation with a positive slope, indicating that electron-donating (-releasing) groups suppress \( T_{1/2} \) in this series. Here, the SCO temperature \( T_{1/2} \) is defined as the temperature at which equimolar fractions of the HS and LS species are present.

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100 K. The pyridine nitrogen position does not show any disorder because the presence of hydrogen bonds between the pyridine nitrogen atoms and the hydroxyl groups from methanol molecules solvated (the Npyridyl···OMeOH distances are 2.820(6) Å for N4pyridyl···O13MeOH and 2.884(5) Å for N8pyridyl···O14MeOH).

**Magnetic Properties in the Solid State.** The present compounds have a potential of SCO near room temperature, which has been confirmed by means of the SQUID magnetic susceptometry. Because the three derivatives (X = N3, Br, and 3Py) have structurally been characterized, their polycrystalline magnetic properties are reported here. As Figure 2a shows, the high-temperature limits of the $\chi_mT$ value were 3.0$−$4.5 cm$^3$ K mol$^{-1}$, typical of the S = 2 HS state of the iron(II) ion. The LS state is characterized with 0 cm$^3$ K mol$^{-1}$. For all the compounds investigated here, the $\chi_mT$ profiles on heating were not reproduced by those of the cooling process. This finding is rationalized by the presence of a crystal solvent molecule, which is assumed to escape during the heating measurements up to 400 K.

The $\chi_mT$ value of the N3 derivative is practically null below 150 K (Figure 2a), but above 320 K, it reached the HS level, indicating that this specimen underwent SCO. The heating process showed a two-step profile, which is in good agreement with the presence of two crystallographically independent molecules. The SCO temperatures were ca. 220 K for the first gradual SCO and 330 K for the second abrupt SCO. On cooling from 400 K, the SCO behavior took place in a single step and broad manner. The high-temperature $\chi_mT$ value of the Br derivative is practically saturated to reach a half level of the theoretical HS value. A possible reason for this behavior is the coexistence of polymorphic crystals of LS, as clarified by

**Table 1. Selected Crystallographic Parameters of [Fe(N3-pybox)$_2$](ClO$_4$)$_2$·0.75MeOH, [Fe(Br-pybox)$_2$](ClO$_4$)$_2$·MeOH, and [Fe(3Py-pybox)$_2$](ClO$_4$)$_2$·2MeOH, Measured at 100 K**

| X     | N3    | Br   | 3Py  |
|-------|-------|------|------|
|       | C$_{22.52}$H$_{31}$Cl$_2$FeN$_{12}$O$_{28.75}$ | C$_{23.52}$H$_{32}$Br$_2$Cl$_2$FeN$_{14}$O$_{23}$ | C$_{34.52}$H$_{36}$Cl$_2$FeN$_{18}$O$_{34}$ |
|       | 792.28 | 879.04 | 907.46 |
| space group | P1 | P1 | orthorhombic |
| a/Å  | 11.085(3) | 9.678(3) | 14.284(2) |
| b/Å  | 16.394(5) | 9.790(3) | 15.268(3) |
| c/Å  | 17.644(5) | 16.669(5) | 17.484(3) |
| α/deg | 71.995(13) | 85.581(15) | 90 |
| β/deg | 83.901(12) | 80.683(16) | 90 |
| γ/deg | 83.563(13) | 81.201(15) | 90 |
| V/Å$^3$ | 3021.6(16) | 1537.8(8) | 3812.8(12) |
| Z     | 4 | 2 | 4 |
| $d_{calcd}$/g·cm$^{-3}$ | 1.695 | 1.898 | 1.581 |
| μ (Mo Kα)/mm$^{-1}$ | 0.759 | 3.345 | 0.615 |
| no. of unique reflections | 10 924 | 6976 | 8717 |
| R(F) (I > 2σ(I))$^a$ | 0.0731 | 0.0438 | 0.1258 |
| wR(F$^2$) (all reflections)$^b$ | 0.1887 | 0.1038 | 0.0495 |
| goodness-of-fit parameter | 1.034 | 1.104 | 1.044 |
| Flack parameter | $−0.009(6)$ |

$^a$R = $\sum|F_o|−|F_c|/\sum|F_o|$. $^b$wR = $[\sum w(F_o^2−F_c^2)/\sum wF_o^2]^{1/2}$.
the crystallographic analysis. Owing to the crystal breakdown, details are unknown in the high-temperature phase. A relatively abrupt $\chi_mT$ jump was recorded at 310 K on heating. The measurements on cooling almost maintained the room-temperature $\chi_mT$ value. The 3Py derivative exhibited an abrupt $\chi_mT$ jump at 340 K on heating and an incomplete decrease on cooling.

The SCO temperatures in the heating process have been recorded as $T_{1/2}$(N$_3$) < $T_{1/2}$(Br) < $T_{1/2}$(3Py). The electron-withdrawing character has the same order in the $\sigma_p$ scale. However, the analysis on the solid-state specimens involves approximation because the various space groups, molecular arrangements, solvation and desolvation effects, and coordination structure distortions were found, but such factors are neglected here. The structural distortion is known to regulate $T_{1/2}$ to a considerable extent. The solution experiments will afford a better venue for the discussion on the substituent effect.

**Magnetic Properties in Solution.** The solution magnetic susceptibilities in acetone were acquired on a SQUID susceptometer. Details of the experimental method have been described elsewhere. Although the SCO profiles were all gradual with a similar shape, an appreciable difference in $T_{1/2}$ was recorded (Figure 2b). The $T_{1/2}$ values are determined as 220, 260, 215, 280, and 270 K for X = Me, 2Th, N$_3$, Br, and 3Py, respectively. The trend observed seems to be approximately related to the electron-accepting/donating properties. Namely, electron-donating substituents (X = Me) stabilized the HS state, whereas electron-withdrawing substituents (X = Br, 3Py) stabilized the LS state, which is qualitatively the same as that of the solid-state experiments.

The results on 12 derivatives in total are accumulated in Figure 3a, and the relation between $T_{1/2}$ and $\sigma_p$ is surveyed to establish a structure−SCO property relationship. Actually, the plot displays a strong positive correlation. A plot using the alternative substituent constant $\sigma_p^*$, suitable for substituent effects to a cationic center exhibits a positive correlation as well (Figure 3b). The $R^2$ correlation coefficients are comparable; 0.780 for $\sigma_p$ and 0.768 for $\sigma_p^*$. The solution data have no structural information, but we suppose that the structural distortion factor would be negligible because of the vast conformational freedom. Accordingly, the solution experiments seem to be more appropriate than the solid-state experiments to assess substituent effects. As previously pointed out, electron-donating substituents suppress $T_{1/2}$ and electron-withdrawing substituents raise $T_{1/2}$.

The substituent dependence of $T_{1/2}$ in [Fe(X-pybox)$_2$](ClO$_4$)$_2$ in acetone solution can be verified with the trend known for $T_{1/2}$ in [Fe(X-1-bpp)$_2$](BF$_4$)$_2$ in acetone or nitromethane solution. Figure 4 displays the plot using the difference of $T_{1/2}$ of an X-substituted derivative from that of the mother X = H compound as $\Delta T_{1/2}$. Because the 4-X-1-bpp and 4-X-pybox series contain the double meridional chelation in common, the steric effects are similar to each other. A relationship is formulated as eq 1 and superposed in Figure 4. The slope close to unity implies that essentially the same substituent effects are operative in both. Moreover, the comparison study indicates that the counter anion dependence or solvent dependence could be negligible in the solution experiments.

$$\Delta T_{1/2}(\text{pybox}) = 1.20(26) \times \Delta T_{1/2}(\text{bpp}) + 17(12) K \quad (1)$$

**Density-Functional-Theory (DFT) MO Calculation.** We investigated the theoretical MO calculation on the series of X-pybox ligands and performed DFT calculation in the Gaussian 03 package. The B3LYP Hamiltonian with the 6-311+G(2d,p) basis set was selected. To reproduce the solution data, the geometry optimization is required, and only the ligand portion (X-pybox) was subjected to calculation. This method would be welcomed for ab initio prediction of $T_{1/2}$ when only the chemical formula of X-pybox is given. There have been several known DFT functionals, B3LYP* and TPSSh, for example, suitable for the analysis of the SCO behavior on the whole coordination compounds. In the present work, the

### Table 2. Fe–N Bond Lengths ($d$) in Å for [Fe(N$_1$-pybox)$_2$](ClO$_4$)$_2$, 0.75MeOH, [Fe(Br-pybox)$_2$](ClO$_4$)$_2$, MeOH, and [Fe(3Py-pybox)$_2$](ClO$_4$)$_2$·2MeOH

| X     | N$_1$ (Fe1) | N$_1$ (Fe2) | Br  | 3Py |
|-------|-------------|-------------|-----|-----|
| d/Å   | 1.985(5)    | 1.967(5)    | 1.974(3) | 1.965(4) |
|       | (Fe1−N1)   | (Fe2−N1)   | (Fe1−N1) | (Fe1−N1) |
|       | 1.917(4)    | 1.907(4)    | 1.905(3) | 1.896(3) |
|       | (Fe1−N2)   | (Fe2−N2)   | (Fe1−N2) | (Fe1−N2) |
|       | 1.987(5)    | 1.970(5)    | 1.958(3) | 1.984(4) |
|       | (Fe1−N3)   | (Fe2−N3)   | (Fe1−N3) | (Fe1−N3) |
|       | 1.994(5)    | 1.973(5)    | 1.988(3) | 1.984(4) |
|       | (Fe1−N7)   | (Fe2−N7)   | (Fe1−N4) | (Fe1−N5) |
|       | 1.922(4)    | 1.905(5)    | 1.900(3) | 1.891(3) |
|       | (Fe1−N8)   | (Fe2−N8)   | (Fe1−N5) | (Fe1−N6) |
|       | 1.981(5)    | 1.968(5)    | 1.976(3) | 1.977(4) |
|       | (Fe1−N9)   | (Fe2−N9)   | (Fe1−N6) | (Fe1−N7) |

$d_m$/Å = 1.97
1.95
1.95
1.95

aThere are two crystallographically independent molecules.
metal-free organic ligand is subjected to the calculation, so that the choice of B3LYP/6-311+G(2d,p) would be reasonable.

Because the crystal field effect is sensitive to the charge or electron population of the ligating atom, the Mulliken atomic charge at the pyridine nitrogen seems to be important. However, it has been pointed out that the natural population analysis gives better results than the Mulliken population analysis when precise basis sets are chosen.37,38 Therefore, the natural orbital population analysis was performed with the natural bond orbital (NBO) option.39

Attention was paid to a conformation problem around the biaryl-type Csp2−Csp2 single bonds. The pybox ligands and related chelatable ligands have a syn conformation in the coordination compounds, though the most stable form often is nearly anti20 (Scheme 3). To reproduce the conformation after complexation, the geometry optimization started from the syn form, eventually giving a conformation with a local potential minimum close to that of an ideal syn form.

The natural charge at the pyridine nitrogen atom, \( \rho(N_{py}) \), and the energy levels of the pyridine C≡N π orbital, \( E(\pi_{py}) \), and the pyridine lone-pair π orbital, \( E(n_{py}) \), were obtained and listed in Table 3. These values are varied depending on the substituent, and the \( T_{1/2} \) versus \( \rho(N_{py}) \) plot (Figure 5a) displays a positive correlation. The molecular electrostatic potential surfaces are demonstrated in Figure 5bc for MeO- and 4Py-pybox, respectively, under the same isosurface conditions. The electronegative character can be seen around heteroatoms, and in particular, the pyridine N atom in the former is more negative than that of the latter. To argue the usefulness of \( \rho(N_{py}) \), correlations were checked by drawing the plots of \( \sigma_p \) and \( \sigma_{p}' \) versus \( \rho(N_{py}) \) (Figure 6). Positive correlations were found with \( R^2 = 0.410 \) and 0.540, respectively, and it is notable that these coefficients are smaller than that of the \( T_{1/2} \) versus \( \rho(N_{py}) \) plot (0.734 in Figure 5a).

The matching of the energy levels has also been taken into consideration when the ligand MOs interact with iron(II) orbitals. Figure 7 illustrates that \( T_{1/2} \) had a negative correlation with \( E(\pi_{py}) \) and \( E(n_{py}) \), though the data points were relatively scattered. It is not surprising that the three calculated values, \( \rho(N_{py}) \), \( E(\pi_{py}) \), and \( E(n_{py}) \), are related to each other because the rich electron population or negatively large \( \rho(N_{py}) \) lifts \( E(\pi_{py}) \) and \( E(n_{py}) \).
DISCUSSION

Substituent Effect from an Empirical Approach. To establish a prediction method of SCO \( T_{1/2} \), the solution data were analyzed in connection with the substituent effect. We plotted the solution \( T_{1/2} \) against \( \sigma_p \) and \( \sigma_p^+ \) (Figure 3), where the data on the known derivatives\(^{16,17} \) are included. We can find a considerably good positive correlation, which indicates that electron-donating substituents suppress \( T_{1/2} \) whereas electron-withdrawing substituents raise \( T_{1/2} \). An empirical relationship equation is expressed as eq 2 (a dashed line superposed in Figure 3a). This method is satisfactory for the prediction of \( T_{1/2} \) when the substituent constant is available.

\[
T_{1/2} = 234(6)K + 170(29)\sigma_p K
\]  
(2)

Substituent Effect from the DFT Calculation Approach. Very recently, Brooker and co-workers reported the relation between the NMR chemical shift of the ligating nitrogen atom and SCO behavior.\(^{20} \) The chemical shifts were obtained by means of spectroscopic and DFT computational methods. In that research, the \(^{15}N\) NMR spectroscopy was applied, but such methods are not easily performed. Novikov et al. reported another way using a paramagnetic shift of \(^1H\) NMR on the ligand protons.\(^{46} \) The pseudocontact shift depends on the calculated mutual geometry between the \(^1H\) nucleus and unpaired electrons, and the contact distributions are given from calculation. Both experimental and computational techniques are needed.

On the other hand, the MO calculation on the ligand is an easier way to approach SCO analysis. The electron density is caused by the substituents, as usually formulated with the \( \sigma_p \) and finally proven with the MO calculation. This method has an intervening parameter (\( \sigma_p \)) in the discussion of the relation between the SCO temperature and the substituent effect. However, it seems to be more convenient if the SCO temperature is directly predicted from the calculation. Furthermore, as the calculation results on \([\text{Fe}(X-\text{pybox})_2]_2(\text{ClO}_4)_2\) (Figure 5a) show, the \( R^2 \) correlation coefficient between \( T_{1/2} \) and \( \rho(N_{py}) \) is better than those of \( \sigma_p \) versus \( \rho(N_{py}) \) and \( \sigma_p^+ \) versus \( \rho(N_{py}) \). A direct correlation using \( \rho(N_{py}) \) seems to be a more reliable and convenient way to predict \( T_{1/2} \).

In short, the substituent constants are not needed any more. A correlation equation is empirically described with eq 3 (a dashed line superposed in Figure 5).

\[
T_{1/2} = 1.68(27) \times 10^3K + 3.98(76) \times 10^3\rho(N_{py})K
\]  
(3)

Application to the 1-bpp Compounds. The present work provides a prediction method for \( T_{1/2} \) only from a chemical formula, enabling us to apply the DFT method to well-known SCO-active \([\text{Fe}^2(X-1-bpp)_2](\text{BF}_4)_2\) involving 4-substituted 1-bpp,\(^{30} \) for example. The calculation protocol was the same as that of the 4-X-pybox series, and the result is displayed in Figure 8. An astonishingly good correlation (\( R^2 = 0.980 \)) appeared, as shown with a dashed line. The best fit line is formulated with eq 4.

\[
T_{1/2} = 1.700(79) \times 10^3K + 3.60(19) \times 10^3\rho(N_{py})K
\]  
(4)

Figure 9 shows the correlations between \( \sigma_p \) versus \( \rho(N_{py}) \) and \( \sigma_p^+ \) versus \( \rho(N_{py}) \). These plots still have a strong correlation but relatively scattered data points, as indicated with \( R^2 = 0.831 \) and 0.932, respectively. As Halcrow et al. pointed out, the \( \sigma_p^+ \) constants are slightly better than the \( \sigma_p \) ones to describe the results of the 1-bpp complexes.\(^{30} \) However, similar to the case of the X-pybox compounds, the best way in the substituent effect analysis is to utilize the \( \rho(N_{py}) \) parameter. Furthermore, the present method is inexpensive in comparison with the usual theoretical treatments including the calculation.

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Figure 5. (a) Plot of \( T_{1/2} \) for \([\text{Fe}(X-\text{pybox})_2]_2(\text{ClO}_4)_2\) in acetone solution vs \( \rho(N_{py}) \) from the DFT natural population analysis. A dashed line represents the best linear fit. (b,c) Molecular electrostatic potential from −0.10 (red) to +0.14 (blue) mapped on the total electron density surface at 0.02 e au\(^{-3} \) for X = MeO (b) and 4Py (c).

Figure 6. Plots of (a) \( \sigma_p \) vs \( \rho(N_{py}) \) and (b) \( \sigma_p^+ \) vs \( \rho(N_{py}) \) for X-pybox. Dashed lines represent the best linear fit.
on the whole coordination compounds. The SCO temperature will be discussed in a generalized manner according to the present method, regardless of the different ligand platforms, such as pybox and 1-bpp.

**Application to the Azine-Substituted Triazole Compounds.** To pursue further generalization of the present method, we expanded the calculation work to another system, the azine (heteroaromatic ring) dependence on $T_{1/2}$ of $[\text{Fe}^{II}(L^{\text{azinyl}})_{2}(\text{NCBH}_3)_2]$ ($\text{azinyl} = 2$-pyridyl, 3-pyridazyl, 4-pyrimidinyl, 2-pyrimidinyl, pyrazinyl). The electronic population on the ligating nitrogen atom ($N_{\text{A}}$; see Scheme 3) varies with respect to the heteroaromatic skeleton itself and not as a substituent on the ring. The natural charge on the ligating azinyl nitrogen atom, $\rho(N_{\text{A}})$, was calculated at the same level as those of the calculations on the 4-X-pybox and 4-X-1-bpp families. In this calculation, the starting structure is restricted to a syn isomer (Scheme 3), like the two previous cases. Figure 10 shows a calculation result and clarifies a distinct positive correlation between $T_{1/2}$ and $\rho(N_{\text{A}})$. The best fit line is expressed as eq 5 with $R^2 = 0.963$.

$$T_{1/2} = 700(44)K + 103(12) \times 10^4 \rho(N_{\text{A}}) K$$ (5)

Apparently, a similar result was obtained here, when compared with the plot of $T_{1/2}$ versus $\delta(N_{\text{A}})$ ($^{15}$N NMR chemical shift) reported by Brooker et al., but there seems to be a different meaning. Both the crystal field effect and NMR chemical shift originate in the atomic charge in common. However, the $^{15}$N chemical shift in the heteroaromatic ring involves an additional deshielding effect from an aromatic ring current. After the deshielding effect is cancelled by accident in the comparison work, a linear relation in the $T_{1/2}$ versus $\delta(N_{\text{A}})$ plot would appear. Therefore, the $T_{1/2}$ versus $\rho(N_{\text{A}})$ plot is concluded to demonstrate a straightforward causal relationship. In short, the NMR chemical shift is not needed in the discussion on $T_{1/2}$.
The charge at the ligating nitrogen atom is concluded to be essential in discussion on SCO. The present DFT MO method would be applicable to other SCO-active Fe(II) complexes carrying substituted pyridine-based N-donor ligands, and even for different ligand systems involving azaaromatic rings. The electron population analysis at the ligating nitrogen atom in a metal-free ligand by means of the DFT MO method provides one of the most convenient and powerful ways to explain and predict the SCO temperature.

**Mechanism.** The substituent effect described here is explained in terms of a perturbation from the substituent. When an electron-donating group is introduced to the pyridine ring, the $t_{2g}$ energy level is raised, and the $e_g-t_{2g}$ energy gap ($\Delta_{eo}$) becomes narrower, favoring the HS state and low $T_{1/2}$ (Figure 11). With an electron-withdrawing group, it is vice versa. The $\sigma_p$ and $\sigma_p^*$ constants contain two major contributions: one is the inductive effect along the $\sigma$ electron system and another is the mesomeric or resonance effect through the $\pi$ electron system. In general, the latter becomes obvious when the 2- or 4-position in the six-membered aromatic ring is substituted. Therefore, the $\sigma_p$ and $\sigma_p^*$ constants are adequate empirical representatives to comprehend the substituent effect in the SCO compounds involving 4-X-substituted pyridine-based ligands.

The DFT calculation supports the proposed mechanism. Figures 5a, 8, and 10 highlight the role of the electron-withdrawing or -donating nature of the substituent group or heteroaromatic skeleton, and the charge of the ligating nitrogen atom is tuned. In the case of the L$n$azinyl series, the substituent effect belongs to the heteroaromatic ring itself. The logic never changes; the electron population on the ligating nitrogen atom increases or decreases, depending on the electronic structure of the heteroaromatic rings.

The $d\pi/d\pi$ symmetry consideration tells us that the $t_{2g}$ energy level is perturbed through the $d\pi$-$\pi$ interaction from the ligand $\pi$ electron system (Figure 11). In addition to the orbital overlap, the matching of the energy level of each orbital has also been taken into account. The electron density at each atom is responsible for the shift of the energy levels of relevant MOs. Although correlations appear for both $E(\pi_{pp})$ and $E(\pi_{pp})$ to $T_{1/2}$, $E(\pi_{pp})$ has a higher energy level than $E(\pi_{pp})$, and there seems to be an advantage in the interaction between the $\pi_{pp}$ and iron(II) $t_{2g}$ orbitals over the interaction between the $\pi_{pp}$ and iron(II) $e_g$ orbitals. In other words, the $d\pi$-$\pi$ interaction serves a major path in tuning $T_{1/2}$.

Finally, we have to make a comment on the validity that a purely enthalpy term de is handled with care, though we have not yet encountered any hazard.

**EXPERIMENTAL SECTION**

**Materials.** Caution! The perchlorate salts should be handled with care, though we have not yet encountered any hazard.

Me$_2$Br, Br, and Cl-pybox were prepared according to the literature methods. Na$_3$pybox: a mixture of Cl-pybox (0.746 g; 2.96 mmol), NaN$_3$ (1.932 g; 29.7 mmol), and N,N-dimethylformamide (10 mL) was heated at 65 °C for 4 h. Anhydrous conditions are required to avoid hydrolysis of the oxazoline rings. After the addition of aq NaHCO$_3$, the organic layer was extracted with dichloromethane and hexane. The organic layer was washed with brine, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. The resultant colorless powder was collected on a filter and washed with tetrahydrofuran. The yield was 0.575 g (2.27 mmol; 77%).

Computational methods. The DFT calculation was implemented using the Dmol program. All structures were optimized using the B3LYP functional with a 6-31G(d,p) basis set. The vibrational frequencies were calculated to check the minimum energy structures. The electronic spectra were calculated using the synchronous transit gradient (STO) method with the same basis set. All calculations were performed on a laptop computer with an Intel Core i7 processor (3.6 GHz) and 8 GB of RAM.
2-Thy-pybox: a mixture of Cl-pybox (0.394 g; 1.57 mmol), 2-thienyl boronic acid (0.198 g; 1.55 mmol), Pd(PPh4)3 (0.0232 g; 0.0201 mmol), and K2CO3 (0.890; 6.44 mmol) in dry N,N-dimethylformamide (4 mL) was heated at 130 °C for 3 days. After the addition of water, the organic layer was separated with ethyl acetate. The organic layer was washed with aq. NaHCO3 and brine, dried over anhydrous MgSO4, with ethyl acetate. The organic layer was washed with water, the organic layer was separated and magnetic analyses. The purity of the target complexes was confirmed with the elemental, spectroscopic, and magnetic analyses.

Complexes [Fe(X-pybox)2](ClO4)2·X(solvent) (X = Me, 2Th, N3, Br, 3Py) were synthesized in a manner similar to those of [Fe(X-pybox)2]ClO4·3MeOH.11−17 The elemental analysis was performed by a usual combustion method (PerkinElmer Series II CHNS/O 2400) on evacuated specimens, and accordingly, the solvation content was often different from those of the X-ray crystallographic analysis. The purity of the target complexes was confirmed with the elemental, spectroscopic, and magnetic analyses.

Crystallographic Study. X-ray diffraction data of [Fe(X-pybox)2]ClO4·nMeOH (X = N3, Br, 3Py) were collected on a Saturn70 CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were directly solved by a heavy-atom method and expanded using Fourier techniques in the CRYSTALSTRUCTURE program package.48 The parameters were refined in the SHELXL program.49 Numerical absorption correction was used. Hydrogen atoms were placed at calculated positions, and their parameters were refined as riding. The thermal displacement factors of nonhydrogen atoms were refined anisotropically. Selected crystallographic data are given in Table 1, and important bond lengths are listed in Table 2. A pseudo-polymer of the X = Br derivative was found. Selected crystallographic parameters are as follows: [Fe(2Th-pybox)2]ClO4·nMeOH, monoclinic P21/c, a = 9.627(2) Å, b = 17.371(4) Å, c = 20.100(5) Å, V = 348.38(13) Å3, Z = 4, d = 1.875 g cm−3, μ(μKα) = 3.090 mm−1, R(F) (I > 2σ(I)) = 0.0661, wR(F2) (all data) = 0.1667, G.O.F. = 1.031, T = 100 K for 7649 reflections.

A crystallographic study on the X = Me and 2Th derivatives clarified the cell parameters as follows: [Fe(Me-pybox)2]ClO4·nMeOH, tetragonal, a = 20.433(7) Å, b = 20.037(5) Å, V = 8366(4) Å3 and Z = 8 at 100 K; [Fe(2Th-pybox)2]ClO4·0.75MeOH, triclinic, P1, a = 17.084(4) Å, b = 17.905(4) Å, c = 24.247(7) Å, α = 90.225(10), β = 99.720(11), γ = 95.326(9), V = 7278(3) Å3, and Z = 8 at 100 K.

CCDC numbers 1836313, 1836314, and 1836315 for [Fe(X-pybox)2]ClO4·nMeOH (X = N3, Br, 3Py, respectively) include the experimental details and geometrical parameter tables.

Magnetic Study. Magnetic susceptibilities of polycrystalline and solution forms of [Fe(X-pybox)2]ClO4·X(solvent) (X = Me, 2Th, N3, Br, 3Py) were measured on a Quantum Design PPMS-XL7 SQUID magnetometer with a static field of 0.5 T. Solution specimens were mounted in a sealed NMR sample tube. Details have been described elsewhere.55

DFT Calculation Study. DFT MO calculation was performed with the GAUSSIAN 03 package on a Windows PC. The geometry was optimized, and the self-consistent-field (SCF) energy was converged on the B3LYP Hamiltonian with the 6-311+G(2d,p) basis set. The criterion of the SCF energy convergence was set to 10−5 au. The NBO analysis was performed with the NBO option executing the Gaussian NBO version 3.1.56 The natural charge at the pyridine nitrogen atom, ρ(Npy), and the MO energy levels, E(σpy) and E(πpy), could be read out from the text output.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01095.

Crystallographic data for [Fe(X-pybox)2]ClO4·nMeOH (X = N3, Br, 3Py) (CIF)
dispensable for discussing ligand
regarded as a convenient metric, an MO consideration is
the present study, the SQUID susceptometry was applied, but
the possible e
van der Waals radii (3.35 Å).29 Distances near the sum of the
for O14MeOH
H17Aoxazoline, 2.319 Å for O14MeOH
O9ClO4 and 2.838(8) Å for O1oxazoline
operative and construct an interactive network.

A versatile system for spin-crossover research. Coord.
Chem. Rev. 2015, 289, 35–47.

one may assume that more negative charge on the donor
interaction giving a decrease of
π
in frame stronger, thus enhancing
Δ
in favor of the LS state. In the present mechanism, the dx−
py interaction giving a decrease of
Δ
is more vigorous than the possible effect mentioned above. Although the charge is regarded as a convenient metric, an MO consideration is indispensable for discussing ligand fields from aromatic ring coordination.

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ADDITIONAL NOTES

Considerably short intermolecular atomic distances are found; 2.906(9) Å for Br1···O10ClO4 and 2.997(4) Å for

The solvated methanol oxygen atoms have another contact with neighboring [Fe(3Py-pybox)2] complex ion; 3.093(7) Å for O13MeOH···

H17Apyridine. Namely, the solvate molecule plays a role of an interaction network bridge. Such an interaction network may enhance an abrupt character of the SCO behavior.

From a closer look at Figures 5a and 8, we can find that the latter displays a better correlation than the former. The oxazoline ring has saturated bonds while the pyrazole ring is aromatic. The calculation was performed on the metal-free oxazoline ring has saturated bonds while the pyrazole ring is aromatic. The calculation was performed on the metal-free oxazoline ring.

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