Quantitative Assessment of Ligand Substituent Effects on $\sigma$- and $\pi$-Contributions to Fe–N Bonds in Spin Crossover Fe$^{II}$ Complexes

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Abstract: The effect of para-substituent X on the electronic structure of sixteen tridentate 4-X-(2,6-di(pyrazol-1-yl))pyridine (bpp) ligands and the corresponding solution spin crossover [Fe(bpp)$_3$]$^{2+}$ complexes is analysed further, to supply quantitative insights into the effect of X on the $\sigma$-donor and $\pi$-acceptor character of the Fe-N$_A$(pyridine) bonds. EDA-NOCV on the sixteen LS complexes revealed that neither $\Delta E_{\sigma,\text{bor}}$ ($R^2 = 0.48$) nor $\Delta E_{\sigma,\text{bor}}$ ($R^2 = 0.31$) correlated with the experimental solution T$_{1/2}$ values (which are expected to reflect the ligand field imposed on the iron centre), but that $\Delta E_{\sigma,\text{bor}}$ correlates well ($R^2 = 0.82$) and implies that as X changes from EDG—EWG (Electron Donating to Withdrawing Group), the ligand becomes a better $\sigma$-donor. This counter-intuitive result was further probed by Mulliken analysis of the N$_A$ atomic orbitals: N$_A$($\sigma$) involved in the Fe–N $\sigma$-bond vs. the perpendicular N$_A$($\pi$) employed in the ligand aromatic $\pi$-system. As X changes EDG—EWG, the electron population on N$_A$($\sigma$) decreases, making it a better $\pi$-acceptor, whilst that in N$_A$($\pi$) increases, making it a better $\sigma$-bond donor; both increase ligand field, and T$_{1/2}$ as observed. In 2016, Halcrow, Deeth and co-workers proposed an intuitively reasonable explanation of the effect of the para-X substituents on the T$_{1/2}$ values in this family of complexes, consistent with the calculated MO energy levels, that M–L $\pi$-backdonation dominates in these M–L bonds. Here the quantitative EDA-NOCV analysis of the M–L bond contributions provides a more complete, coherent and detailed picture of the relative impact of M–L $\sigma$-versus $\pi$-bonding in determining the observed T$_{1/2}$, refining the earlier interpretation and revealing the importance of the $\sigma$-bonding. Furthermore, our results are in perfect agreement with the $\Delta$E(HS-LS) vs. $\sigma_\pi$ ($X$) correlation reported in their work.

Introduction

Predictable fine tuning of the electronic structure of metal complexes is highly desirable, not least in order to optimise them for use in practical applications, such as molecular electronics,[6] emissive devices,[7] catalysis[1] or photovoltaics.[5]

The choice of substituent X present in a 5- or 6-membered aromatic ring is an important and frequently employed tool for fine-tuning the electronic structure of organic and inorganic compounds.

Substituent effects are commonly parameterised using the Hammett constant ($\sigma(X)$) or $\sigma^+(X)$: $\sigma(X)$ comes from acid/base dissociation of para/meta substituted benzoic acids, whereas $\sigma^+(X)$ comes from nucleophilic substitution at the carbonyl carbon in para/meta substituted benzoic acid derivatives and better reflects resonance effects.[3-6] The Hammett parameters for para-X substituents, $\sigma_p(X)$ and $\sigma_{p}^+(X)$, range from those for very Electron Donating Groups (EDG, X = Me$_2$; $\sigma_p = -0.83$, $\sigma_{p}^+ = -1.70$) to those for very Electron Withdrawing Groups (EWG, X = NO$_2$; $\sigma_p = 0.78$, $\sigma_{p}^+ = 0.79$). As expected, meta-Y substituents have far less electronic impact so have a much narrower range of $\sigma_{m}^+(Y)$ values, from the lowest EDG (Y = Me: $\sigma_m = 0.04$, $\sigma_{m}^+ = -0.07$) to the highest EWG (Y = NO$_2$; $\sigma_m = 0.71$, $\sigma_{m}^+ = 0.67$).[7]

Many studies have tried, with varying success, to rationalise how ligand substituent modifications affect key properties such as the molecular orbital (MO) energies,[6] redox potentials[6] as well as spin crossover (SCO) switching temperatures.[18,19] The focus herein is on SCO, which occurs when the metal ion M (usually 3$d^9$ to 3$d^7$ electronic configuration in octahedral geometry) can be switched between the high spin (HS) and low spin (LS) states through a trigger stimulus such as temperature, pressure, host-guest interaction, external magnetic field or light irradiation.[11] Systems showing thermal SCO in the solution phase are particularly suitable candidates for monitoring the X
(or Y) effects on the M–L bond, as they are not complicated by the effects of crystal packing or solvatomorphs;[12] so, providing speciation is not a problem, variations in the ligand field strength due to X (or Y) substituent, are more clearly observed in solution[13,14,15] than in the solid state SCO. For thermal SCO, the switching temperature $T_{1/2}$ (the temperature at which there is a 50:50 ratio of HSLs) is determined in order to monitor these variations.[16,13,15]

A landmark study on the effects of para-X (and meta-Y) substituents on solution SCO $T_{1/2}$ values was reported by Deeth, Halcrow and co-workers in 2016.[16] and this was followed up with further papers by them in 2018[16,17] and 2019.[12] They focused on the largest known family of solution SCO active complexes, [Fe(bpp)X]$_2^+$ (where bpp$^X$ = 4-X,2,6-di(pyrazol-3-Y)-1-yl)pyridine; Figure 1 shows only the 16 complexes focused on herein, for which the ‘meta’ pyrazole substituent is held constant as Y = H whilst the para substituent X is varied), which had been prepared and studied by various authors across the years.[16,17] In their landmark paper[16] they found a strong positive correlation ($R^2 = 0.92$) of $\sigma^+$(X) vs. $T_{1/2}$ and as expected a weaker, but also negative, correlation ($R^2 = 0.61$) of $\sigma^-$ (Y) vs. $T_{1/2}$. They also found, by using quantum-chemical calculation based on Density Functional Theory (DFT), that (a) the difference between the HS and LS total energies, $\Delta E_f$(HS-LS), correlated strongly with $\sigma^+$(X) ($R^2 = 0.89$) and less strongly with $\sigma^-$ (Y) ($R^2 = 0.67$); and (b) $\sigma^+$(X) and $\sigma^-$ (Y) correlated extremely well ($R^2 = 0.93$–0.99) with the average energy levels, $<E(t_0)>$ and $<E(e_0)>$, calculated for LS [Fe(bpp)X]$_2^+$ ($R^2 = 0.94$–0.93) and LS [Fe(bpp)X]$_2^-$( $R^2 = 0.99$–0.98). They concluded that there is a “fine balance between opposing M–L $\alpha$- and $\pi$-bonding effects”, and that for the present family: (a) Fe–N $\pi$-backbonding effects must be dominating for para-X substituents because EDG–EWG increases the observed $T_{1/2}$, the rationale being that this is expected to decrease the energy of the ligand $\pi^*$ MOs and therefore increase the M–L $\pi$-backbonding, increasing the ligand field strength and $T_{1/2}$, whereas (b) Fe -- N $\alpha$-bonding effects must be dominating for the meta-Y substituents as EDG--EWG decreases the observed $T_{1/2}$, the rationale being that this is expected to decrease the energy of the lone pairs, making them poorer M–L $\alpha$-donors, decreasing the ligand field strength and hence also the $T_{1/2}$.[16] The quantitative EDA-NOCV analysis carried out herein enables us to refine this interpretation, and reveals the importance of the $\alpha$-bonding (see later).

The present study was motivated by the above findings[16] and by the promise shown in our first use of EDA-NOCV theory, which is a combination of EDA (Energy Decomposition Analysis)[16] with the NOCV (Natural Orbitals for Chemical Valence)[16] concept that provides quantitative and chemically intuitive analysis of bonding – to a solution SCO system, specifically a family of five [Fe(PS$_{2}$)$_2$(NCBH)$_2$] complexes.[16] The latter study[16] first established a new and general fragmentation protocol (M+L) for computationally evaluating M–L bond strength in any kind of metal complex, diamagnetic or paramagnetic. Such corrected approach overcomes limits of partial ML$_x$ fragmentations (ML$_x$+L$_{x}$), proposing a common ground state (the ‘naked’ metal ion M) to treat any complex independently from the ligand coordination pocket. Then this protocol was applied to the family of five [Fe(PS$_{2}$)$_2$(NCBH)$_2$] complexes, revealing a strong correlation ($R^2 = 0.99$) between $\Delta E_{\text{EDGNOV}}$ for the Fe–N bonds and the experimental $T_{1/2}$ for solution SCO.

Another important study aimed at improved our detailed understanding of $\alpha$- and $\pi$-tuning operated by para-X substituents was reported by Ashley and Jakubikova in 2018.[18] They carried out a DFT and EDA-NOCV study on a family of LS iron(II) complexes of para-X substituted bipyrindine ligands, [Fe-(bpp)$_2$]$_2^+$, and found that the ligands show both $\pi$-acceptor and $\pi$-donor character, but recommend that the results should be taken with caution until they can be experimentally verified in some way. They also commented that use of substituents X should be a good way to make small adjustments of ligand field, and hence precisely tune the $T_{1/2}$ in an SCO complex (without pushing the complex either LS or HS). Clearly $T_{1/2}$ is an experimental outcome that can be used to validate theoretical predictions of how a change in X will tune the ligand field. Such a validation in silico predictions, pre-synthesis, is key as it will enable future synthetic efforts to focus on only preparing the best candidate for a desired $T_{1/2}$ or indeed spin state. Given that spin state is key to properties and function, including catalytic, the importance of this is clear.[18]

Herein, EDA-NOCV methodology is applied for only the second time to an SCO system – in this case to the large family of sixteen para-X substituted [Fe(PS$_{2}$)$_2$]$_2^+$ complexes (Figure 1), in order to quantify the relative importance of the $\alpha$- and $\pi$-contributions to the M–L bonds as X is varied as EDG–EWG, and look for correlations between the obtained parameters and

![Figure 1](image-url)
the experimentally observed $T_{1/2}$ values. As this led to unexpected results, an in-depth Mulliken charge analysis of the N-donor atomic orbitals (AOs) population was also performed, to provide further insights and explanations.

Finally, the correlations obtained are employed (a) to test how well the known Hammett $\sigma_p(X)$ parameters for $X = \text{SOME}$ and $\text{SO}_2\text{Me}$ were reproduced, and (b) to predict approximate values for the unknown $\sigma_p(X)$ for these two substituents $X$.

**Introduction to EDA-NOCV**

The EDA-NOCV method involves a “classical” EDA followed by a NOCV procedure. In this work, it is used to single out and quantify the various energy contributions to M–L bonding. After geometry optimisation, the compound is formally separated into two or more non-interacting fragments, and the intrinsic, instantaneous interaction energy $\Delta E_{\text{int}}$ of the bonds formed between the fragments in the frozen (unrelaxed) geometry of the molecule is then assessed (Eq. (1)) in a stepwise fashion. The general fragmentation that we developed and validated in a previous study is employed herein (fragmentation 5 in ref. Figure S1): fragment 1 (corrected) = Fe° and fragment 2 = L (herein both tridentate bpp ligands).

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$$

Where: $\Delta E_{\text{elstat}}$ is the electrostatic interaction (usually negative/attractive), $\Delta E_{\text{Pauli}}$ is the Pauli repulsion (repulsive/positive), $\Delta E_{\text{orb}}$ is the orbital interaction (attractive/negative, see also Equation (2), below), and $\Delta E_{\text{disp}}$ is the dispersion term (attractive/negative) accounting for long-range interaction.

Subsequently, NOCV analysis decomposes $\Delta E_{\text{orb}}$ (Eq. (2)) into several contributions, reflecting electron flows (i.e., deformation densities $\Delta p$) between (a) two MOs on different fragments to give the individual orbital contributions to the $\sigma$, $\pi$ and $\delta$ bonds formed ($\Delta E_{\text{orb},i,j} = \sigma, \pi, \delta$; identified by visual inspection of $\Delta p$) and (b) two MOs on the same fragment to give the polarization term ($\Delta E_{\text{orb,pol}}$).

$$\Delta E_{\text{orb}} = \Delta E_{\text{orb},\sigma} + \Delta E_{\text{orb},\pi} + \Delta E_{\text{orb,pol}} + \Delta E_{\text{orb,pol}}$$

Information about the magnitude of the charge flow is given via the corresponding eigenvalues. Of the many contributions to $\Delta E_{\text{orb}}$, those of key importance in octahedral transition metal complexes are six $\sigma$-type interactions ($\Delta E_{\sigma}$) between the M AOs ($d_{x^2}$, $d_{xy}$, $d_{yz}$, $d_{pz}$, $p_x$, $p_y$, and $s$ orbitals) and the MOs with the corresponding symmetry in the L 6 fragment, plus three $\pi$-type interactions ($\Delta E_{\pi}$) between the remaining $\text{M}$ AOs ($d_{xy}$, $d_{yz}$, $d_{z^2}$) and the $L_6$ MOs of appropriate symmetry.

Note that the development and validation of this general fragmentation method ($\text{M} + 6 \text{L}$), for dia- and para-magnetic complexes and the application of it to SCO complexes for the first time in Ref. [20], and again herein, opens the door quantifying the nature of M–L bonding in more families of SCO complexes (in which the ligand field strength is very delicately poised) and we expect the resulting findings will continue to be revelatory.

**Results and Discussion**

DFT optimisation of [Fe($\text{bppp}$)$_2$]$^{2+}$ (LS and HS)

The geometry optimisation computational protocol employed for the sixteen LS and sixteen HS [Fe($\text{bppp}$)$_2$]$^{2+}$ complexes was chosen based on the functional screening we performed previously. The same computational protocol was applied to all of the candidates, in the same CPCM solvent, acetone, albeit the LS forms of the X = NH$_2$ or NH$_3$ complexes were not observed experimentally. Calculating the Root-Mean-Square-Deviation (RMSD) of each atomic position (Eq. S1) in the structures of these [Fe($\text{bppp}$)$_2$]$^{2+}$ complexes from that of the respective LS or HS state of the X = H parent complex, [Fe($\text{bppp}$)$_2$]$^{2+}$, confirmed that the variation of the para-substituent $X$ causes no significant deviations (RMSD < 0.01 Å in all cases, Table S1). The six, out of the sixteen [Fe($\text{bppp}$)$_2$]$^{2+}$ complexes, where the experimental $T_{1/2}$ values were measured in nitromethane solvent were subjected to a geometry re-optimisation, and then to a RMSD evaluation between the final geometries calculated in acetone vs. nitromethane. Again, the RMSD for each atomic position confirmed that, as expected, changing the dielectric constant in the CPCM model, from acetone to nitromethane, has a negligible effect on the optimised structures obtained in these two different solvents (RMSD < 0.01 Å in all cases, Table S1).

EDA analysis of effects of $X$ in [Fe($\text{bppp}$)$_2$]$^{2+}$ (LS and HS)

EDA, using the previously established optimal fragmentation 5e ($\text{M} + 6 \text{L}$) (Table S2, see Computational Details section below for details), were performed on the sixteen HS and sixteen LS [Fe($\text{bppp}$)$_2$]$^{2+}$ complexes (Figure 1). This quantified the overall interaction energy, $\Delta E_{\text{int}}$, which accounts for the strength of the binding by the coordination sphere onto the iron(II) centre. The $\Delta E_{\text{int}}$ contribution for HS was half that for LS [Fe($\text{bppp}$)$_2$]$^{2+}$ complexes (Table 1).

This is consistent with the HS state being less enthalpically stable than the LS state; note these results are obtained at 0 K. Furthermore, as $\sigma_p(X)$ (X) increases (EDG–EWG, NH$_2$–NO$_2$), the stabilising energy $\Delta E_{\text{elstat}}$ drops in all cases: from about −250 to −200 kcal/mol for the LS complexes (NH$_2$–NO$_2$) and from −120 to −70 kcal/mol (NH$_3$–NO$_2$) for the HS complexes (Figure 2, Tables 1, 2). In the detailed analysis of the various energetic contributions to the $\Delta E_{\text{int}}$ term, the $\Delta E_{\text{elstat}}$ term—which accounts for the ionic bonding between the fragments—is observed to correlate well with $\sigma_p(X)$ for LS [Fe($\text{bppp}$)$_2$]$^{2+}$ ($R^2 = 0.89$, Table S3, Figure S2) and moderately well for HS [Fe($\text{bppp}$)$_2$]$^{2+}$ ($R^2 = 0.73$, Table S4 and Figure S3). In both cases, this behaviour can be understood as follows: as X becomes more electron poor ($\sigma_p(X)$ increases) it drains more electron density away from the coordinating nitrogen (Figure 1),
decreasing the favourable electrostatic interactions with the Fe$^{II}$ ion (Tables S3-S4).

From $X = \text{NMe}_2$ to $X = \text{NO}_2$, $\Delta E_{\text{bond}}$ decreases by just $-60$ kcal/mol (+15%) in the LS $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ and decreasing by just $-35$ kcal/mol (+12%) in the HS $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ complexes. In contrast, the $\Delta E_{\text{int}}$ interaction, which accounts for the covalent bonding between the fragments, remains almost constant across the whole range of $\alpha^*$ values: from $X = \text{NMe}_2$ to $X = \text{NO}_2$, $\Delta E_{\text{int}}$ increases by just +20 kcal/mol (+3.5%) in the LS $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ and decreased by just $-5$ kcal/mol (−1.5%) in the HS $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ complexes. Comparing these EDA results with those for the $[\text{Fe}(\text{L}^{\text{azin}})(\text{NCBH}_3)]$ family ($\text{L}^{\text{azin}} = 3-(2$-azinyl)-4-tolyl-5-phenyl-1,2,4-triazole; (Table 2))$^{[20]}$ few differences can be grouped up. The $\Delta E_{\text{int}}$ energies for the $[\text{Fe}^I(\text{L}^{\text{azin}})(\text{NCBH}_3)]$ family are twice the size of those for the $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ family$^{[20]}$ but yet, the $\Delta E_{\text{bond}}$ values are almost the same (Table 2). The cause of the big difference in $\Delta E_{\text{int}}$ values is the drop in magnitude observed for the $\Delta E_{\text{int}}$ term in the $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ family vs. the $[\text{Fe}(\text{L}^{\text{azin}})(\text{NCBH}_3)]$ family.

This is due to the fact that the two $\text{BF}_3$ (or two $\text{PF}_3$) anions are not directly bonded on the iron(II) ion in $[\text{Fe}(\text{bpp})]^2^{\text{II}}$; whereas the two NCBH$_3^-$ anions are directly bonded to the iron(II) ion in $[\text{Fe}(\text{L}^{\text{azin}})(\text{NCBH}_3)]$ (Table 2)$^{[8b]}$. Finally, it should be noted that the ratio between ionic and covalent contributions ($\Delta E_{\text{int}}/\Delta E_{\text{bond}}$ ratio) is important in describing the bonding between fragments$^{[20]}$. For the $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ complex the ionic:covalent ratio becomes more ionic on going from LS (44:55) to HS (50:47). This is very different from the $[\text{Fe}(\text{L}^{\text{azin}})(\text{NCBH}_3)]$ complex where the ionic bonding is already dominating in the LS state ($\Delta E_{\text{int}}$/$\Delta E_{\text{bond}}$ 55:45), and this further increases in the HS state (65:35) (Table 2)$^{[20]}$. In conclusion, EDA analysis of these families of complexes, which feature very different types of coordination environments, is shown to correctly incorporate

### Table 1. EDA results (frag. 5e) for the sixteen LS and HS $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ complexes: all energies are reported in kcal/mol (Note: 1 eV = 23 kcal/mol = 8100 cm$^{-1}$). Results are presented in order of increasing Hammett parameter ($\alpha^*$). $*$Values estimated in this study.

| X       | $\alpha^*$ | State | $\Delta E_{\text{int}}$ | $\Delta E_{\text{bond}}$ | $\Delta E_{\text{el}}$ |
|---------|------------|-------|--------------------------|--------------------------|-------------------------|
| NMe$_2$ | −1.70      | LS    | −255.0                   | −413.8                   | −305.5                  |
| NH$_3$  | −1.30      | HS    | −120.1                   | −330.6                   | −503.9                  |
| OH      | 164        | LS    | −232.0                   | −396.2                   | −307.7                  |
| OMe     | 158        | HS    | −98.1                    | −320.0                   | −499.5                  |
| SMe     | 194        | HS    | −104.0                   | −320.1                   | −501.6                  |
| Me      | 216        | LS    | −101.5                   | −314.3                   | −502.8                  |
| F       | 215        | LS    | −219.5                   | −385.0                   | −296.9                  |
| SH      | 246        | HS    | −83.0                    | −302.9                   | −499.3                  |
| H       | 248        | LS    | −229.1                   | −393.7                   | −296.6                  |
| Cl      | 226        | LS    | −212.7                   | −383.1                   | −311.8                  |
| I       | 236        | LS    | −224.5                   | −382.5                   | −304.1                  |
| Br      | 234        | HS    | −229.2                   | −383.1                   | −301.8                  |
| CO$_2$H | 281        | LS    | −83.5                    | −301.1                   | −505.6                  |
| NO$_2$  | 309        | LS    | −205.7                   | −365.4                   | −508.7                  |
| SOMe*   | 284        | LS    | −71.6                    | −296.6                   | −314.9                  |
| SO$_2$Me* | 294    | HS    | −81.0                    | −368.0                   | −510.5                  |

### Table 2. Range of $\Delta E_{\text{int}}$, $\Delta E_{\text{bond}}$, and $\Delta E_{\text{el}}$ values obtained from EDA analysis, in both HS and LS spin states (using fragmentation 5e), of the sixteen $[\text{Fe}(\text{bpp})]^2^{\text{II}}$ complexes, compared with those previously obtained for five $[\text{Fe}(\text{L}^{\text{azin}})(\text{NCBH}_3)]$ complexes$^{[20]}$. All energies are reported in kcal/mol.

| $\text{Fe}(\text{bpp})]^2^{\text{II}}$ | $\Delta E_{\text{int}}$ | $\Delta E_{\text{bond}}$ | $\Delta E_{\text{el}}$ |
|-------------------------------------|--------------------------|--------------------------|-------------------------|
| LS                                 | −250−200                 | −415−365 (−45%)          | −510−500 (−55%)         |
| HS                                 | −120−70                  | −330−290 (−55%)          | −315−295 (−45%)         |
| $[\text{Fe}(\text{L}^{\text{azin}})]^2$ | −530−500                 | −635−620 (−55%)          | −520−500 (−45%)         |
| (NCBH$_3$)$_2$                       | −385−370                 | −585−570 (−65%)          | −330−325 (−35%)         |
| bpp* vs. $\text{L}^{\text{azin}}$   | −53%−80%                 | −35%                     | −0.5%                   |
| HS                                 | −59%−81%                 | −40%                     | −5%                     |
details of the change in nature of the coordinative bond, regardless of the origin of the change.

NOCV analysis of the effects of X on Fe-N σ- and π-bonding in [Fe(bpp)$_2$]$_2^+$ (LS and HS)

The full NOCV results obtained using the previously optimised fragmentation 5b$^{[28]}$ are reported in Tables S5–S6, with selected data shown and discussed in the following sections. From the breakdown of the $\Delta E_{\text{orb}}$ term, the nine M-L$_6$ bonding interactions (described by Hoffman theory$^{[28]}$) can be identified by visual inspection and quantitatively assessed (Figure S1): six $\sigma$- ( $\Delta E_{\text{orb},\sigma}$), and three $\pi$-contributions ( $\Delta E_{\text{orb},\pi}$) to the ML$_6$ interactions are sought (Figure 3 and Figure 4, Tables 3, S5–S6).

For both spin states of the sixteen complexes, the $\Delta E_{\text{orb},\sigma}$ ( $\Delta E_{\text{orb},\sigma}$) contribution remains constant as X varies (Figures S5–S10). For all sixteen LS [Fe(bpp)$_2$]$_2^+$ complexes, the six $\sigma$-bonds ( $\Delta E_{\text{orb},\sigma}$) account for about 85% of the $\Delta E_{\text{orb},\sigma}$ contribution to M–L bonding, leaving only 15% of the stabilisation energy to come from the three $\pi$-bonds. The same is observed for all sixteen HS [Fe(bpp)$_2$]$_2^+$ complexes ( $\Delta E_{\text{orb},\pi}$) in the LS state the overall $\sigma$-strength is mostly due to the two M–L $\sigma$-bonds formed by the Fe$_6$(d$_{x^2-y^2}$) and Fe$_6$(d$_{z^2}$) orbitals ( $\Delta E_{\text{orb},\sigma}$ ( $\Delta E_{\text{orb},\sigma}$) $< -100$ kcal/mol; $\nu_i > 0.90$; Figure 3 (left) and Figures S5–S7).

In the sixteen HS [Fe(bpp)$_2$]$_2^+$ complexes in which these two $\epsilon_2$ anti-bonding orbitals are half-occupied, not empty, the $\Delta E_{\text{orb},\sigma}$ stabilisation energy drops by 55% relative to the analogous LS state complex (Tables 3 and S5–S6). In compar-

![Figure 2: Results of EDA analysis of three representative [Fe(bpp)$_2$]$_2^+$ complexes: X = NMe$_2$ (left), X = H (center) and X = NO$_2$ (right), in the LS (top) vs. HS (bottom) state (using fragmentation 5b$^{[28]}$). For each spin state the pair of bar graphs shows the four components of $\Delta E_{\text{ox}}$ (see Equation (1); only $\Delta E_{\text{Pauli}}$ is positive) and the sum of them, $\Delta E_{\text{ox}}$ (yellow).]

![Figure 3: Example of M(d$_{x^2}$)–L$_4$(MO) $\sigma$-donation (left) and M(d$_{z^2}$)–L$_4$(MO) $\pi$-backdonation (right) in LS [Fe(bpp)$_2$]$_2^+$ the direction of the charge flow is yellow—turquoise (cut-off: $\rho > 0.003$ e$^-$). A complete description of each engaged bond obtained by EDA-NOCV analysis is reported in Figures S5–S10.]

![Figure 4: Results of NOCV decomposition of $\Delta E_{\text{ox}}$ of three representative [Fe(bpp)$_2$]$_2^+$ complexes: X = NMe$_2$ (left), X = H (center) and X = NO$_2$ (right), in the LS (top) vs. HS (bottom) state (using fragmentation 5b$^{[28]}$). For each spin state the bar graph shows the four components of $\Delta E_{\text{ox}}$ (see Equation (2)).]
ison, in the LS [Fe(Lamn)(NCBH)2] complexes the six α-bonds (ΔE_α_bond) account for even more, about 92%, of the ΔE_ortho−para, the only exception for L^min=L^pref were the α-contribution drops to 84%; this is very likely due to a mixing between the α- and π-contribution.\(^\text{20}\) As well, for HS [Fe(Lamn)(NCBH)2] complexes, an even more inhomogeneity between ΔE_ortho and ΔE_ortho−para is observed (ΔE_ortho−para=98:2).

The three π-acceptor M−L bonds are composed by two stronger degenerate π-bonds involving the Fe(\(d_{dz^2}\)) and Fe(\(d_{dz^2−y^2}\)) orbitals (Figures S5–S10), and a weaker π-bond involving the Fe(\(d_{dz^2}\)) orbital (Figures S5–S10). For LS [Fe(bpp)\(^{2+}\)], these three π(M−L) interactions (slightly bonding MOs) contribute −47 kcal/mol. For HS [Fe(bpp)\(^{2+}\)], these three π(M−L) bonds contribute only −25 kcal/mol due to the SCO from LS→HS reducing the population of the t\(^2_y\)-like orbitals, i.e., π-backdonation reduction. Overall, on LS→HS, stabilisation by ΔE_ortho−para, drops by about 40% and the overall ΔE_ortho−para drops by about 50%. In comparison, for the [Fe(Lamn)(NCBH)2] complexes, the ΔE_ortho term drops by about 50%, ΔE_ortho−para drops by about 90%, and the overall ΔE_ortho−para drops by about 60%.

### EDA-NOCV analysis: Correlations with \(\sigma_\pi\)\(^+\)(X)

For the LS [Fe(bpp)\(^{2+}\)] family, when the Hammett constant \(\sigma_\pi\)\(^+\)(X) changes from EDG (X=NMe\(_2\)) to EWG (X=NO\(_2\)), a strong correlation is observed with ΔE_ortho−para (R\(^2=0.88\), Figure 5a), a poor correlation is observed with ΔE_ortho−ortho (R\(^2=0.31\), Figure 5b), and a weak correlation is observed with the overall ΔE_ortho−para (R\(^2=0.43\), Figure 5c). No correlations are observed for the HS [Fe(bpp)\(^{2+}\)] complexes: \(\sigma_\pi\)\(^+\)(X) vs. ΔE_ortho−para (R\(^2=0.30\), Figure S17); ΔE_ortho−ortho (R\(^2=0.01\), Figure S18); ΔE_ortho−para (R\(^2=0.34\), Figure S19). Compared to the previous studies\(^\text{21}\) the effects of X on π-backdonation (ΔE_ortho−para) in this LS [Fe(bpp)\(^{2+}\)] family are less linear and predictable than for the π-donation term ΔE_ortho−para shows a weak and opposite trend with the Hammett constant \(\sigma_\pi\)\(^+\)(X).

It is important to note that this divergence is not linked with the employed level of theory, as both studies employed the same DFT theory. Herein, as X varied as EDG→EWG (−1.70→+0.79), a quantitative ΔE_ortho−para stabilisation of about 5 kcal/mol is observed, along with a much less significant ΔE_ortho, destabilisation of about 1.5 kcal/mol (Tables 3, S5–S6). Not surprisingly, the π-donor properties again dominate the π-acceptor properties, with the latter playing only a secondary role in the ligand field tuning operated by the X substituent.

### Table 3. NOCV results (frag. 5b) for the sixteen LS and HS [Fe(bpp)\(^{2+}\)] complexes: all energies are reported in kcal/mol. Results are presented in order of increasing Hammett parameter (\(\sigma_\pi\)\(^+\)). *Hammett values estimated in this study. T_c values for 10 of these complexes were obtained in acetone whereas the 6 marked with * were obtained in nitromethane.

| X       | T_{c,2} | \(\sigma_\pi\)\(^+\) | State | ΔE_ortho−para | ΔE_ortho−ortho | ΔE_ortho−para |
|---------|---------|----------------------|-------|---------------|---------------|--------------|
| NMe\(_2\) | H5      | −1.70                | LS    | −378.5        | −323.2        | −52.5        |
|         |         |                      |       | −167.7        | −142.1        | −25.5        |
| NH\(_3\) | H5      | −1.30                | LS    | −374.8        | −326.4        | −50.1        |
|         |         |                      |       | −161.9        | −135.8        | −26.0        |
| OH      | 164     | −0.92                | LS    | −374.6        | −326.9        | −48.4        |
|         |         |                      |       | −168.9        | −145.6        | −23.3        |
| OMe     | 158     | −0.78                | LS    | −376.1        | −326.4        | −49.6        |
|         |         |                      |       | −156.3        | −130.9        | −25.3        |
| SMe     | 194     | −0.60                | LS    | −378.5        | −326.1        | −52.4        |
|         |         |                      |       | −165.9        | −141.7        | −24.1        |
| Me      | 216     | −0.31                | LS    | −376.2        | −327.7        | −48.2        |
|         |         |                      |       | −170.6        | −147.4        | −23.1        |
| F       | 215     | −0.31                | LS    | −374.4        | −326.7        | −48.5        |
|         |         |                      |       | −169.2        | −142.4        | −26.7        |
| SH      | 246     | −0.03                | LS    | −378.6        | −327.6        | −51.0        |
|         |         |                      |       | −170.2        | −145.9        | −24.3        |
| H       | 248     | 0.00                 | LS    | −375.0        | −328.7        | −47.3        |
|         |         |                      |       | −168.9        | −142.3        | −26.6        |
| Cl      | 226     | +0.11                | LS    | −376.9        | −327.9        | −49.0        |
|         |         |                      |       | −169.1        | −145.7        | −23.3        |
| I       | 236     | +0.14                | LS    | −378.9        | −328.5        | −50.4        |
|         |         |                      |       | −169.7        | −142.8        | −26.8        |
| Br      | 234     | +0.15                | LS    | −377.6        | −327.9        | −49.6        |
|         |         |                      |       | −169.7        | −142.9        | −26.8        |
| CO\(_2\)H | 281   | +0.42                | LS    | −379.7        | −331.1        | −48.5        |
|         |         |                      |       | −171.7        | −148.3        | −23.3        |
| NO\(_2\) | 309    | +0.79                | LS    | −379.7        | −331.8        | −48.8        |
|         |         |                      |       | −171.5        | −147.7        | −23.7        |
| SOMe*   | 284     | +0.25*               | LS    | −375.8        | −328.5        | −49.7        |
|         |         |                      |       | −165.2        | −142.5        | −22.6        |
| SO\(_2\)Me* | 294 | +0.54*              | HS    | −378.2        | −330.3        | −47.8        |
|         |         |                      |       | −170.1        | −147.7        | −22.9        |

EAD-NOCV analysis: Correlations with T_{1/2}

Herein, EDA-NOCV analysis reveals that the observed T_{1/2} is also in extremely good correlation with ΔE_ortho−para for LS [Fe(bpp)\(^{2+}\)].
Figure 5. Correlation of $\alpha_{p}^{+}(X)$ Hammett parameter with (a) $\Delta E_{orb,\sigma}$ ($R^2 = 0.91$); (b) $\Delta E_{orb,\pi}$ ($R^2 = 0.31$) and (c) $\Delta E_{orb,\sigma^{*}}$ ($R^2 = 0.43$) for the family of fourteen [Fe(bpp)$^2$$^{2+}$] complexes (X=SOMe, SOMe are absent as $\alpha_{p}^{+}(X)$ is not available from literature).

(Figure 6, red line, $R^2 = 0.82$ and Figure S11). On the other hand, $T_{1/2}$ does not correlate with $\Delta E_{orb,i}$ ($R^2 = 0.09$ Figure S12), and only very weakly correlates with $\Delta E_{orb,i+\pi}$ ($R^2 = 0.48$ Figure S13). It should be recalled (see above) that for this [Fe(bpp)$^2$$^{2+}$] family, $\Delta E_{orb,i}$ provides 85% of the overall bonding stabilisation ($\Delta E_{orb,i+\pi}$) so it is likely to dominate over changes in $\Delta E_{orb,i+\pi}$. In contrast, for the HS [Fe(bpp)$^2$$^{2+}$] complexes none of the $\Delta E_{orb,i}$ terms ($i = \sigma, \pi, \sigma^{*} + \pi$) shows a promising correlation with the $T_{1/2}$ values: $\Delta E_{orb,i}$ ($R^2 = 0.36$, Figure S14), $\Delta E_{orb,\sigma}$ ($R^2 = 0.07$, Figure S15) and $\Delta E_{orb,\sigma+\pi}$ ($R^2 = 0.31$, Figure S16).

Therefore, these EDA-NOCV results indicate that the LS state is the key spin state, as it is the one for which the electronic effect of X on the bonding properties of the [Fe(bpp)$^2$$^{2+}$] complex can be observed, through the cross-correlation of $\Delta E_{orb,i}$ vs. $T_{1/2}$ (Figure 6, red line, $R^2 = 0.82$) and $\Delta E_{orb,i}$ vs. $\alpha_{p}^{+}$ (Figure 6, blue line, $R^2 = 0.88$) and $T_{1/2}$ vs. $\alpha_{p}^{+}$ (Figure 6, green line, $R^2 = 0.92$)\cite{8b}.

However, the finding herein that in LS [Fe(bpp)$^2$$^{2+}$] only $\Delta E_{orb,i}$ not $\Delta E_{orb} or \Delta E_{orb,i+\pi}$ correlates with $T_{1/2}$ is not consistent with either (i) the intuitive rationale of the M–L bonding provided by Deeth, Halcrow and co-workers\cite{26} that M–L $\pi$-backboning dominates the tuning by X; or (ii) the finding observed for the [Fe(L$^{\text{amine}}$)$_2$(NCBH)$_2$$^{2+}$] family of a strong correlation for $\Delta E_{orb,i+\pi}$ vs. $T_{1/2}$ ($R^2 = 0.99$) and weak correlations for $\Delta E_{orb,i}$ vs. $T_{1/2}$ ($R^2 = 0.76$), $\Delta E_{orb,i}$ vs. $T_{1/2}$ ($R^2 = 0.88$)\cite{26}.

For issue (i), a deeper comparison of Deeth, Halcrow and co-workers\cite{26} finding vs. the present finding will be discussed shortly. For issue (ii), a deeper comparison of the EDA-NOCV results for the [Fe(bpp)$^2$$^{2+}$] (X substituent in dicationic complex) and [Fe(L$^{\text{amine}}$)$_2$(NCBH)$_2$$^{2+}$] (CH/N replacement in neutral complex) families\cite{26} is too early at this stage as these are the only two SCO families studied using EDA-NOCV to date: investigations of more such families are required and indeed warranted.

The results obtained on the SCO families under study also indicate that EDA-NOCV analysis works much better when the number of unpaired electrons is zero (diamagnetic) i.e. for LS (better than HS). This is a consequence of using DFT as the main theoretical investigation tool in the first steps of the EDA-NOCV analysis, along with having a d$^0$ ion, as Fe$^+$, instead of using a (computationally prohibitively expensive) multi-reference approach to capture and evaluate all relevant microstates. Being intrinsically a mono-determinantal approach, DFT cannot correctly capture static correlation effects. Thus, the closed-shell LS Fe$^+$ system can be correctly described while the open shell HS Fe$^+$ system is less well described and hence is less reliable. Moreover, as the LS state is the most stable species at 0 K, prediction of temperature effects for it is inherently limited. Conversely, temperature effects are important for the HS state, but cannot be explicitly considered unless more time-consuming DFT-based ab-initio molecular dynamic (AIMD) calculations are used.

Figure 6. Three strong pairwise correlations (blue, red and green lines), and a cross-correlation (black dots; grey arrow is only a guide to the eye) between the ligand donation properties ($\Delta E_{orb,\sigma}, \Delta E_{orb,\pi}$, calculated by EDA-NOCV for the LS complexes using fragmentation 5b), the Hammett constant of X ($\alpha_{p}^{+}$), and the switching temperature ($T_{1/2}$) for the twelve SCO-active complexes for which $\alpha_{p}^{+}(X)$ is known in this family of [Fe(bpp)$^2$$^{2+}$] complexes (X = SOMe, SOMe, NH$_2$, NMe$_2$ are absent, as $\alpha_{p}^{+}(X)$ is not known for the first two, and the last two remain HS).

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EDA-NOCV analysis: Correlations with δNₐ

Finally, NOCV results are explored from another perspective, not yet explicitly discussed in this study. This follows from an approach first proposed by Brooker and co-workers in 2009,[31,31] then followed up in 2017,[33] and further extended in 2021 to 5 families (42 complexes),[31b] in which the $^{13}$N NMR chemical shift ($\delta N_\alpha$) of the coordinating nitrogen $N_\alpha$ of the free ligand (easy to measure or calculate) provides a quantitative report on an N-donor ligand that has been shown to correlate well with the observed $T_{1/2}$ for the corresponding complex, in families of closely related complexes, including the bpp⁴ family of interest herein.[32]

Herein, the calculated $\delta N_\alpha$ of the bpp⁴ ligands is shown to correlate with one of the NOCV results, establishing a correlation between the properties of the bpp⁴ ligand before (free bpp⁴ ligand) and after coordinating the Fe²⁺ ion ([Fe²⁺(bpp⁴)]²⁺ complex).

For LS [Fe²⁺(bpp⁴)]²⁺, $\delta N_\alpha$ shows an extremely good correlation with $\Delta E_{orb,i}$ ($R^2 = 0.95$, Figure 7a), but only a very weak correlation with $\Delta E_{orb,x}$ ($R^2 = 0.39$, Figure 7b) or $\Delta E_{orb,x,y}$ ($R^2 = 0.23$, Figure 7c).[13] In contrast, for HS [Fe²⁺(bpp⁴)]²⁺, no correlations are observed for $\delta N_\alpha$ with any $\Delta E_{orb,i}$ ($i = \sigma; \pi; \sigma + \pi$) term: $\Delta E_{orb,i}$ ($R^2 = 0.35$, Figures S20), $\Delta E_{orb,x}$ ($R^2 = 0.04$, Figures S21) and $\Delta E_{orb,x,y}$ ($R^2 = 0.30$, Figures S22).

This is in full agreement with all of the findings discussed previously: the X substituent, the effect of which can be quantified through use of $\sigma_\alpha^>(X)$, operates as a tuner of the coordinating nitrogen ligand field strength, by enriching or impoverishing the electron density, which in turn is reflected in the chemical shift, $\delta N_\alpha$. This tweak of the nitrogen electron density is intimately entangled with the ligand $\sigma$-donating properties ($\Delta E_{orb,i}$) of the, enthalpically most stable, LS state that, finally, leads to an increase in the experimental $T_{1/2}$.

Mulliken population analysis

The EDA-NOCV results just reported project a different interpretation of the experimental results than those proposed by Deeth, Halcrow et al. in 2016.[36] They concluded that the dominant effect of X changing EDG—EWG was increased $\pi$-backdonation, which increased the ligand field splitting ($\Delta A$) and the observed solution $T_{1/2}$ values. In contrast, the above quantitative EDA-NOCV analysis indicates, rather counter-intuitively at first glance, that as X changes as EDG—EWG, the dominant effect is increased $\sigma$-donation $M$—L, and hence increased ligand field splitting and observed solution $T_{1/2}$ values (Figure 8).

To try to understand how X changing EDG—EWG could increase the ability of the N-donor to act as a stronger $\sigma$-donor to Fe⁰, here the associated changes in the population of the key atomic orbitals (AOs) of the coordinating nitrogen, $\Delta N\alpha$(AO), when the X substituent changes from EDG (NMeth, $\sigma_\alpha^+ = -1.70$) to EWG (NO₂, $\sigma_\alpha^+ = +0.79$) are probed by looking at the Mulliken charges, $N\alpha$(AO), for each atomic orbital,[22] as these provide a simple electronic population analysis. This investigation was performed on the relaxed trans-geometry of the free ligands, optimised using the same basis set employed for the related iron(II) complexes. It is worth mentioning that the observed trends are fully consistent with those obtained for the cis-geometry of these ligands, which is closer to the coordination geometry but is less energetically stable (Tables S7, S9). Furthermore, it is important to note that the effects of varying X, which is para to the pyridine ring N donor atom ($N_\alpha$), are much greater on $N_\alpha$ than on the coordinating nitrogen ($N_{NP}$) of the relatively remotely attached pyrazolyl ring, and, most importantly, the latter reveals the same trend as $N_\alpha$ does with $\sigma_\alpha^>(X)$ (Figure S4, Tables S10–S11). Hence, as Deeth, Halcrow and co-workers also did,[36] it is reasonable that the following discussion focuses attention only on the effect of varying X on $N_\alpha$.

Examining the population of the individual valence orbitals on $N_\alpha$ uncovers information otherwise lost when only the overall electron density is considered, as is case when looking at the overall atomic charge ($\rho(N_\alpha)$)[30a] or at the $^{13}$N NMR chemical shift, $\delta N_\alpha$ (Figures S26 and S32).[15]

Mulliken charges were therefore calculated for each valence orbital on the $N_\alpha$ donor atom ($s$, $p_x$, $p_y$, $p_z$), as the Hammett parameter of X in the ligand was changed (EDG—EWG, Figures S27–S30). The hybridised $sp^2$ is also reported vs. $\sigma_\alpha^>(X)$ (Figure S31, with the electronic population taken as the average...
of the $s$, $p_{x}$, $p_{y}$ orbital population. In the defined framework, in which all of the Fe-pyridine moiety is contained in the $xy$ plane (Figure 8), the $p_{x}$ ligand orbital is responsible for accepting electron density from the metal in a $\pi$-backbonding interaction (M$\rightarrow$L), while the $p_{y}$ ligand orbital provides the lone-pair that enriches for the $N_{x}(p)$ in $\{\text{Fe}^{2+}(\text{bpp})_{2}\}$ and $\{\text{Fe}^{2+}(\text{bpp})_{2}\}$.

Correlations between two of the $N_{x}(\text{AOs})$, $N_{y}(p_{x})$, and $N_{y}(p_{y})$, and $\alpha_{xy}^{p}(X)$ are seen (Figure 9a). Specifically, as the para-substituent X changes EDG$\rightarrow$EWG, the associated increase in the Hammett parameter, $\alpha_{xy}^{p}(X)$, correlates extremely well ($R^{2} = 0.91$, pink line in Figure 9a) with electron depletion of the $p_{x}$ orbital $N_{y}(p_{x})$ and correlates well ($R^{2} = 0.79$, purple line in Figure 9a) with electron accumulation in the $p_{y}$ orbital $N_{y}(p_{y})$. Overall, from $\text{NMe}_{2} \rightarrow \text{NO}_{2}$, the decrease in population of the $p_{y}$ orbital is $\Delta N_{y}(p_{y}) = +0.08$ e, while the increase in the population of the $p_{x}$ orbital is more modest, $\Delta N_{y}(p_{x}) = -0.03$ e.

Therefore, whilst electronic population in $N_{y}(p_{x})$ is decreased as the X substituent becomes more EWG, making it a better acceptor for M$\rightarrow$L $\pi$ backbonding, the $N_{y}(p_{y})$ population is increased, resulting in more available electron density in the lone-pair, which facilitates stronger M$\rightarrow$L $\alpha$ bonding and with it an increase in $T_{1/2}$ - in alignment with the common interpretation from crystal field theory first principles.

For completeness, it should be noted that para-X substituent only has tiny effects on the $N_{x}(s)$ ($\Delta e < -0.002$, $\text{NMe}_{2} \rightarrow \text{NO}_{2}$) and $N_{y}(p_{x})$, $N_{y}(p_{y})$ atomic orbitals ($\Delta e < -0.004$, $\text{NMe}_{2} \rightarrow \text{NO}_{2}$), which also results in a lack of correlations with $\alpha_{xy}^{p}(X)$ ($R^{2}(\Delta N_{y}(s)) = 0.27$, Figure S27 and $R^{2}(\Delta N_{y}(p_{x})) = 0.02$, Figure S29). Combining these to form the $N_{x}(sp^{2})$ hybrid orbital, the result is a good correlation with $\alpha_{xy}^{p}(X)$ ($R^{2}(\Delta N_{x}(sp^{2})) = 0.73$, Figure S31).

As the $N_{x}(s)$ and $N_{y}(p_{x})$ atomic orbitals look almost unaffected by the electronic nature of the X substituent, it can be assumed that the $N_{y}(p_{y})$ atomic orbitals are intimately affecting each other. For EDG substituents, this behavior can be explained as arising from the enrichment of $\pi$-density ($N_{x}(p_{x})$) inducing a compensating electrostatic draining of $\alpha$-density ($N_{y}(p_{y})$), all of which directly influences the bonding properties of the coordinated $N_{x}$ atom. The opposite trend is expected for the EWG substituents.

In previous studies it was observed that $\delta N_{x}$ is intimately connected with $T_{1/2}$ and hence also with $\alpha_{xy}^{p}(X)$. Therefore,
herein possible relationships of $\delta N_A$ with the Mulliken population analysis results are probed (Figure 9b). Unsurprisingly, the results are in full agreement with the observations just reported for $N_A(\text{AOs})$ vs. $\alpha_\pi^e(\text{X})$ trends (Figure 9a). Indeed, the correlations with $N_A(p_\alpha)$ and $N_A(p_\pi)$ are even stronger when using $\delta N_A$, which has the advantages of being an easily calculated but also experimentally verifiable value for the specific ligand used, rather than using $\alpha_\pi^e(\text{X})$ for the substituent used.

An excellent correlation of increasing $\delta N_A$ with decreasing $N_A(p_\alpha)$ ($R^2 = 0.99$, pink line in Figures 9b, S36) and with increasing $N_A(p_\pi)$ ($R^2 = 0.93$, purple line in Figures 9b, Figure S34) is observed. Again no correlation is observed for $\delta N_A$ vs. $N_A(s)$ ($R^2 = 0.41$, Figure S33) or vs. $N_A(p_\sigma)$ ($R^2 = 0.0002$, Figure S35).

When combined, a very good correlation is observed for $\delta N_A$ with $N_A(s^p)$ ($R^2 = 0.93$, Figure S37). As well, very good correlations are also observed for the experimental $T_{1/2}$ vs. $N_A(p_\sigma)$ ($R^2 = 0.88$, purple line in Figures 9c and S40) and $N_A(p_\pi)$ ($R^2 = 0.75$, pink line in Figures 9c and S42). Experimental $T_{1/2}$ was also tested vs. $\rho(N_A)$ ($R^2 = 0.85$, Figure S38), $N_A(s)$ ($R^2 = 0.22$, Figure S39), $N_A(p_\sigma)$ ($R^2 = 0.03$, Figure S41), and the combined $N_A(s^p)$ ($R^2 = 0.74$, Figure S43).

Herein, the two orbital populations $N_A(p_\alpha)$ and $N_A(p_\pi)$ were also tested vs. the orbital energy terms $\Delta E_{\text{orb,orbit}}$, $\Delta E_{\text{orb,\sigma}}$, and $\Delta E_{\text{orb,\sigma+\pi}}$ (Figure 10). The $\Delta E_{\text{orb,\sigma}}$ term correlates extremely well with both $N_A(p_\pi)$ ($R^2 = 0.84$, Figure 10a) and $N_A(p_\sigma)$ ($R^2 = 0.93$, Figure 10b), revealing how the variation of occupancy in these two orthogonal orbitals contributes to the σ-donating properties of the ligand.

Not surprisingly, given the poor correlations of $\Delta E_{\text{orb,\sigma}}$ or $\Delta E_{\text{orb,\sigma+\pi}}$ with either the Hammett parameter $\alpha_\pi^e(\text{X})$ or observed $T_{1/2}$ or calculated chemical shift $\delta N_A$ (see above), poor correlations were found for $\Delta E_{\text{orb,\sigma}}$ with $N_A(p_\alpha)$ ($R^2 = 0.49$, Figure S44) or $N_A(p_\pi)$ ($R^2 = 0.36$, Figure S45), and for $\Delta E_{\text{orb,\sigma+\pi}}$ with $N_A(p_\alpha)$ ($R^2 = 0.29$, Figure S46) or $N_A(p_\pi)$ ($R^2 = 0.46$, Figure S47).

For above findings to be useful, it is critical that they are not dependent on the specific method of charge analysis employed, so the same analysis was also performed using the Loewdin framework in the atomic charge assessment (Table S8, Figures S48-S50), and this confirmed the above findings.

Comparison of these results with the literature

In their landmark 2016 paper, Halcrow, Deeth and coworkers\(^{[28,29]}\) proposed an intuitively reasonable explanation, also consistent with the calculated MO energy levels of the $[\text{Fe}^6(\text{bpp})]^{2+}$ complexes, of the effect of the $\text{para}$-$\text{X}$ substituents on the $T_{1/2}$ values in this family of SCO active complexes: that $\text{M}=\text{L}$ $\pi$-backdonation dominates in these $\text{M}$-$\text{L}$ bonds. Hence, in the quantitative EDA-NOCV analysis of the $\text{M}-\text{L}$ bond contributions performed herein, a correlation between $\Delta E_{\text{orb,\sigma}}$ and $T_{1/2}$ was expected - but was not observed ($R^2 = 0.09$, Figure S12).

However, the proposed dominance of the $\text{M}=\text{L}$ $\pi$-backdonation was based on the observation of a slope difference between the correlation lines for $\alpha_\pi^e(\text{X})$ vs. $\text{Fe}^6 < E(t_{1g}) >$ ($-0.39$) and $< E(e) >$ ($-0.32$)\(^{[27]}\). Error bars would have helped in analysing the significance of this small difference in slope. Indeed, a larger variance is expected for $\text{Fe}^6 E(t_{1g})$ than for $\text{Fe}^6 E(e)$, so what was claimed as a “greater effect on the averaged $< E(t_{1g}) >$ orbital energies than on the $< E(e) >$ orbitals” could be an overstatement. Also, in ref\(^{[28]}\) the halogen $\text{X}$ substituents (four dots: $\text{X} = \text{F, Cl, Br, I}$) had to be separately grouped from all of the other electron-withdrawing $\text{X}$ substituents. They behave differently to the other $\text{X}$ groups, specifically they have a greater effect on the $E(e)$ than on the $E(t_{1g})$ $\text{MOs}$. All of these effects are accurately reflected in the present EDA-NOCV analysis, which therefore provides a coherent and detailed picture of the relative impact of $\text{M}=\text{L}$ $\sigma$- versus $\pi$-bonding in determining the observed $T_{1/2}$, effectively refining the earlier interpretation by Halcrow, Deeth and co-workers.\(^{[29]}\) In support of this, the perfect agreement between our results and the $\Delta E(\text{HS-LS})$ vs. $\alpha_\pi^e(\text{X})$ reported in their work is revelatory.\(^{[7b]}\)

Predicting $\alpha_\pi$ and $\alpha_\pi^e$ for $\text{X} = \text{SOMe, SOeMe}$

In this study, several correlations have been identified whereby the electronic tuning by $\text{X}$ modifies the electron density over the coordinating nitrogen $N_A$, and consequently, its coordinating properties in engaging in the $\text{Fe-N}$ bond in these sixteen $[\text{Fe}^6(\text{bpp})]^{2+}$ complexes. These correlations, weight averaged by the relative $R^2$ values, can be employed to predict the Hammett constants for substituents $\text{X}$ for which they are not known. For two out of the sixteen $[\text{Fe}^6(\text{bpp})]^{2+}$ complexes, those with $\text{X} = \text{SOMe}$ and $\text{X} = \text{SOeMe}$, whilst the $\alpha_\pi^e(\text{X})$ parameter is known, the $\alpha_\pi^e(\text{X})$ parameter is not available.\(^{[28,29]}\)
Firstly, this approach was trialled for estimating the known $\sigma_p(X)$ parameters,[82] giving $\sigma_p$(SOMe)$\approx 0.31$ vs. the literature value of 0.49, and similarly, $\sigma_p$(SO$_2$Me)$\approx 0.52$ vs. the literature value of 0.72, with both predicted values lying about 0.2 units below the literature values. A general underestimation of the literature values is observed in all the explored correlations (Table S12).

Secondly, in the same way, the set of seven correlations, Equations S1–S7, identified in this study were used to predict the unknown values of $\sigma_p^*(X)$ for $X=$ SOMe and $X=$ SO$_2$Me (Table 4, Table S13), as $\approx 0.25$ and $\approx 0.54$, respectively.

Finally, we note that in future studies by us and others, consideration could be given to using parameters designed for azine (and azole) derivatives,[12] in place of the Hammett parameter which arises from consideration of benzoic acid derivatives.[9]

**Conclusion**

Inspired by the 2016 landmark study by Deeth, Halcrow and co-workers,[4] the effect of the $\text{para}$-substituent $X$ on the electronic structure of sixteen solution SCO active [Fe$^\text{II}$$(\text{bpp})_2]^\text{2+}$ complexes has been investigated in more depth herein, by quantifying the contributions to the $\text{M}$$\rightarrow$ $\text{L}$ bonds through use of EDA-NOCV analysis, and then, due to the unexpected findings from that study, a Mulliken charge analysis was also conducted.

Specifically, the EDA-NOCV results unexpectedly revealed a strong correlation between the $\sigma$-donor strength ($\Delta E_{\text{orb}}$) of the bpp$^*$ ligand in the LS $[\text{Fe}^\text{II}(\text{bpp})_2]^\text{2+}$ complex and the measured $T_{1/2}$ of the complex ($R^2 = 0.82$), but not with $\Delta E_{\text{ehyb}}$ or $\Delta E_{\text{ehyb}+\pi}$. Furthermore, $\Delta E_{\text{ehyb}}$ also correlated strongly with the $\text{15N}$ NMR chemical shift $\Delta \delta_{\text{N}}(\text{bpp})^*$ ($R^2 = 0.95$), and with $\sigma_p^*(X)$ ($R^2 = 0.88$).

These correlations, of $\Delta E_{\text{ehyb}}$ with $T_{1/2}$ vs $\sigma_p^*(X)$ and $\Delta \delta_{\text{N}}$, were further probed by analysis of the Mulliken charges for the $\text{N}$ $\text{a}$ valence orbitals. Moving from EDG to EWG $\text{para}$-substituents $X$, the analysis of the Mulliken charges showed that the electron population in the $N_j(p)$ orbital decreases (as it is delocalised in the ligand $\pi$-system towards the $X$ substituent), whilst the population in the nitrogen lone pair, $N_j(p)_l$, orthogonal to $N_j(p)$, increases. An enhancement of the $\sigma$-donation (Fe$^\text{III}$$\rightarrow$N$\text{a}$) is therefore expected, as is enhancement of the $\pi$-acceptor character (Fe$^\text{III}$$\rightarrow$N$\text{a}$). Both of these effects lead to an increase in the ligand field and hence an increase of $T_{1/2}$, as experimentally observed. The key difference from Halcrow and Deeth’s intuitive finding is that the EDA-NOCV quantitative analysis indicates that the $\sigma$-donation Fe$^\text{III}$$\rightarrow$N$\text{a}$ dominates, whereas they proposed that the $\pi$-acceptor character Fe$^\text{III}$$\rightarrow$N$\text{a}$ dominates. Indeed, a critical look at Halcrow and Deeth’s results shows a similar dependence of both $\sigma$-donation and $\pi$-acceptor for [Fe$^\text{II}$-(bpp)$_2$]$^{2+}$, depicting a picture not too different from ours.

It is also interesting to note that the EDA-NOCV findings for the [Fe$^\text{II}$-(bpp)$_2$]$^{2+}$ family studied herein (correlations only with $\Delta E_{\text{ehyb}}$ not with $\Delta E_{\text{ehyb}+\pi}$ or $\Delta E_{\text{ehyb}+\sigma}$) differ from those found for the only other SCO-active family studied to date, wherein a correlation was found only with $\Delta E_{\text{ehyb}+\sigma}$ not $\Delta E_{\text{ehyb}}$ or $\Delta E_{\text{ehyb}+\pi}$.[20] This might indicate that EDA-NOCV analysis may be sensitive to different coordination bond schemes (i.e. kinds of ligands), but the important point is the confirmation that excellent trends between EDA-NOCV parameters and $T_{1/2}$ values are found for the different Fe(II) families studied to date. Nevertheless, it must be borne in mind that to date these are the only two in depth studies of SCO-active families so it is too soon to draw conclusions from this. Rather, it is clear that further such studies are warranted.

Finally, it is also important to note that while the above EDA-NOCV analysis captures the majority of enthalpic effects, it does not account for any explicit entropic contributions. Indeed, the $T_{1/2}$ values arise from a delicate balance of very subtle effects of these two contributions, that can have drastic consequences on the SCO. Hence the future development of this approach for applications in the SCO field should also involve finding ways to evaluate if, and how, entropic contributions need to be included in the EDA-NOCV analysis when systems that are structurally very different are considered.

**Computational Details**

Calculations were performed using ORCA 4.1[172] and ADF (version 2018.106) code.[14] The ORCA code was used to optimise the structure of sixteen of the [Fe$^\text{II}$-(bpp)$_2$]$^{2+}$ complexes (in both HS and LS states); the absence of negative eigenvalues for the Hessian matrix confirmed the all computed geometries are in real minima.

Firstly, using the atomic coordinates of the sixteen LS and sixteen HS [Fe$^\text{II}$-(bpp)$_2$]$^{2+}$ complexes available from the DFT study at RI-BP86-D3(BJ)/def2-SVP/J + COSMO(acetone) level of theory in the paper by Deeth, Halcrow et al.[4] a geometry re-optimisation was performed using different RI-BP86-D3(BJ)/def2-TZVPP + CPCM level of theory,[23,120] i.e. RI$\rightarrow$ resolution of identity[56d] with a BP86

| Table 4. Predicted values of $\sigma_p^*(X)$ for the two X substituents for which this value is not reported in literature, using the correlations identified in this study with the best correlation factor, followed by the weighted average value highlighted in yellow. |
|-----------------|-----------------|-----------------|-----------------|
|                  | $\sigma_p^*(X)$ | $\sigma_p^*(X)$ | $\sigma_p^*(X)$ |
|                  | $X=$ SOMe       | $X=$ SO$_2$Me   | $\text{R}^2$    |
| LS $[\text{Fe}^\text{II}(\text{bpp})_2]^\text{2+}$ |                  |                  |                  |
| Exp.             |                  |                  |                  |
| bpp$^*$          | $\Delta E_{\text{ehyb}}$ | 0.20 | 0.65 | 0.89 |
|                  | $\Delta E_{\text{ehyb}+\pi}$ | 0.01 | 0.50 | 0.88 |
|                  | $T_{1/2}$ | 0.53 | 0.64 | 0.92 |
|                  | $\delta^+\text{N}^\text{a}$ | 0.58 | 0.62 | 0.92 |
|                  | $p(\text{N})_l$ | 0.23 | 0.66 | 0.93 |
|                  | $N_j(p)$ | 0.28 | 0.51 | 0.79 |
|                  | $N_j(p)_l$ | 0.23 | 0.62 | 0.91 |
| weight.av. ($\sigma_p^*$) | 0.25 | 0.54 | 0.91 |
functional[25,26] with D3 dispersion correction (including BJ damping)[27] def2-TZVPP basis set,[28,29] and the solvent modelled by PCM,[30,31] The same was done for the trans and cis forms of the sixteen free bpp ligands.

Secondly, the optimised structures of the complexes were used for the EDA-NOCV[32] method that combines classical EDA[33] with NOCV[34] which were performed using the ADF2019.106 program package at the BP86-D3(BJ)/TZ2P level of theory.[35,36] It should be noted that the EDA-NOCV is implemented with no possibility to include any solvation model. Finally, the fully optimised geometries of the ligands were used for the Mulliken and Loewdin analyses.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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