Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


# Supporting Information

## Exploring the Computational Design of Anionic Spin-Crossover Systems

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S1. DFT Benchmark for the $[Fe(OEt\text{-}L_1\text{-}pH)(NCS)_3]^-$ system

| ***Method*** | ***ΔE*** | ***ΔH*** | ***ΔS*** | $T_{1/2}$ |
|---|---|---|---|---|
| TPSSh | 6.94 | 5.59 | 24.67 | 226 |
| OPBE | 2.39 | 0.79 | 22.29 | 35 |
| OLYP | -9.39 | -10.89 | 21.44 | -508 |
| B3LYP | -7.83 | -9.14 | 23.78 | -384 |
| B3LYP* | -5.54 | -6.86 | 21.65 | -317 |
| M06L | -4.84 | -6.30 | 19.77 | -319 |

Table 1: Computed ΔE, ΔH, ΔS and $T_{1/2}$ for the $[Fe(OEt\text{-}L_1\text{-}pH)(NCS)_3]^-$ systems. Electronic Energies and Enthalpies in $kcal \cdot mol^{-1}$. Entropies in $cal \cdot K^{-1} \cdot mol^{-1}$ and all temperatures in K. Experimental value for $T_{1/2} = 132$ K

S2. Experimental values for different $[Fe(R_1\text{-}L_1\text{-}pR_2)(L_2)_3]^-$ reported systems.

| *System* | *Counterion* | $T_{1/2}$ | *Refcode* | *reference* |
|---|---|---|---|---|
| $[Fe(OEt\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NEt_4]^+$ | 135 | IROMOU | 1 |
| $[Fe(OEt\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[Fe(py_3C\text{-}OEt)_2]^+$ | 205 | ZANLEJ | 2 |
| $[Fe(OEt\text{-}L_1\text{-}pH)(NCBH_3)_3]^-$ | $[Fe(py_3C\text{-}OEt)_2]^+$ | 245(1), 380(2) | ZANLOT[a] | 2 |
| $[Fe(OH\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NEt_4]^+$ | 224($T^{\uparrow}$) 246($T^{\downarrow}$) | XOPDAJ | 3 |
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NBu_4]^+$ | 330 | IHEKEN | 4 |
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[PPh_4]^+$ | 290 | UXOHEW | 5 |
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NMe_4]^+$ | 313.4 | - | 6 |
| $[Fe(Et\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NMe_4]^+$ | 338.2 | - | 6 |
| $[Fe(nPr\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NMe_4]^+$ | 298.4 | VULHES | 6 |
| $[Fe(nBu\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NMe_4]^+$ | 315.4 | KUYFES | 6 |
| $[Fe(Py\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[Fe(py_4C)_2]^+$ | 161 | GECHED | 7 |
| $[Fe(nR\text{-}L_1\text{-}pH)(NCS)_3]^-$ | $[NMe_4]^+$ | 185.6 | RIDGUJ | 8 |

[a] = two-step transition
$py_3C$-OEt = tris(2-pyridyl)ethoxymethane
$py_4C$ = tetrakis(2-pyridyl)methane
nR = nonadecane

References:


1 E. Cuza, C. D. Mekuimemba, N. Cosquer, F. Conan, S. Pillet, G. Chastanet and S. Triki, *Inorg. Chem.*, 2021, **60**, 6536–6549.
2 E. Cuza, S. Benmansour, N. Cosquer, F. Conan, S. Pillet, C. J. Gómez-García and S. Triki, *Magnetochemistry*, 2020, **6**, 26.
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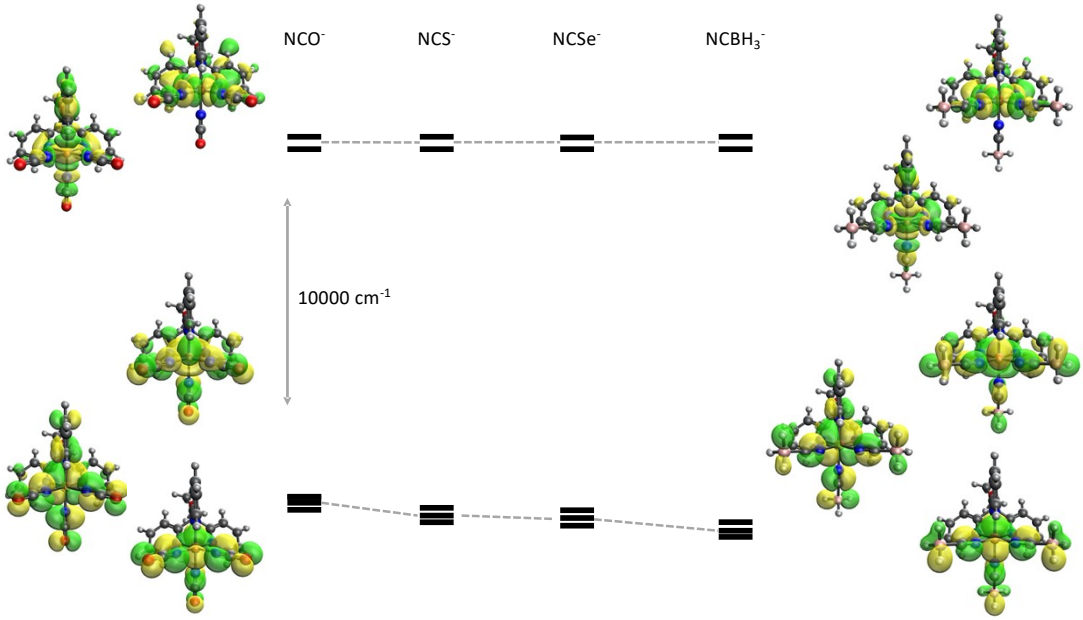
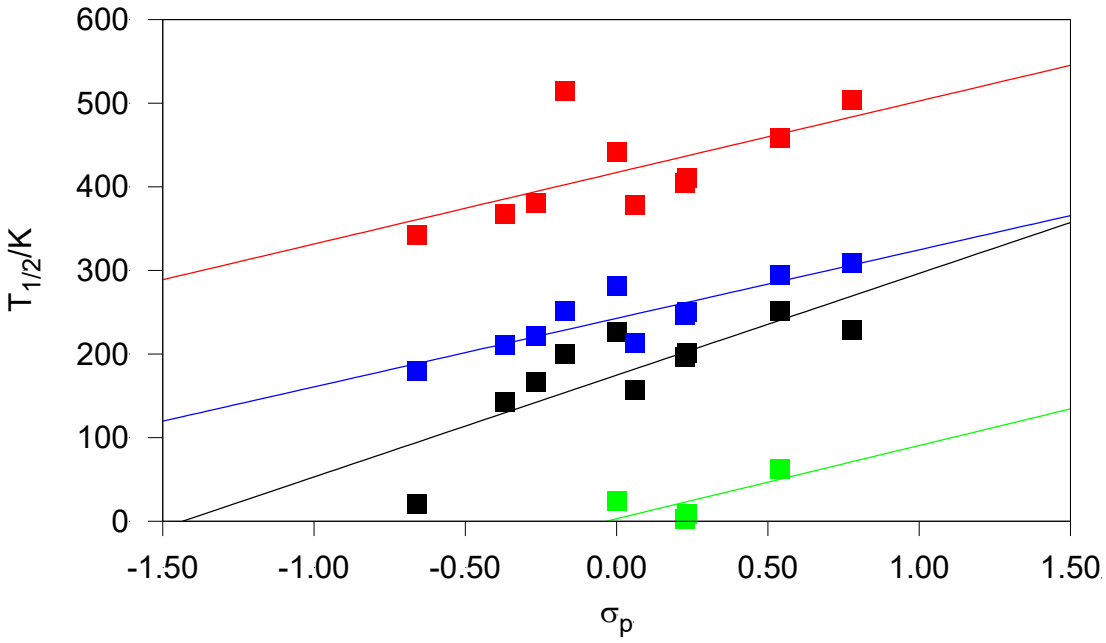
S3. Schematic d-based Molecular Orbital Diagrams for the $[Fe(OEt\text{-}L_1\text{-}pH)(L_2)_3]^-$ systems ($L_2$ = $NCO^-$, $NCS^-$, $NCSe^-$ and $NCBH_3^-$). Bottom table, energies (in $cm^{-1}$) of the five d-based MOs upon the AILFT interpretation of the NEVPT2 calculation on the S=0 optimized geometry.




| $NCO^-$ | $NCS^-$ | $NCSe^-$ | $NCBH_3^-$ |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 259.1 | 307.9 | 315.6 | 307 |
| 544.8 | 599.9 | 610.3 | 618 |
| 17199.5 | 17717.7 | 17827.2 | 18255.8 |
| 17858.2 | 18390.2 | 18513.9 | 18950.1 |

S4. Computed $T_{1/2}$ vs. the $\sigma_p$ Hammett parameter for the $[Fe(OEt\text{-}L_1\text{-}pR_2)(L_2)_3]^-$ systems. $L_2$ are in green ($NCO^-$), black ($NCS^-$), blue ($NCSe^-$) and red ($NCBH_3^-$), and $R_2$ = -$NH_2$, -OH, -OMe, -Me, -F, -H, -Cl, -Br, -$CF_3$ and -$NO_2$.




The corresponding $R^2$ values are 0.75, 0.64, 0.76 and 0.40respectively for $NCO^-$, $NCS^-$, $NCSe^-$ and $NCBH_3^-$.

S5. Computed ΔE and $T_{1/2}$ for the $[Fe(OEt\text{-}L_1\text{-}pR_2)(NCO)_3]^-$ systems. All energies in kcal·mol$^{-1}$ and all temperatures in K.

| $[Fe(OEt\text{-}L_1\text{-}pR_2)(NCX)_3]^-$ | ***NCO*$^-$** | |
|---|---|---|
| | ***ΔE*** | ***$T_{1/2}$*** |
| $R_2$ = OH | 0.25 | -38 |
| $R_2$ = OMe | -5.07 | -307 |
| $R_2$ = Me | 1.20 | -2 |
| $R_2$ = H | 1.73 | 24 |
| $R_2$ = Cl | 1.33 | 3 |
| $R_2$ = Br | 1.48 | 9 |
| $R_2$ = $CF_3$ | 2.64 | 62 |

**S6**. A data set collection of computational results is available in the ioChem-BD repository[1] and can be accessed via https://doi.org/10.19061/iochem-bd-6-152

[1] Álvarez-Moreno, M.; de Graaf, C.; Lopez, N.; Maseras, F.; Poblet, J.M.; Bo, C. J. Chem. Inf. Model. 2015, 55, 95,103.

**S7.** Counterion effect control calculations

The effect of adding counterions to the studied systems was calibrated doing two sets of control calculations.

First, we studied if adding different counterions had a significant impact on the spin-state energy gaps. This was done by computing the $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3][C]$ where C could be $[NMe_4]^+$, $[NEt_4]^+$ or $[PPh_4]^+$. Results are summarized below:

| *System* | *Refcode* | *Counterion* | *ΔE* | *ΔE(BSSE)* | *ΔH* | *ΔS* | $T_{1/2}$ |
|---|---|---|---|---|---|---|---|
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | | - | 10.48 | 10.48 | 9.15 | 23.50 | 389 |
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | IHEKEN | $[NBu_4]^+$ | 12.55 | 11.71 | 11.29 | 21.075 | 536 |
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | UXOHEW | $[PPh_4]^+$ | 12.37 | 11.46 | 11.04 | 24.136 | 458 |
| $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ | VULHES | $[NMe_4]^+$ | 12.83 | 12.63 | 11.49 | 21.361 | 538 |

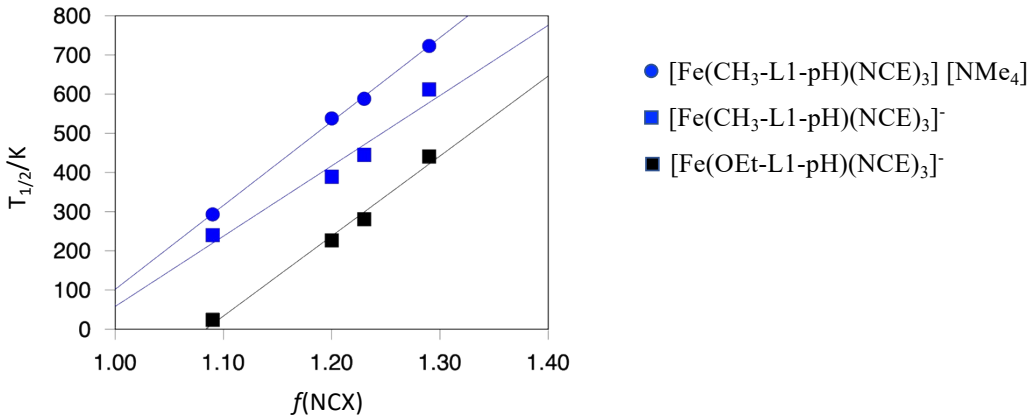
Computed spin-state energy gap (ΔE), enthalpy (ΔH), entropy (ΔS) and estimated $T_{1/2}$ for the $[Fe(CH_3\text{-}L_1\text{-}pH)(NCS)_3]^-$ molecule, without and with different counterions. Energy and enthalpy in kcal/mol, entropy in $cal\cdot K^{-1}\cdot mol^{-1}$, and temperatures in K

As can be seen, once the spin-state energy gap is corrected for the basis set superposition error (BSSE), the spin-state energy gap changes very little, and the computed values are also quite close to the spin-state energy gap without counterion. Remarkably, the calculations can model the decrease in $T_{1/2}$ when the counterion is $[PPh_4]^+$, as observed experimentally (see table S2).

The second test was done by computing the whole series of $[Fe(CH_3\text{-}L1\text{-}pH)(NCE)_3]$- (E = O, S, Se or $BH_3$) with and without counterions, and comparing this results with the ones computed for the $[Fe(OEt\text{-}L1\text{-}pH)(NCE)_3]$- system. Results are provide in the table below.

| *NCE* | *f* | $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3][NMe_4]$ | $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3]^-$ | $[Fe(OEt\text{-}L_1\text{-}pH)(NCE)_3]^-$ |
|---|---|---|---|---|
| $NCS^-$ | 1.2 | 538 | 389 | 226 |
| $NCSe^-$ | 1.23 | 588 | 445 | 281 |
| $NCBH_3^-$ | 1.29 | 723 | 612 | 441 |
| $NCO^-$ | 1.09 | 293 | 240 | 24 |

*f* factors and computed transition temperatures for the $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3][NMe_4]$, $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3]$- and $[Fe(OEt\text{-}L_1\text{-}pH)(NCE)_3]$- (E = S, Se, O, $BH_3$) systems.




Correlation between the computed $T_{1/2}$ and the *f* factor for the $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3][NMe_4]$ (blue circle), $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3]^-$ (blue square) and $[Fe(CH_3\text{-}L_1\text{-}pH)(NCE)_3]^-$ (black square) (E = O, S, Se and $BH_3$).

As can be seen in the above figure, the effect of adding counterions does not alter the trends, and is inferior to the one produced by changing $R_1$ = -$CH_3$ to $R_1$ = -OEt.

From this results, one can see firstly that the reported trends do not change upon inclusion of the counterion. Secondly, the main driving effect is replacing the $R_2$ group from -OEt to -$CH_3$, thus proving one more time that the electronically driven effects are properly captured by the reported methodology.