CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Metal Controlled Anion Binding Tendencies of the Thiourea Unit of Thiosemicarbazones

Valeria Amendola,[a] Massimo Boiocchi,[b] Luigi Fabbrizzi,*[a] and Lorenzo Mosca[a]

[a] *Dr. Valeria Amendola, Prof. Luigi Fabbrizzi, Dr. Lorenzo Mosca*
Dipartimento di Chimica Generale
Università di Pavia
via Taramelli 12, 27100 Pavia, Italy

[b] *Dr. Massimo Boiocchi*
Centro Grandi Strumenti
Università di Pavia
via Bassi, 27100 Pavia, Italy

SUPPORTING INFORMATION

Information on crystallographic data: CCDC 685928 and 685929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

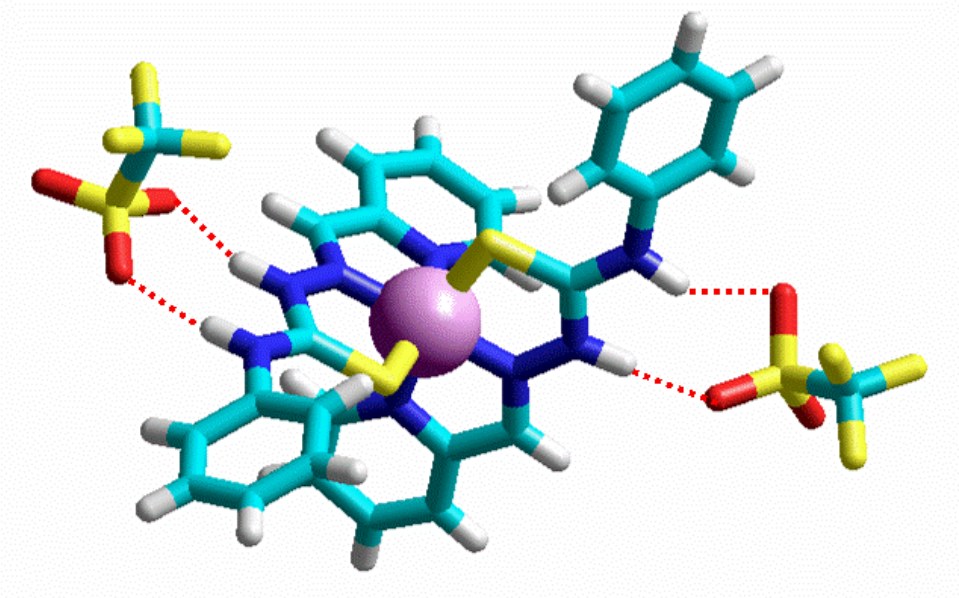

Figure S1. Bifurcate hydrogen bonding interactions between triflate ions and the thiourea subunits of the crystalline complex salt $[Fe^{II}(\mathbf{3})_2](CF_3SO_3)_2 \cdot H_2O$. The water molecule has been omitted in the Figure.

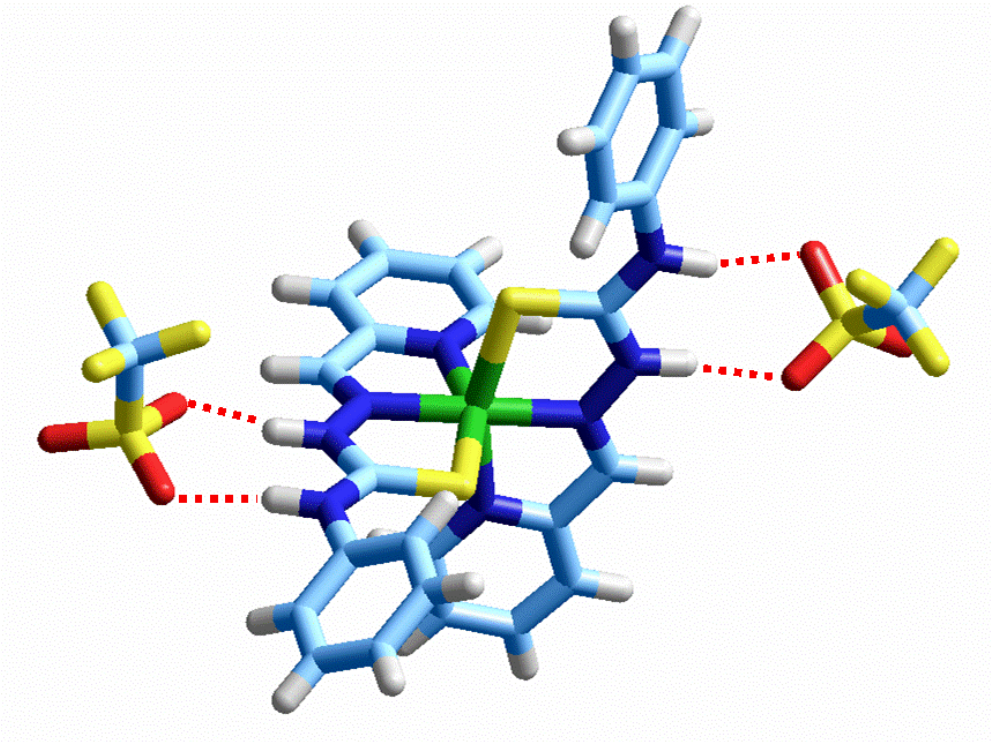

Figure S2. Bifurcate hydrogen bonding interactions between triflate ions and the thiourea subunits of the crystalline complex salt $[Ni^{II}(\mathbf{3})_2](CF_3SO_3)_2 \cdot MeCN$. The MeCNr molecule has been omitted in the Figure.

Figure S3. Colours of $CHCl_3$ solution 5×10^{-5} M of $[Fe^{II}(LH)_2]^{2+}$ complex after the addition of 0, 1, 2 equiv. of Proton Sponge® , **13** (from left); LH = **3**.

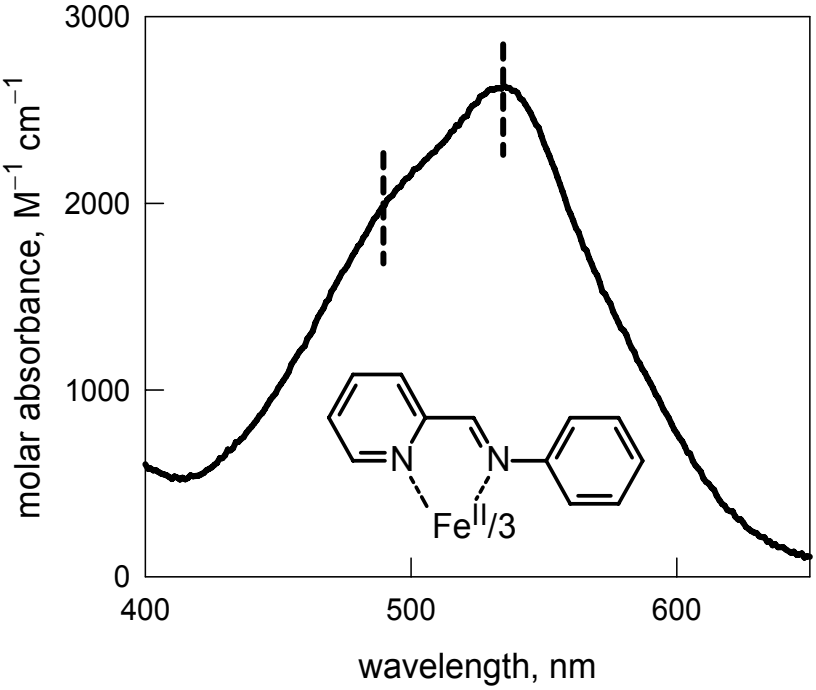

Figure S4. MLCT spectrum of the 1:3 complex of Fe^{II} with N-phenyl-pyridine-2-yleneamine. MeCN solution 1.13×10^{-4} M in the complex.

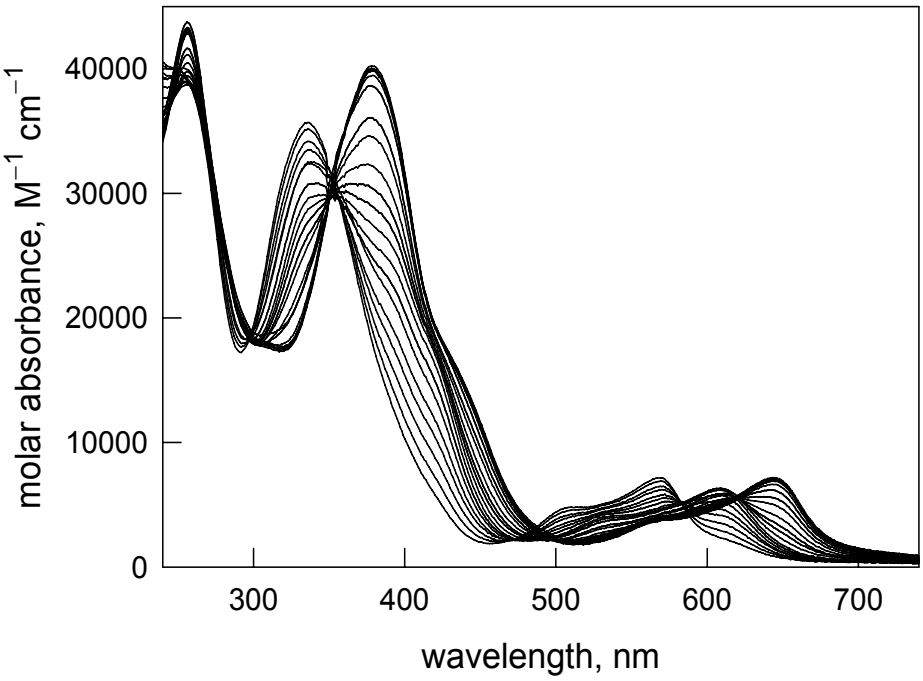

Figure S5. Spectra obtained over the course of the titration of a 1.01×10^{-4} M solution of $[Fe^{II}(\mathbf{3})_2]^{2+}$ in $CHCl_3$ with a solution of $[Bu_4N]NO_2$ in $CHCl_3$ (LH = **3**).

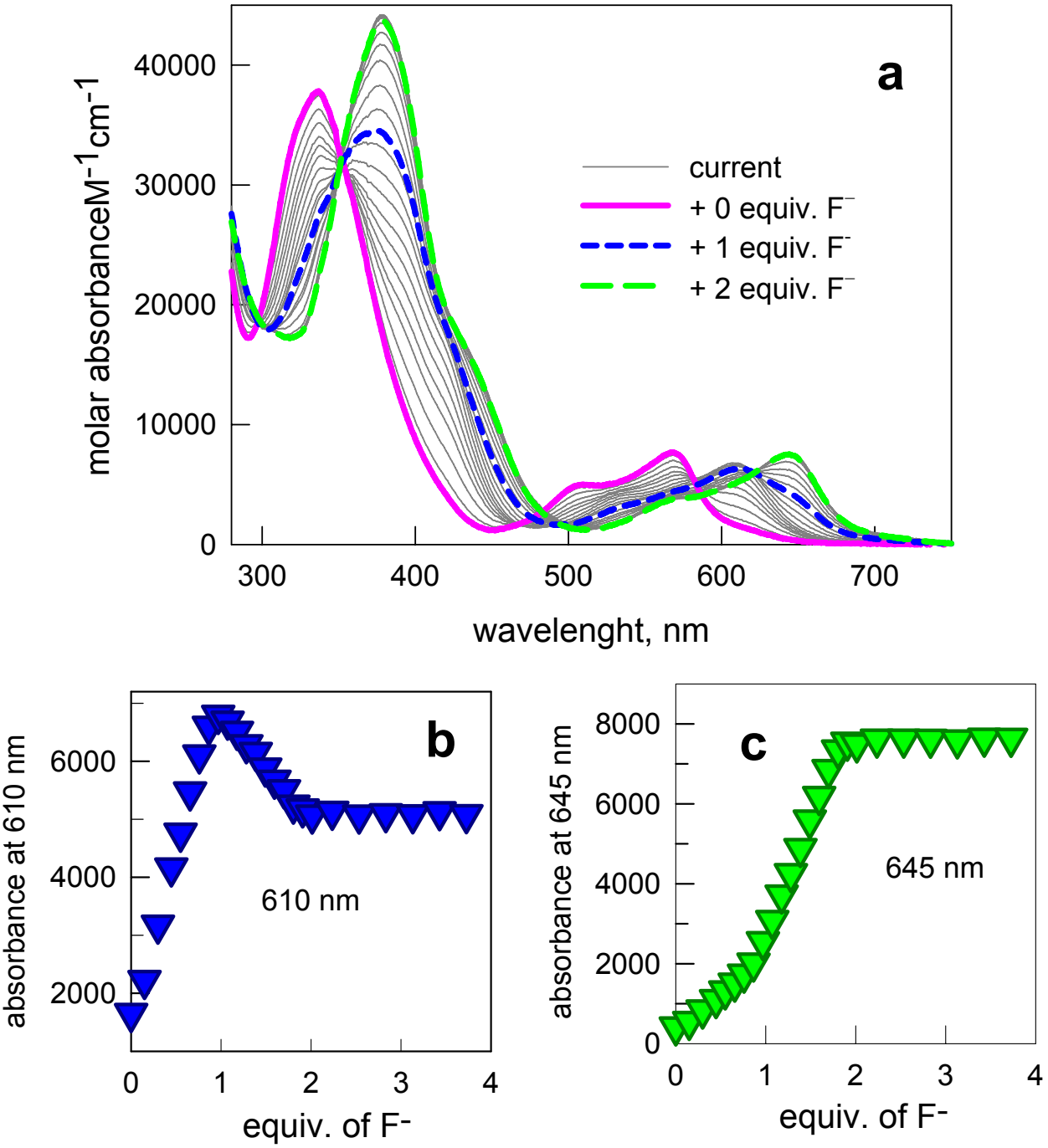

Figure S6. (a) Spectra obtained over the course of the titration of a 1.06×10^{-4} M solution of $[Fe^{II}(\mathbf{3})_2]^{2+}$ in $CHCl_3$ with a solution 1.58×10-2 M $[Bu_4N]F{\cdot}3H_2O$ in $CHCl_3$ (LH = **3**); (b) titration profile on the lower energy MLCT band, corresponding to the $[Fe^{II}(LH)(L)]^{+}$ species; (c) titration profile on the lower energy MLCT band, corresponding to the $[Fe^{II}(L)_2]$ species.

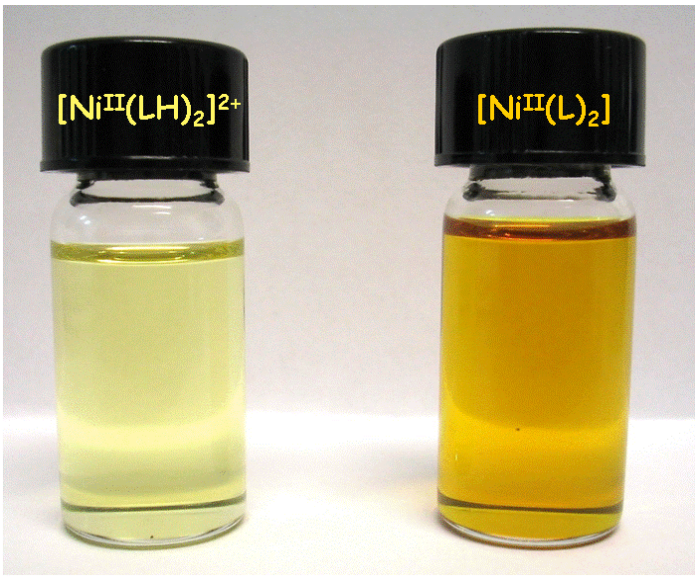

Figure S7. Colours of a $CHCl_3$ solution 5×10^{-5} M of $[Ni^{II}(LH)_2]^{2+}$ complex before (left) and after (right) the addition 2 equiv. of Proton Sponge®; LH = **3**.

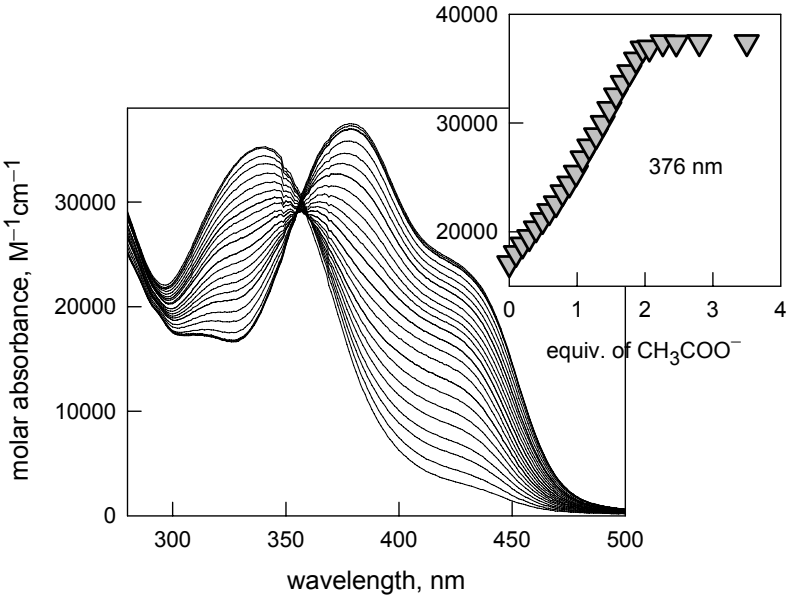

Figure S8. (a) spectra obtained over the course of the titration of a 1.22×10^{-4} M solution of $[Ni^{II}(LH)_2]^{2+}$ in $CHCl_3$ with a solution 1.20×10^{-2} M of $[Bu_4N]CH_3COO$ in $CHCl_3$ (LH = **3**); inset: titration profile at 376 nm.

Table S1. Selected bond lengths (Å) and bond angles (°) around the metal center (Me) in the Fe^{II} and Ni^{II} molecular complexes of **3**. δ is the difference of corresponding bond distances in the Ni^{II} and Fe^{II} complexes.

	$[Fe^{II}(\mathbf{3})_2](CF_3SO_3)_2 \cdot H_2O$	$[Ni^{II}(\mathbf{3})_2](CF_3SO_3)_2 \cdot MeCN$	δ
Me–N(1)	1.896(21)	2.005(3) 0.11	0.11
Me–N(2)	1.971(22)	2.105(3) 0.14	0.14
Me–N(5)	1.878(19)	2.007(2) 0.13	0.13
Me–N(6)	1.974(21)	2.119(3) 0.15	0.15
Me–S(1)	2.283(8)	2.402(1) 0.12	0.12
Me–S(2)	2.301(7)	2.431(1) 0.13	0.13
N(1)–Me–N(2)	80.6(10)	78.1(1)	
N(1)–Me–N(6)	97.7(9)	97.2(1)	
N(1)-Me-S(1)	84.8(8)	82.3(1)	
N(1)-Me-S(2)	96.8(7)	102.9(1)	
N(2)-Me-N(5)	97.4(9)	99.2(1)	
N(2)-Me-N(6)	90.0(9)	89.2(1)	
N(2)-Me-S(2)	91.1(6)	91.7(1)	
N(5)-Me-N(6)	80.7(9)	78.3(1)	
N(5)-Me-S(1)	97.2(6)	100.2(1)	
N(5)-Me-S(2)	84.8(6)	81.5(1)	
N(6)-Me-S(1)	90.6(7)	92.3(1)	
S(1)-Me-S(2)	91.9(3)	93.7(1)	