Supporting Information

In air a spin crossover active iron(II) complex of amine/$NCBH_3^-$ ligands is converted to a low spin complex of imine/CN^- ligands

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Synthesis of [$NiL_1(NCBH_3)_2$]. To a solution of L_1 (L_1 = N,N'-bis(2-pyridylmethyl)-1,2-ethanediamine, 0.024g, 0.1mmol) in a mixed solution of MeOH (10 mL) and MeCN (5 mL) was added $NiCl_2 \cdot 6H_2O$ (0.024 g, 0.1 mmol) and $NaNCBH_3$ (0.013g, 0.2mmol) in the air. The resulting reaction mixture was stirred for 1 h in air and then left for evaporation. Flake lavender crystals of $NiL_1(NCBH_3)_2$ were obtained after one week in 75% yield (0.029 g). Elemental analysis, Calcd: C, 50.48; H, 6.35; N, 22.07. Found: C, 50.71; H, 6.43; N, 21.78.

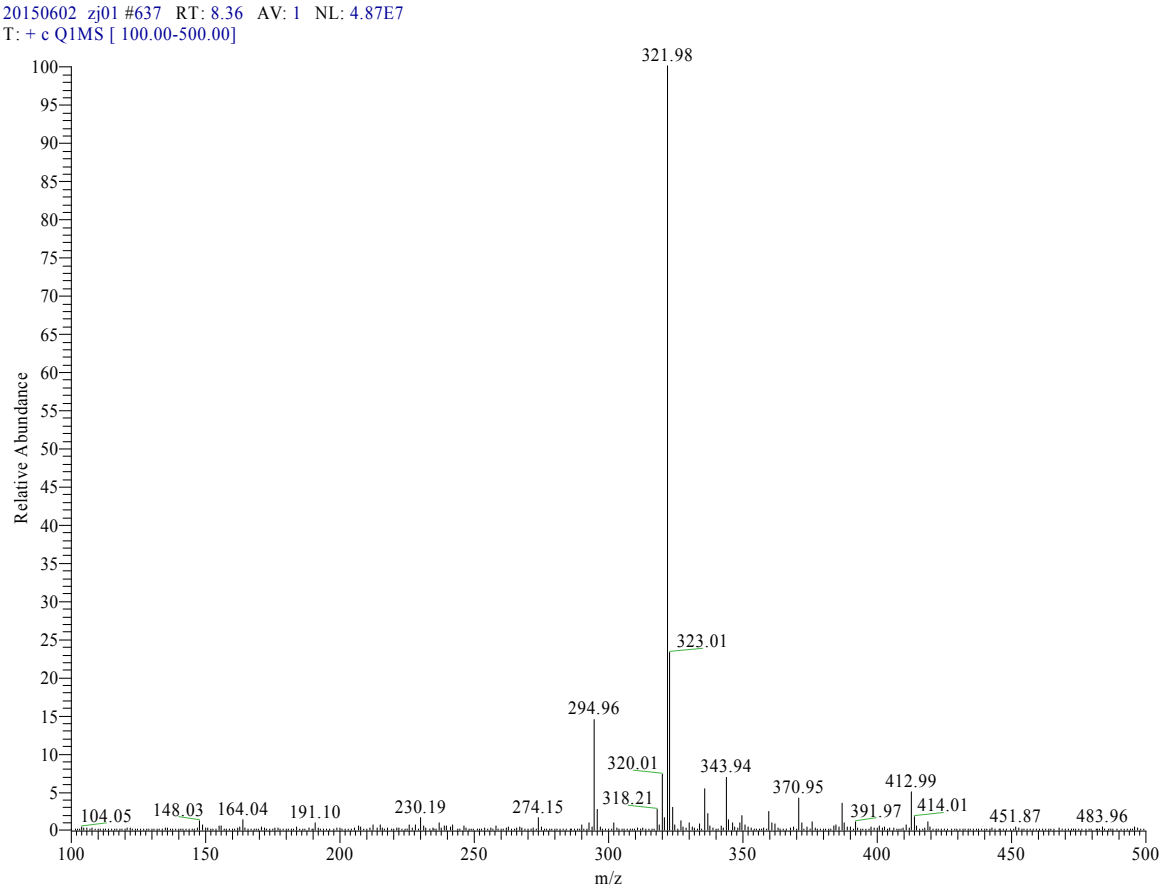

Figure S1. ESI-MS spectrum for complex **2**. The intense peak at *m/z* 321.98 corresponds to $[FeL_2(CN)]^+$ (calc.: 322.09).

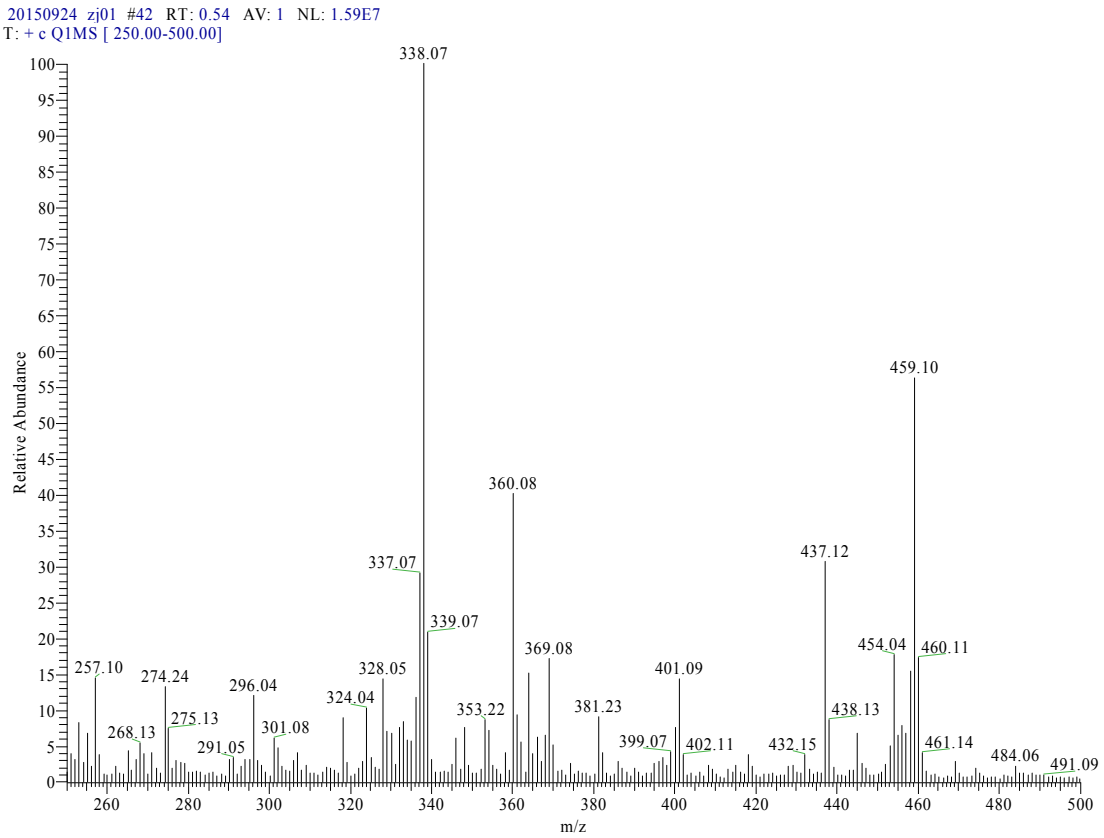

Figure S2. ESI-MS spectrum taken immediately after mixing the reactants. The strongest peak at *m*/*z* 338.07 corresponds to $[FeL_1(NCBH_3)]^+$ (calc.: 338.12) and a very weak peak at 324.04 corresponding to $[FeL_1(CN)]^+$ (calc.: 324.09).

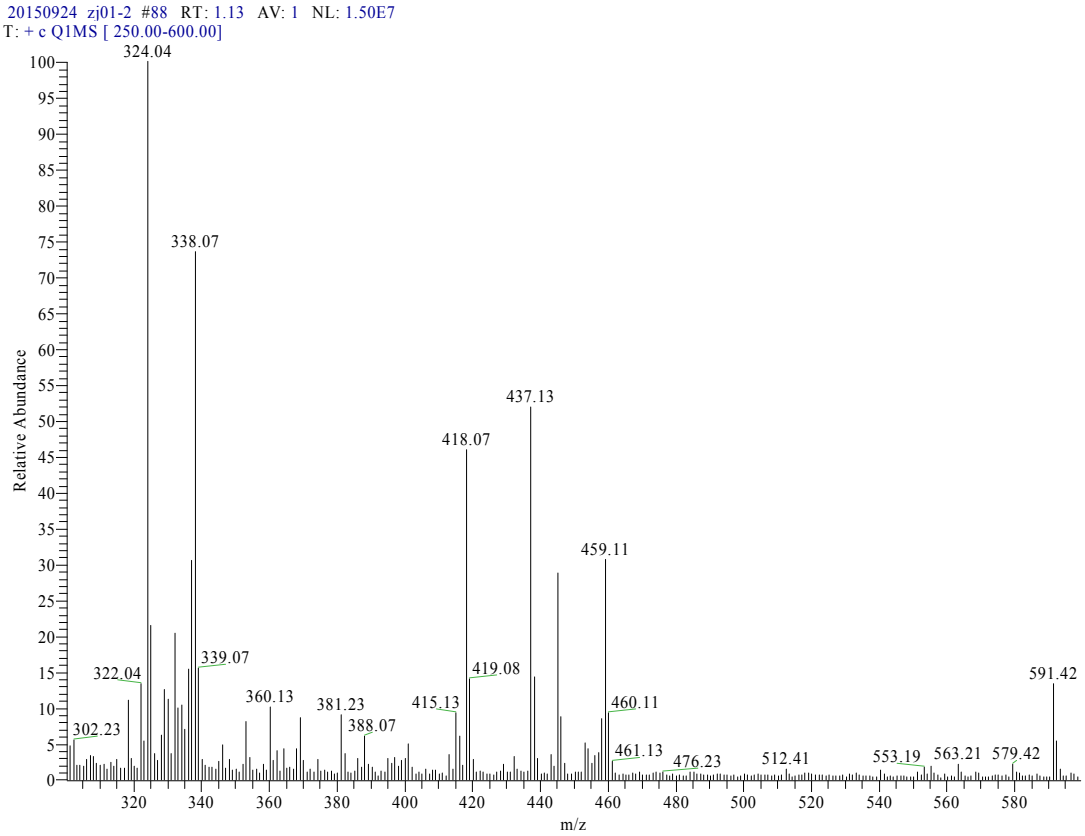

Figure S3. ESI-MS spectrum taken 5 minutes later after mixing the reactants. The peak of $[FeL_1(CN)]^+$ at 324.04 (calc.: 324.09) became the strongest and a weak peak at 322.04 corresponding to $[FeL_2(CN)]^+$ (calc.: 322.09) was observed .

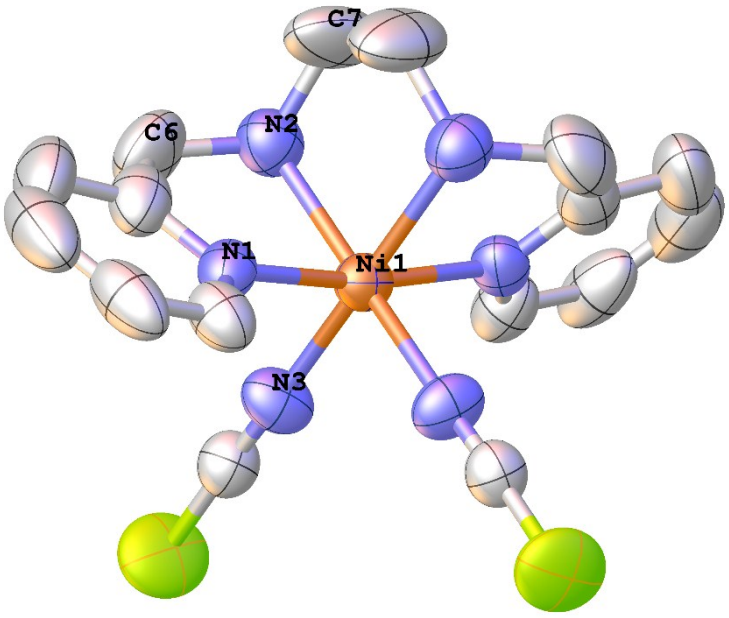

Figure S4. View of the molecular structures of $[NiL_1(NCBH_3)_2]$. Color code: C, gray; Ni, orange; B, green; N, blue. H atoms are omitted for clarity.

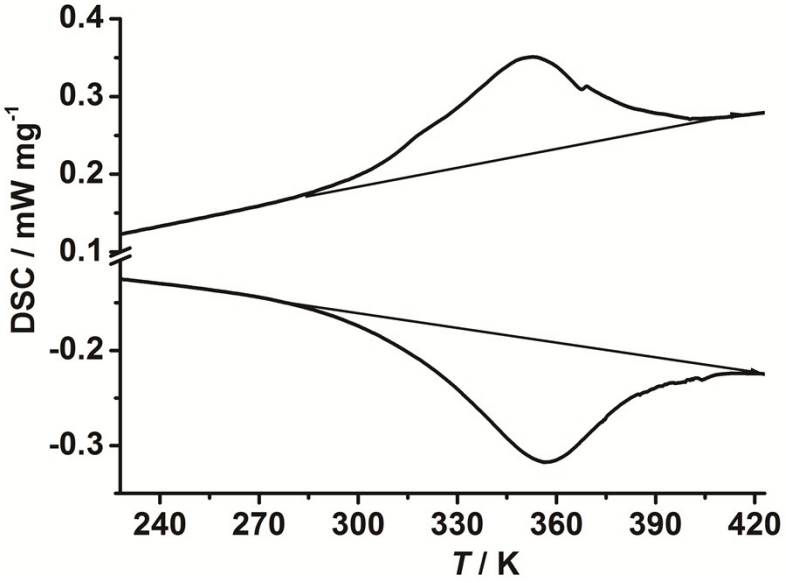

Figure S5. DSC curve of **1** showing the baseline to obtain Δ*H*.

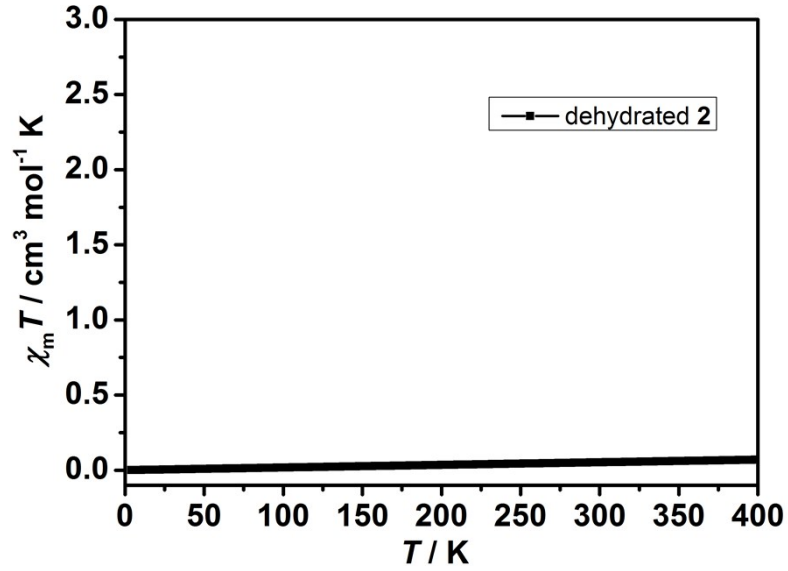

Figure S6. Variable-temperature magnetic susceptibility studies of dehydrated **2**. Data recorded in both cooling and heating modes at a scan rate of 2 K min^{-1}.

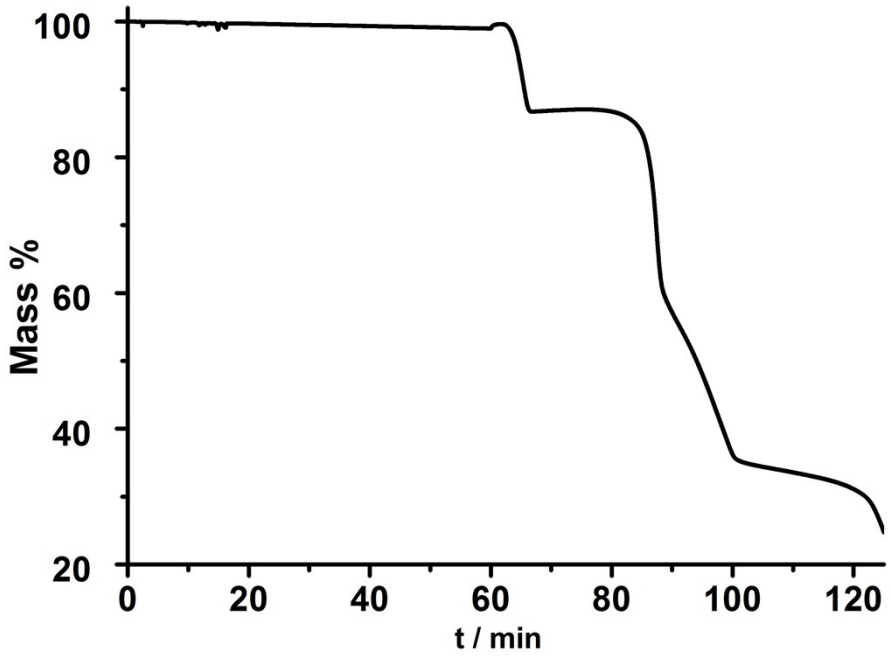

Figure S7. Time dependent TG curve for **2**. In the first 60 minutes the sample was kept at 30 °C and no weight loss was observed at this temperature.

Table S1. ^{57}Fe Mössbauer parameters of **1** at different temperatures.

T (K)	Component	$\delta \pm 0.01$ (mm/s)	$\Delta E_Q \pm 0.01$ (mm/s)	RA ± 1(%)	Assignment
80	Singlet	0.46	-----	100	LS Fe^{II}
500	Singlet	0.42	-----	5	LS Fe^{II}
	Doublet	1.35	1.92	95	HS Fe^{II}

Table S2. Unit cell and selected refinement parameters for **$NiL_1(NCBH_3)_2$**.

	$NiL_1(NCBH_3)_2$
Temperature / K	298
Empirical formula	$C_{64}H_{96}B_8N_{24}Ni_4$
Formula weight / g mol^{-1}	1522.96
Crystal system	Orthorhombic

Space group	*C*2*cb*
***a* / Å**	9.216(3)
***b* / Å**	15.403(5)
***c* / Å**	14.342(5)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	2035.9(11)
Z	1
ρ_{calc} / mg mm^{-3}	1.242
μ / mm^{-1}	0.964
***F*(000)**	800
Reflections collected	5662
Independent reflections	1840 R_{int} = 0.0595,
Goodness-of-fit on F^2	1.05
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0365 wR_2 = 0.0580
Final *R* indexes [all data]	R_1 = 0.0784 wR_2 = 0.0657
Largest diff. peak/hole / e Å^{-3}	0.26/-0.28
Flack parameter	0.03(2)

Table S3**.** Selected bond lengths and angles for **$NiL_1(NCBH_3)_2$**.

	$NiL_1(NCBH_3)_2$
Temperature / K	298
Ni−N_{NCBH3} / Å	2.037(6)
Ni−N_{py} / Å	2.093(4)
Ni−N_{amine} / Å	2.112(6)
Ni-$N_{average}$ / Å	2.08
N2-C6 / Å	1.463(11)
***cis* N−Ni−N / °**	80.0(2)-93.7(2)
***trans* N−Ni−N / °**	170.6(3) -171.9(3)
Σ_{Ni} / °	52.9