Mononuclear Fe^{II} and Heterobinuclear $Fe^{II}Ni^{II}$ Thiolate Complexes Derived from a Compartmental Hexaazadithiophenolato Ligand: Synthesis, Structure and Properties

Vanessa Stephan,[a] Christian Zocher,[a] Martin Börner,[a] Jennifer Klose,[a] Daniel Fuhrmann,[a] and Berthold Kersting[a]

[a] *Institut für Anorganische Chemie und Kristallographie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany, E-mail: b.kersting@uni-leipzig.de Fax: +49(0)341-97-36199.*

Supporting Information

Content

1) Mass spectrometric results of mixed-metal product 3 and of redistribution experiments

The amount of by-product during synthesis of the hetero-binuclear $Fe^{II}Ni^{II}$ complex **3** was established according to the isotope pattern of mass spectra under the application of a system of linear equations. For referencing, the signals with *m/z* 839.35 (equation (I)), 841.35 (equation (II)) and 843.35 (equation (III)) were applied. Thus, x corresponds to the amount of complex **3**, y to complex **4** and z to complex **5**. The isotope pattern of the desired complex, **3**, and the respective homo-binuclear by-products, Fe_2 **4** and Ni_2 **5**, were simulated by MestReNova v. 11.0.2 (Figure S 1). The measured mass spectra of the product **3** using either the Fe^{II} or Ni^{II} complex as precursor are illustrated in Figure S 2. Accordingly, a summary of the calculated ratio of the desired complex to by-products is given in Table S 1.

$$(I) \quad 6.14\,x + 100.00\,y + 0\,z$$
$$(II) \quad 100.00\,x + 23.14\,y + 0\,z$$
$$(III) \quad 59.38\,x + 1.89\,y + 100.00\,z$$

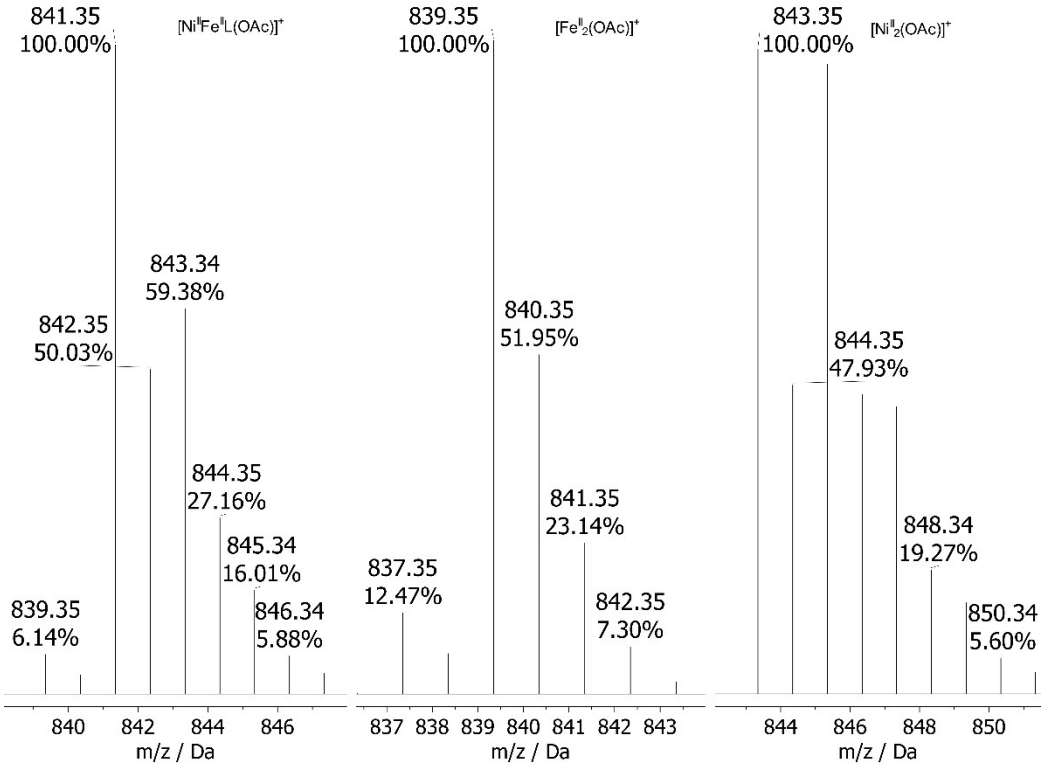

Figure S 1. Simulated isotope patterns of the respective complexes **3**, **4** and **5** generated by MestReNova.

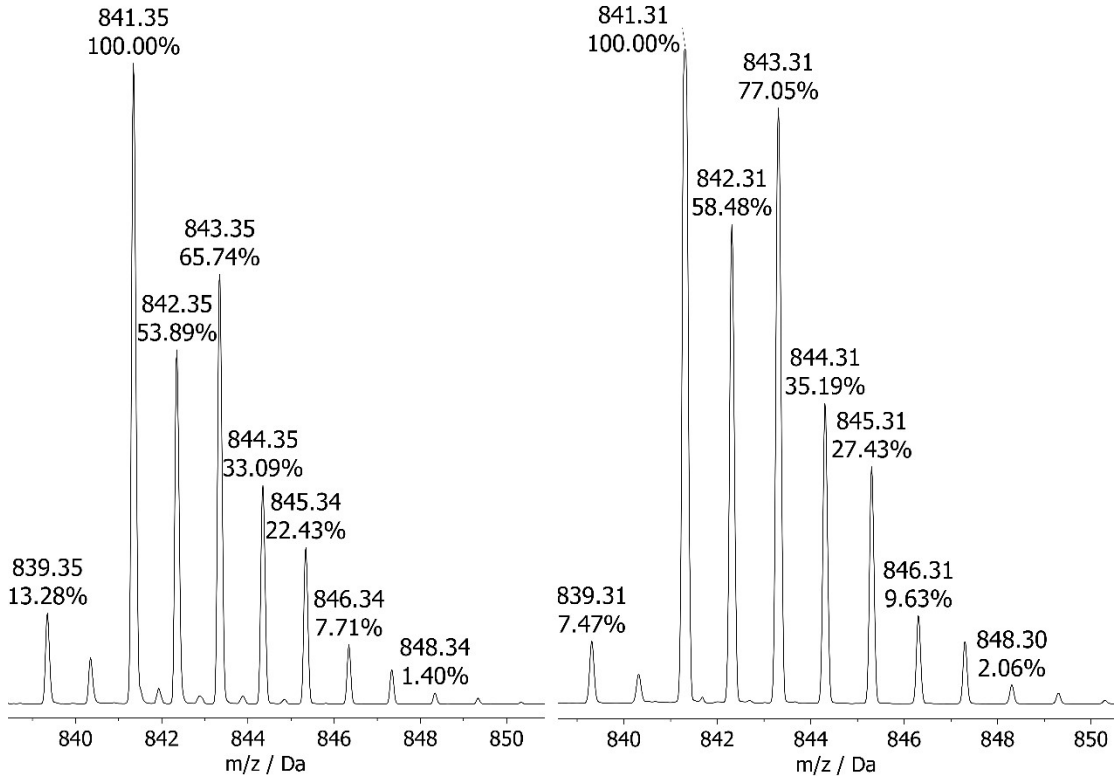

Figure S 2. Measured isotope pattern of the product signal of complex **3** utilizing the Fe^{II} complex **1** (left) and Ni^{II} complex **2** (right) as starting material.

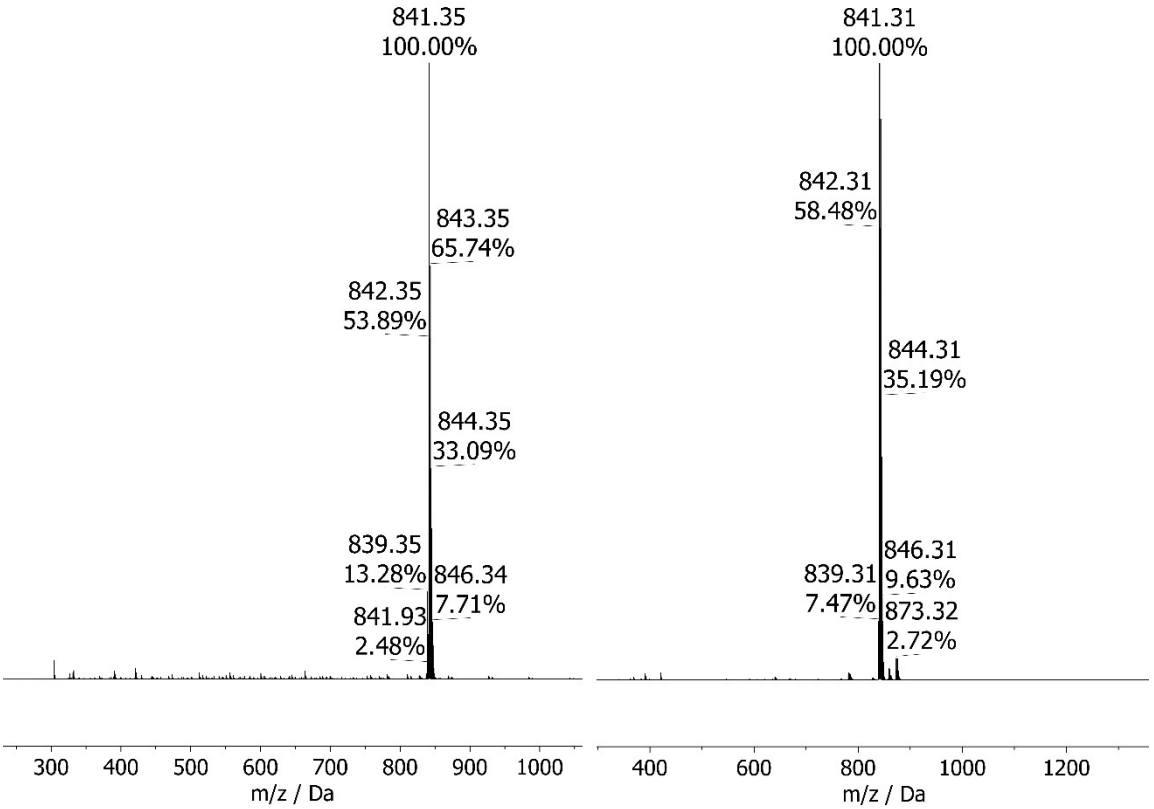

Figure S 3. Full MS spectra of complex **3** utilizing the Fe^{II} complex **1** (left) and Ni^{II} complex **2** (right) as starting material.

Table S 1. Summary of calculated ratio of complex **3**:**4**:**5** based on using the Fe^{II} complex or the Ni^{II} complex as starting material.

Precursor	Ratio **3**:**4**:**5**	Amount of complex **3** / %	Yield / %
$[Fe(H_2L)]^{2+}$	14:1:1	87.5	42
$[Ni(H_2L)]^{2+}$	75:1:13	84.3	80

For a redistribution experiment. a 1:1 mixture of genuine samples of the homobinuclear complexes **4** and **5** was left to stir in MeOH/MeCN (1:1) for several days at room temperature. Similarly, a solution of complex **3** was stirred for several days. The outcome of the experiment was evaluated based on mass spectrometric data. No changes in the stoichiometric composition could be detected in case of both approaches.

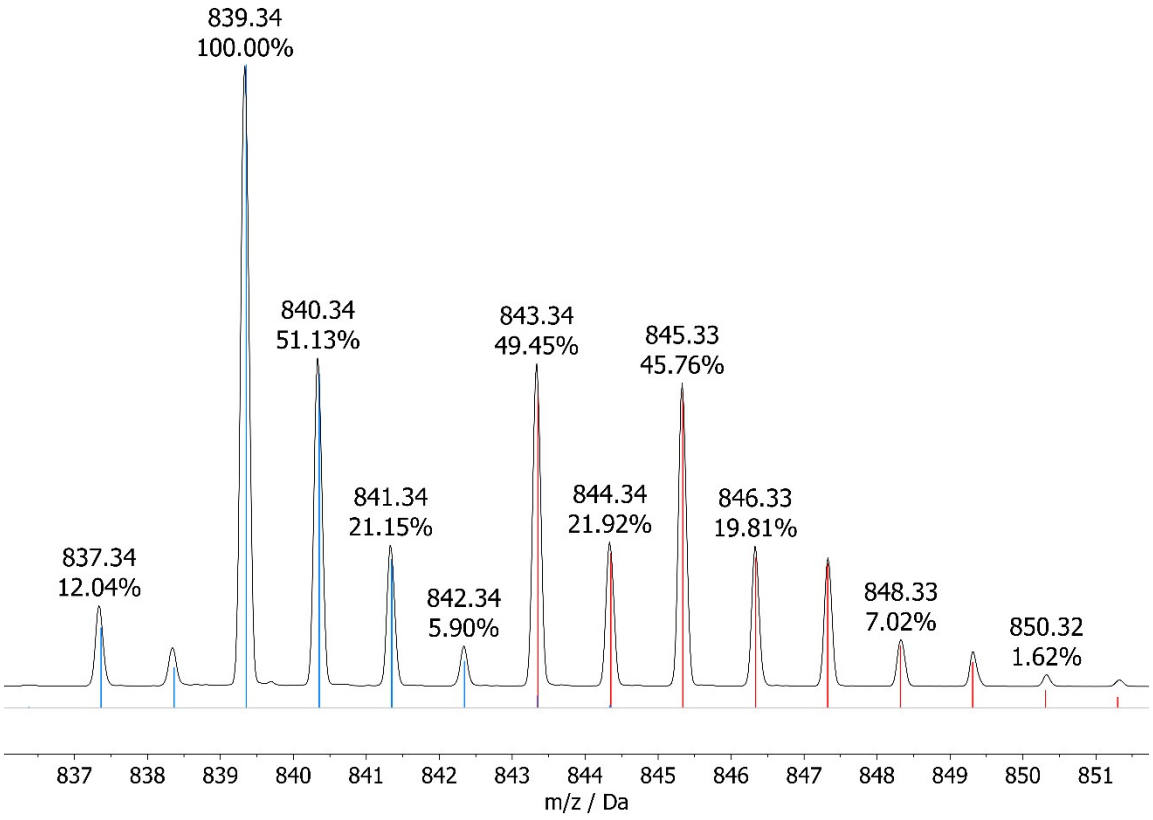

Figure S 4. Mass spectrum of the redistribution reaction with complex **4** and **5**; predicted isotope patterns in blue and red. respectively.

2) Spectroscopic characterization of complexes 1 and 3

A UV-vis-NIR spectrum of complex **1** was measured in MeCN (c = 10^{-3} M, 295 K) in N_2 atmosphere and with exposure to air after 16 h and 3 d. Spectral changes in the vis-NIR region occur due to oxidation of Fe^{II} to Fe^{III} in solution.

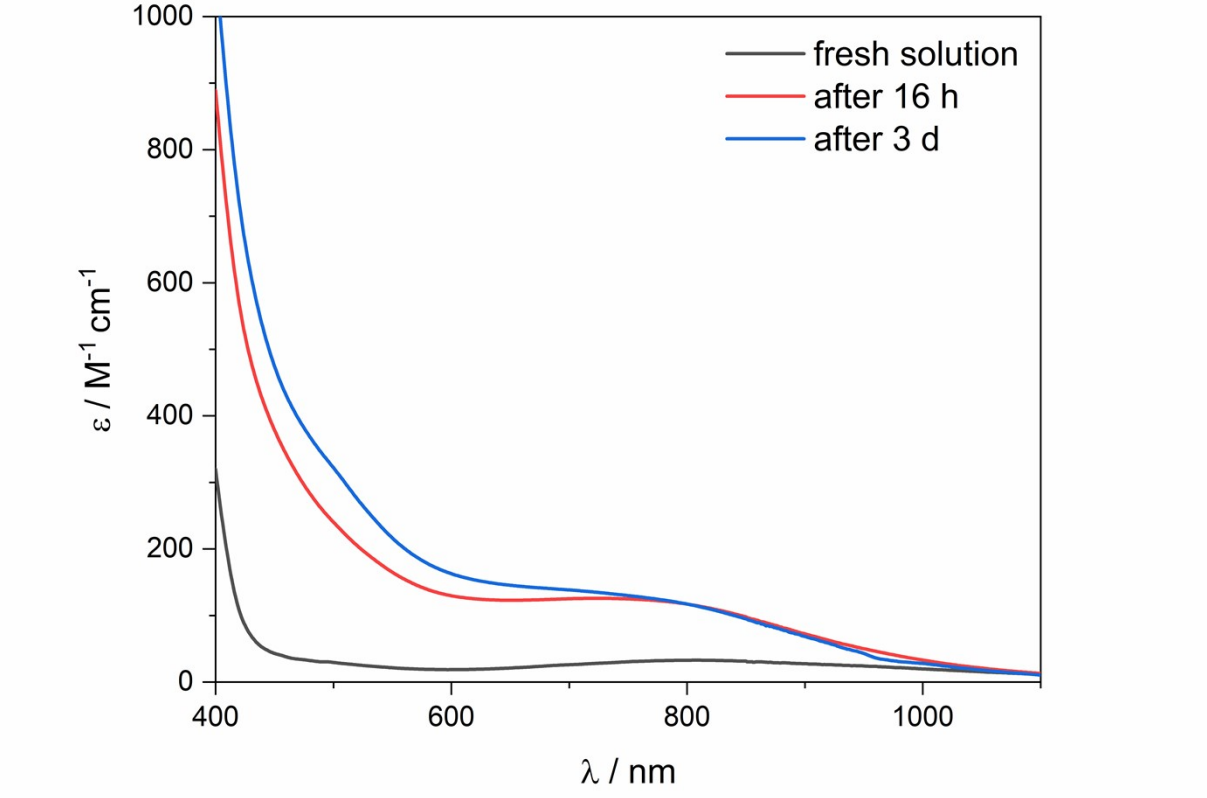

Figure S 5. The vis-NIR region of **1** measured in MeCN (c = 10^{-3} M, 295 K) measured in N_2 atmosphere and with exposure to air after 16 h and 3 d.

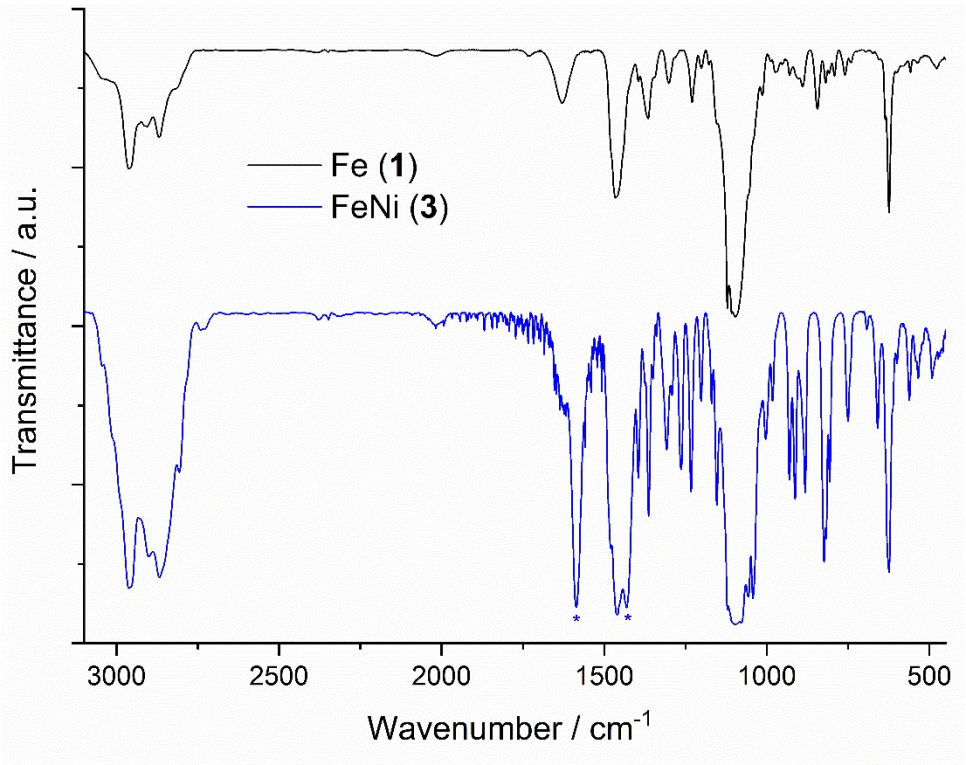

Figure S 6. FTIR spectra of the complexes **1** and **3** in KBr at room temperature; bands for the acetate-group in complex **3** are marked by a blue star.

3) Selected crystallographic data of complex 1 and 3

Table S 2. Selected distances [Å] and bond angles [°] of the heterobinuclear complex **3'**·MeCN measured at 180 K. M1 and M2 are indicative of the metal ions Fe^{II} and Ni^{II}. Since the metal ions are statistically distributed, bond distances are indicative.

Distance [Å]	**3'**·MeCN	Distance [Å]	**3'**·MeCN
M1–S1	2.5211(9)	M–N1	2.3498(20)
M2–S1	2.5313(7)	M–N2	2.1931(21)
M1–S2	2.4729(7)	M–N3	2.2835(29)
M2–S2	2.4739(9)	M–N4	2.2852(17)
M–O1	2.0222(19)	M–N5	2.1944(23)
M–O2	2.0171(19)	M–N6	2.3335(26)
Bond angle [°]	**3'**·MeCN	Bond angle [Å]	**3'**·MeCN
O1–M1–S1	93.49(5)	O2–M2–S1	94.47(5)
O1–M1–S2	97.19(5)	O2–M2–S2	96.98(5)
O1–M1–N2	160.68(8)	O2–M2–N5	161.17(8)
O1–M1–N1	86.80(7)	O2–M2–N4	87.85(7)
O1–M1–N3	87.09(9)	O2–M2–N6	86.93(7)
S2–M1–S1	80.81(2)	S2–M2–S1	80.58(2)
N1–M1–S2	170.47(6)	N5–M2–S2	98.13(6)
N1–M1–S1	90.33(5)	N5–M2–S1	99.03(6)
N3–M1–S2	89.57(6)	N5–M2–N4	80.92(7)
N3–M1–S1	170.37(6)	N5–M2–N6	80.13(7)
N3–M1–N1	99.30(7)	N4–M2–S2	90.24(6)
N2–M1–S2	98.44(6)	N4–M2–S1	170.74(6)
N2–M1–S1	100.14(7)	N4–M2–N6	99.43(7)
N2–M1–N1	79.55(8)	N6–M2–S2	169.72(5)
N2–M1–N3	81.76(10)	N6–M2–S1	89.65(5)

M1–O1–C39	134.14(17)	M2–O2–C39	133.56(18)

Table S 3. Selected bond angles [°] of the complex **1**·MeOH for the determination of the structure factor τ; measured at 180 K.

Angle [°]	**1**·MeOH
N1–Fe–N3	157.29(6)
N1–Fe–S1	94.84(4)
N1–Fe–S2	92.86(5)
N1–Fe–N2	80.27(7)
N3–Fe–S1	103.62(5)
N3–Fe–S2	93.22(5)
N3–Fe–N2	80.07(7)
S1–Fe–S2	109.76(2)
S1–Fe–N2	114.58(5)
S2–Fe–N2	135.51(5)
τ[a]	0.36

[a] The structure factor τ is defined by eq. (2) in Experimental.

4) Powder X-ray diffraction of complex 1·MeOH

The PXRD of complex **1**·MeOH matches well with the reflections of the simulated pattern from the crystal structure (CCDC: 2392032). The diffractogram shows an elevated background, likely due to partial amorphization during sample preparation (mortaring). The presence of an amorphous by-product can be excluded, which is proven by elemental analysis in the Experimental Section. The synthesized material initially contained only well-defined crystalline material, as verified by microscopy. The observed loss of crystallinity is thus most likely associated with the release of solvent molecules from the crystal lattice.

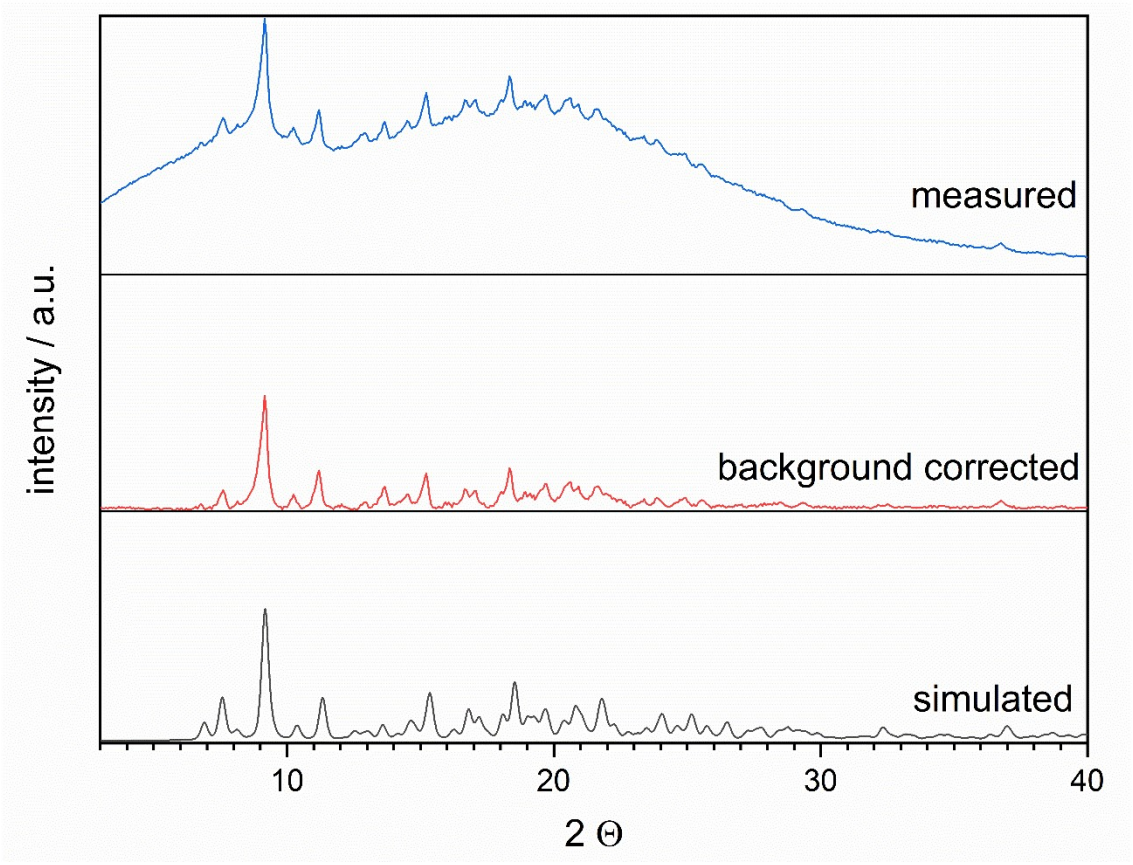

Figure S 7. PXRD of a crystalline sample of complex **1**·MeOH; the measured (blue), background-corrected (red), and simulated diffractogram based on the crystal structure (black, CCDC 2392032) are shown.

5) Optimized XYZ coordinates obtained by DFT calculations for 1 and 3

Table S 4. Optimized coordinates X, Y, and Z for **1** (Final Single Point Energy = -3875.625081395762 Eh).

Atom	X	Y	Z
Fe	8.17666	10.55306	16.26168
S	7.68057	11.78325	14.32324
S	8.69612	8.35957	15.63115
N	5.96165	10.01763	16.68503
N	7.86272	11.62921	18.14472
N	7.40863	13.82125	12.05898
H	7.90257	13.00166	12.46467
N	10.359	11.15328	16.77994
N	8.16815	8.43342	12.51049
H	7.98112	8.88299	13.42857
N	8.13513	11.583	10.39623
C	14.58608	7.57327	12.40981
H	14.73627	7.00199	13.32718
H	15.54073	7.62816	11.8844
H	13.89158	7.01855	11.77736
C	6.43087	13.27556	11.06357
H	5.85184	14.10978	10.66722
H	5.75344	12.63807	11.62494
C	15.13555	9.72574	13.54453
H	14.83764	10.75077	13.77582
H	16.06338	9.77662	12.97451
H	15.35583	9.20859	14.48006
C	4.95917	11.58993	14.96183
C	7.11752	12.52358	9.9312
H	6.32926	12.03841	9.33563
H	7.60409	13.23342	9.26353
C	1.96614	15.24314	15.44756
H	0.96952	15.68328	15.50409
H	2.6379	15.99627	15.03272

H	2.29505	15.01901	16.46405
C	14.07091	8.99118	12.72268
C	12.73928	8.88515	13.46503
C	3.34035	13.37785	14.51913
C	9.08567	11.31999	18.9184
H	9.08997	10.24464	19.10573
H	9.07369	11.82366	19.89209
C	1.45776	14.31925	13.16295
H	1.43169	13.43196	12.52724
H	2.10372	15.05988	12.68936
H	0.45133	14.73838	13.19854
C	8.64015	9.46904	11.53313
H	9.12628	8.92195	10.72765
H	9.39033	10.06	12.0522
C	5.1495	10.18139	15.4529
H	4.16019	9.73884	15.61398
H	5.64993	9.58507	14.68572
C	10.91476	12.13678	15.83361
H	10.9204	11.71863	14.8308
H	11.9397	12.4195	16.10065
H	10.2887	13.02625	15.8288
C	11.18177	9.90426	16.77841
H	10.71034	9.20123	17.46577
H	12.17823	10.14162	17.16546
C	7.54467	10.38409	10.99398
H	6.92529	9.84569	10.25956
H	6.90298	10.68822	11.82183
C	4.38102	14.10125	13.93884
H	4.17935	15.07985	13.52185
C	11.64918	8.25604	12.86345
H	11.75261	7.84505	11.86694
C	1.93183	13.96632	14.58555
C	6.00007	12.34933	14.40906
C	10.24506	8.6239	14.80898
C	9.29124	7.4451	12.81533

H	8.84126	6.67825	13.44264
H	9.58831	7.00713	11.86447
C	11.31619	9.28719	15.41574
C	9.07356	11.26381	9.31557
H	9.93163	10.71688	9.70165
H	9.45135	12.18739	8.87989
H	8.61004	10.67167	8.51304
C	12.53231	9.397	14.74172
H	13.34149	9.90437	15.24734
C	5.85053	8.60971	17.11233
H	6.13999	7.95441	16.29465
H	4.82201	8.37334	17.40733
H	6.51288	8.40678	17.95029
C	13.85431	9.76251	11.40646
H	13.13819	9.25941	10.7545
H	14.79465	9.84518	10.85949
H	13.48772	10.77261	11.60315
C	5.67994	13.61525	13.88002
C	3.66833	12.12042	15.01221
H	2.89504	11.50599	15.4508
C	10.33266	11.72649	18.15126
H	10.38206	12.81053	18.07327
H	11.21717	11.41995	18.71646
C	6.65318	11.07284	18.79297
H	6.32596	11.71472	19.61762
H	6.91788	10.10802	19.22351
C	6.93616	7.70836	12.0984
H	7.12705	7.17698	11.16817
H	6.12034	8.41226	11.96441
H	6.68352	7.00022	12.88356
C	6.73028	14.47599	13.24828
H	7.54019	14.69194	13.94569
H	6.30647	15.41311	12.89199
C	8.42482	14.73086	11.466
H	7.92074	15.5578	10.96965

H	9.03331	14.17687	10.75907
H	9.05592	15.11048	12.26575
C	5.53338	10.9093	17.77884
H	4.63654	10.52411	18.27759
H	5.27054	11.87377	17.35121
C	10.4287	8.12199	13.50842
C	0.92639	12.98749	15.20218
H	1.1862	12.72979	16.2308
H	0.8472	12.06618	14.62166
H	-0.06197	13.4466	15.22289
C	7.7039	13.08261	17.93433
H	8.50685	13.47013	17.3148
H	7.69975	13.61427	18.89159
H	6.77021	13.27976	17.41508
Fe	8.17666	10.55306	16.26168
S	7.68057	11.78325	14.32324
S	8.69612	8.35957	15.63115
N	5.96165	10.01763	16.68503
N	7.86272	11.62921	18.14472
N	7.40863	13.82125	12.05898
H	7.90257	13.00166	12.46467
N	10.359	11.15328	16.77994
N	8.16815	8.43342	12.51049
H	7.98112	8.88299	13.42857
N	8.13513	11.583	10.39623
C	14.58608	7.57327	12.40981
H	14.73627	7.00199	13.32718
H	15.54073	7.62816	11.8844
H	13.89158	7.01855	11.77736
C	6.43087	13.27556	11.06357
H	5.85184	14.10978	10.66722
H	5.75344	12.63807	11.62494
C	15.13555	9.72574	13.54453
H	14.83764	10.75077	13.77582
H	16.06338	9.77662	12.97451

H	15.35583	9.20859	14.48006
C	4.95917	11.58993	14.96183
C	7.11752	12.52358	9.9312
H	6.32926	12.03841	9.33563
H	7.60409	13.23342	9.26353
C	1.96614	15.24314	15.44756
H	0.96952	15.68328	15.50409
H	2.6379	15.99627	15.03272
H	2.29505	15.01901	16.46405
C	14.07091	8.99118	12.72268
C	12.73928	8.88515	13.46503
C	3.34035	13.37785	14.51913
C	9.08567	11.31999	18.9184
H	9.08997	10.24464	19.10573
H	9.07369	11.82366	19.89209
C	1.45776	14.31925	13.16295
H	1.43169	13.43196	12.52724
H	2.10372	15.05988	12.68936
H	0.45133	14.73838	13.19854
C	8.64015	9.46904	11.53313
H	9.12628	8.92195	10.72765
H	9.39033	10.06	12.0522
C	5.1495	10.18139	15.4529
H	4.16019	9.73884	15.61398
H	5.64993	9.58507	14.68572
C	10.91476	12.13678	15.83361
H	10.9204	11.71863	14.8308
H	11.9397	12.4195	16.10065

Table S 5. Optimized coordinates X, Y, and Z for **3** (Final Single Point Energy = -5609.210436651824).

Atom	X	Y	Z
Ni	-0.74957	8.36172	3.29661
Fe	-0.64055	5.00797	4.13546

S	1.06420	6.77920	3.86782
S	-1.66880	6.26869	2.20950
O	-1.81445	8.13727	4.99498
N	0.18440	9.28196	1.53705
N	0.38554	10.05235	4.33365
N	-2.56413	9.57207	2.46745
O	-1.77232	5.95301	5.51946
N	-2.35508	3.40534	4.01960
N	0.55739	4.14181	5.87595
N	0.38571	3.40597	3.04454
C	1.57117	7.21775	5.50070
C	-3.36283	6.32206	2.73335
C	-2.14403	7.14330	5.68252
C	1.01629	10.44529	1.97078
C	-0.92178	9.71881	0.63955
C	1.02977	8.33643	0.76892
C	-3.37044	3.82436	3.00433
C	-1.72636	2.16167	3.49973
C	-3.06283	3.11880	5.26977
C	1.74818	9.62343	4.78200
C	-0.29084	10.66225	5.49895
C	0.56708	11.06867	3.27547
C	-3.57626	8.65892	1.83616
C	-3.28737	10.40456	3.45459
C	-2.03265	10.42454	1.37812
C	1.88187	4.78706	6.06810
C	0.80313	2.75243	5.44984
C	-0.14187	4.15241	7.18222
C	-0.65026	2.48422	2.49336
C	1.27846	2.68571	4.01785
C	1.20251	3.91851	1.91356
C	-4.00047	5.16695	3.21507
C	-5.28021	5.26442	3.75370
C	1.77116	8.56245	5.84845
C	2.10602	8.89907	7.15203
C	-5.97607	6.47029	3.84398
C	-5.36120	7.58138	3.24734
C	-7.36190	6.57523	4.49052
H	-4.08937	3.14404	2.98591
H	-2.93780	3.82140	2.11379
H	-5.82899	8.40810	3.23383

C	-4.09022	7.52186	2.67279
H	-5.69869	4.47410	4.07448
C	1.84577	6.23947	6.46400
C	2.19089	6.60553	7.75041
H	2.35807	5.92161	8.38817
C	2.30447	7.93474	8.15315
H	2.23088	10.41852	5.12096
H	2.24529	9.28694	3.99482
C	-7.78999	5.32058	5.19873
C	-7.26051	7.65461	5.65328
C	-8.37425	7.07304	3.52357
H	0.99192	11.13630	1.26233
H	1.95556	10.14695	2.06695
H	2.20453	9.81714	7.37574
C	-3.12524	7.41189	6.81350
C	2.66386	8.32723	9.58149
H	-1.29419	8.92563	0.17801
H	-0.55597	10.32628	-0.05084
H	2.39414	4.70591	5.22484
H	2.37542	4.28579	6.76470
H	1.79616	8.06452	1.31643
H	1.35095	8.77406	-0.04717
H	0.50243	7.54606	0.52998
H	-3.17488	8.27784	1.01532
H	-4.35127	9.20778	1.55639
H	-1.15776	11.02520	5.22031
H	0.26512	11.38441	5.85861
H	-0.42919	9.98111	6.18990
H	1.24144	11.73079	3.57063
H	-0.28754	11.54718	3.13182
H	-2.41838	1.59577	3.07346
H	-1.33341	1.65149	4.25139
H	-0.21585	1.64369	2.20297
H	-1.06590	2.90187	1.69746
H	-2.44158	2.71225	5.91031
H	-3.80048	2.49846	5.09253
H	-3.41790	3.95172	5.64276
H	-3.61291	9.83712	4.18411
H	-4.04643	10.84362	3.01790
H	-2.68004	11.08411	3.81553
H	-1.68988	11.27160	1.75894

H	-2.76173	10.64505	0.74569
C	2.50643	9.74124	9.86185
C	1.38540	7.61424	10.45626
C	3.83404	7.62167	10.01284
H	2.18655	3.07491	3.96574
H	1.34213	1.73537	3.74849
H	-3.04034	8.34410	7.10563
H	-2.92928	6.81537	7.56576
H	-4.03940	7.25116	6.49863
H	-0.03180	2.22909	5.54315
H	1.48593	2.34543	6.04063
H	0.61570	4.34221	1.25178
H	1.68389	3.17540	1.49380
H	1.84649	4.57796	2.24710
H	-0.23247	5.07583	7.49780
H	0.37530	3.63419	7.83447
H	-1.03141	3.75339	7.08079
H	-8.63425	5.48424	5.66914
H	-7.10138	5.05886	5.84364
H	-7.91528	4.60291	4.54335
H	-6.98211	8.51473	5.27645
H	-6.60249	7.35911	6.31638
H	-8.13578	7.75381	6.08337
H	3.17109	10.25174	9.35472
H	2.63351	9.90095	10.82068
H	1.60565	10.02836	9.60071
H	-8.43566	6.45408	2.76666
H	-8.10874	7.95935	3.20066
H	-9.24642	7.13483	3.96678
H	0.54036	8.04478	10.21095
H	1.54325	7.72867	11.41732
H	1.33834	6.65803	10.24564
H	3.67163	6.65702	9.95866
H	4.04038	7.86752	10.93836
H	4.58898	7.85925	9.43502

6) Magnetism data of complex 1 and 3

Table S 6. Effective magnetic moment and susceptibility of complex **1** and **3** as a function of the temperature. For complex **1**: **s**ample mass = 4.340 mg; M_r = 924.3 g mol^{-1}. H = 0.05 T. For complex **3**: Sample mass = 21.310 mg; M_r = 942.12 g mol^{-1}. H = and 0.5 T.

Temperature [K]	χ_MT of **1** [cm^3 K mol^{-1}]	μ_{eff} of **1** [μ_B]	Temperature [K]	χ_MT of **3** [cm^3 K mol^{-1}]	μ_{eff} of **3** [μ_B]
300.37	3.66	5.41	299.46	4.96	6.30
290.38	3.66	5.41	289.47	4.93	6.28
280.37	3.65	5.40	279.49	4.88	6.25
270.37	3.65	5.40	269.54	4.85	6.23
260.38	3.65	5.40	259.56	4.82	6.21
250.39	3.63	5.39	249.57	4.78	6.18
240.38	3.62	5.38	239.63	4.74	6.16
230.37	3.62	5.38	229.65	4.70	6.13
220.36	3.62	5.38	219.64	4.65	6.10
210.36	3.61	5.37	209.66	4.61	6.07
200.34	3.59	5.36	199.78	4.56	6.04
190.33	3.59	5.36	189.80	4.52	6.01
180.32	3.58	5.35	179.80	4.47	5.98
170.30	3.58	5.35	169.85	4.41	5.94
160.18	3.57	5.34	159.86	4.35	5.90
150.27	3.51	5.30	149.89	4.29	5.86
140.24	3.55	5.33	139.90	4.24	5.82
130.23	3.55	5.33	129.91	4.16	5.77
120.22	3.54	5.32	119.91	4.09	5.72
110.19	3.54	5.32	109.94	3.99	5.65
100.17	3.53	5.31	99.96	3.89	5.58
90.14	3.53	5.31	89.98	3.78	5.50
80.12	3.51	5.30	80.02	3.65	5.40
70.08	3.50	5.29	70.05	3.47	5.27
60.06	3.47	5.27	60.06	3.26	5.11
50.02	3.45	5.25	50.05	3.00	4.90
40.00	3.42	5.23	40.00	2.66	4.61
30.00	3.66	5.18	30.00	2.21	4.20
20.00	3.66	5.09	19.99	1.63	3.61
19.00	3.65	5.05	19.01	1.58	3.55

18.00	3.65	5.04	18.00	1.51	3.48
17.00	3.65	5.02	17.00	1.45	3.41
16.00	3.63	5.00	16.00	1.39	3.33
15.00	3.62	4.97	15.00	1.33	3.26
14.02	3.62	4.95	14.05	1.27	3.19
13.01	3.62	4.92	13.03	1.21	3.11
12.00	3.61	4.89	12.01	1.18	3.07
11.02	3.59	4.85	11.02	1.10	2.96
10.00	3.59	4.81	10.01	1.04	2.88
9.00	3.58	4.78	9.01	0.99	2.81
8.00	3.58	4.74	8.01	0.93	2.73
7.01	3.57	4.70	7.01	0.87	2.64
6.03	3.51	4.65	6.01	0.81	2.55
5.01	3.55	4.59	5.00	0.74	2.44
4.03	3.55	4.53	4.00	0.66	2.30
3.00	3.54	4.46	3.00	0.55	2.10
2.00	3.54	4.44	1.99	0.42	1.83

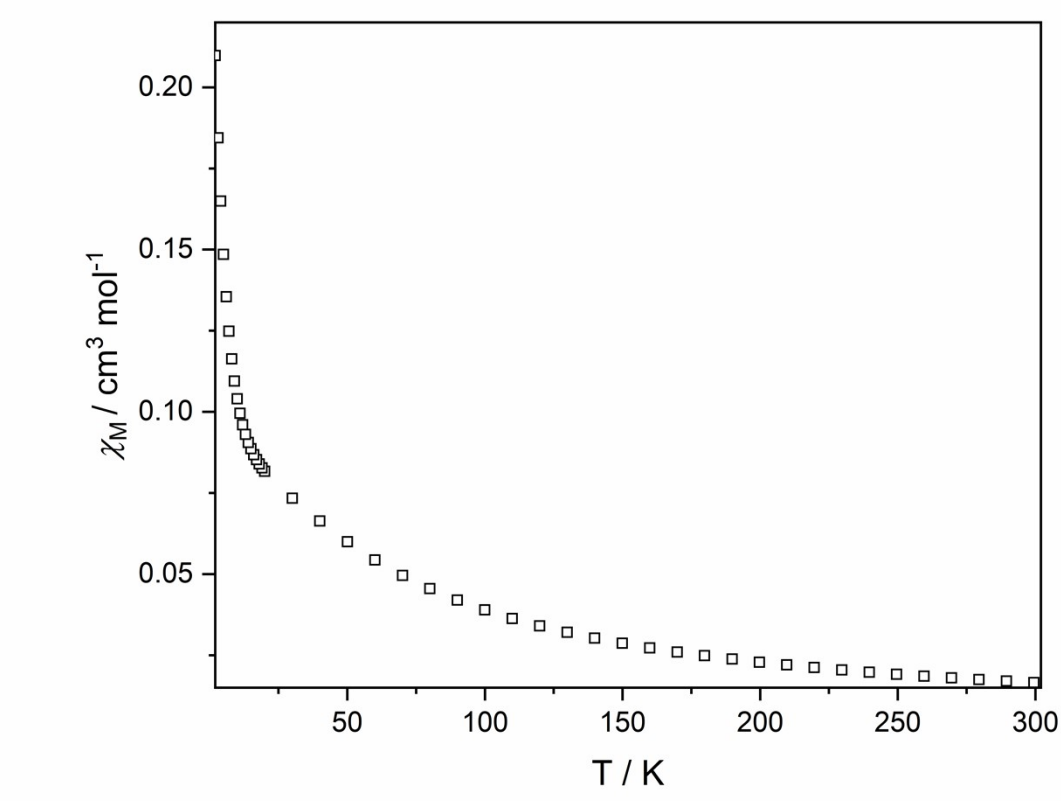

Figure S 8. The χ_M vs. T plot for the heterobinuclear complex **3** at 0.5 T.

7) Broken-symmetry DFT calculations

7a) Results for complex **3**

Table S 7. Calculated Mulliken spin density and *J* values of complex **3** at the PBE0/def2-TZVPP level of theory.

	state	Fe	Ni	S1	S2	O1	O2	N1-N6	Total spin	*J* / cm$^{-1,a}$
3	HS	3.720	1.597	0.145	0.150	0.048	0.023	0.045 – 0.053 (3x) 0.010 – 0.021 (3x)	6	-7.42
	BS	3.707	-1.585	-0.024	-0.026	-0.038	0.025	-0.046 – -0.055 (3x) +0.011 – +0.024 (3x)	2	

[a)] The *J* values are based on the energy difference between the high-spin and broken-symmetry solutions as calculated by the Yamaguchi formula, i.e. $J = -(E_{HS} - E_{BS})/ (\langle S^2\rangle_{HS} - \langle S^2\rangle_{BS})$.

7b) Results for complexes **3″**

In order to evaluate the coupling through the thiophenolato and carboxylato bridges in the present complexes, we utilized a breakdown approach, in which the carboxylate ligands were virtually removed from the structure of **3** to obtain the hypothetical $[FeNi(L)]^{2+}$ dication **3″**. The resulting structure was also subjected to broken symmetry DFT density functional theory calculations. This method has previously shown to be a powerful tool to unravel the contribution of the various bridging co-ligands for dinuclear nickel complex of the type $[Ni_2L(\mu\text{-}L')]^+$, where L′ = F^-, Cl^-, Br^-, N_3^-, and OH^-.[i] The coupling constants (J_{SR}) calculated for the $[FeNi(L)]^{2+}$ cation **3″** (J = -17.11 cm^{-1}) was found to be slightly larger than for the carboxylato bridged species (indicative of an orbital counter-complementary effect).

[i] A. Jeremies, S. Gruschinski, S. Schmorl, T. Severin, B. Kersting, *New. J. Chem.* **2018**, 42, 7630–7639.

Table S 8. Calculated Mulliken spin density and *J* values of complexes **3″** at the PBE0/def2-TZVPP level of theory.

	state	Fe	Ni	S1	S2	N1-N6	Total spin	*J* / cm$^{-1,a}$
3′	HS	3.800	1.610	0.144	0.145	0.005 – 0.008 (3x) 0.004 – 0.020 (3x)	6	-17.11
	BS	3.791	-1.600	-0.033	-0.035	-0.050 – -0.081 (3x) 0.007 – 0.020 (3x)	2	

[a)] The J values are based on the energy difference between the high-spin and broken-symmetry solutions as calculated by the Yamaguchi formula, i.e. $J = -(E_{HS}-E_{BS})/ (\langle S^2\rangle_{HS}-\langle S^2\rangle_{BS})$.

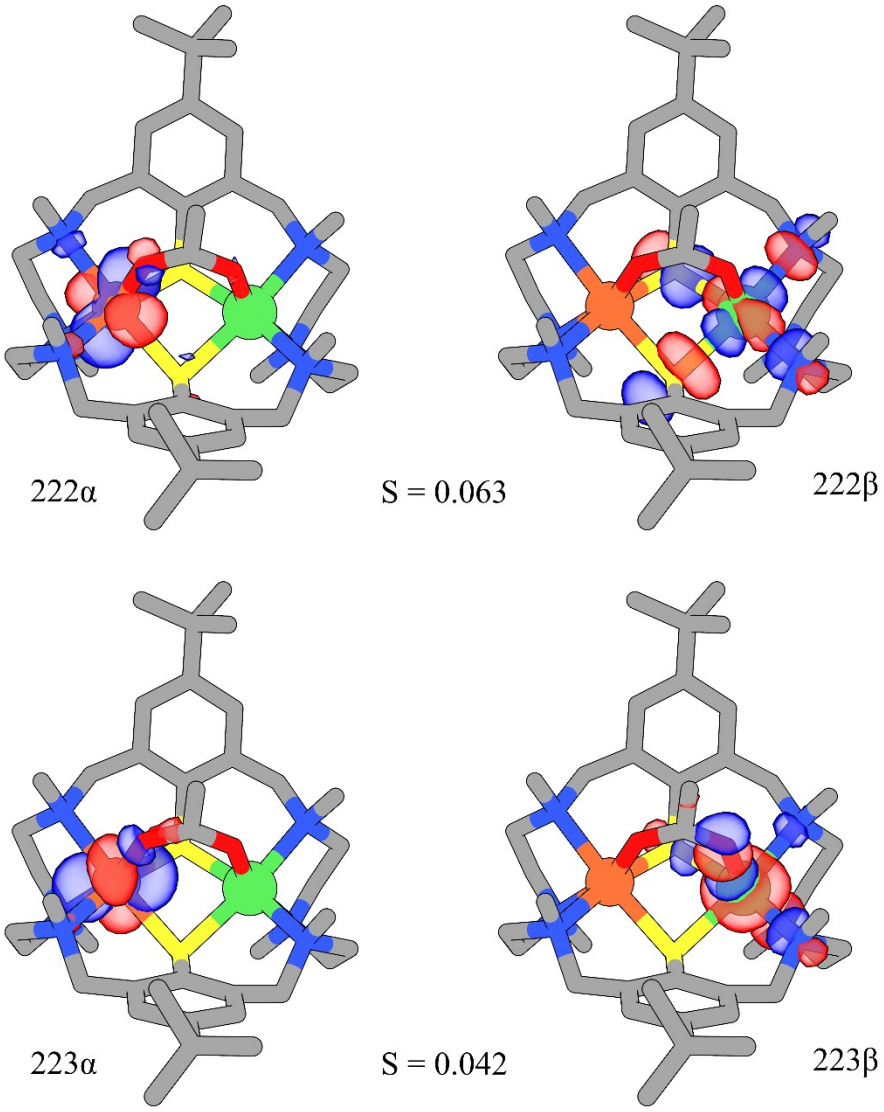

Figure S 9. Pairs of 'magnetic orbitals' for **3** derived from the corresponding orbital transformation of the broken-symmetry DFT determinant. The *S* values correspond to the values of overlap integrals for the corresponding orbital pairs.

8) SEM-EDX mapping on a single crystal of 3'·MeCN

Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) mapping was conducted on single crystals of compound **3'**·MeCN crystallized from different solvent media (Figures S 10 and S 11). The analyses reveal that Fe and Ni are uniformly distributed throughout all crystals analysed. Representative EDX spectra (Figure S 12) from two well-defined single crystals obtained from a MeCN/EtOH mixture confirm the consistent Fe/Ni distribution along an individual crystal.

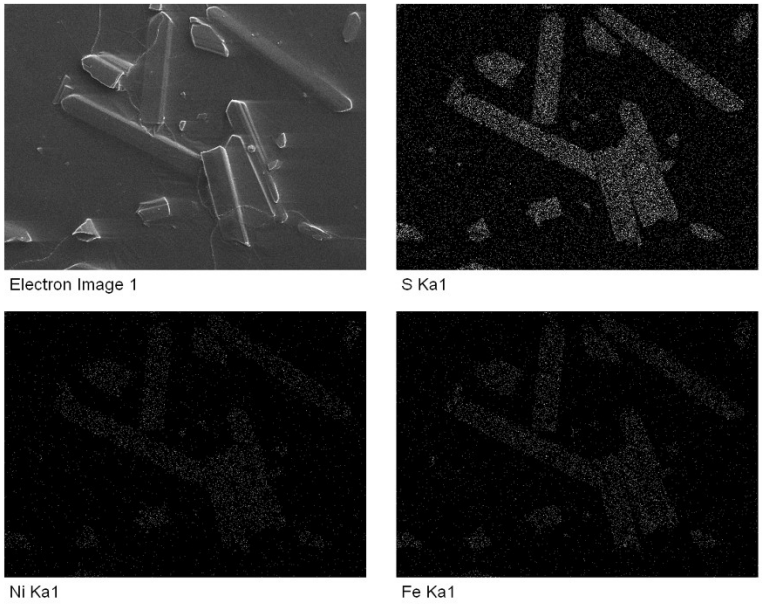

Figure S 10. SEM image of single crystals obtained by slow evaporation from MeCN/^{i}PrOH (top left) and EDX mapping of S, Ni and Fe; magnification 70x.

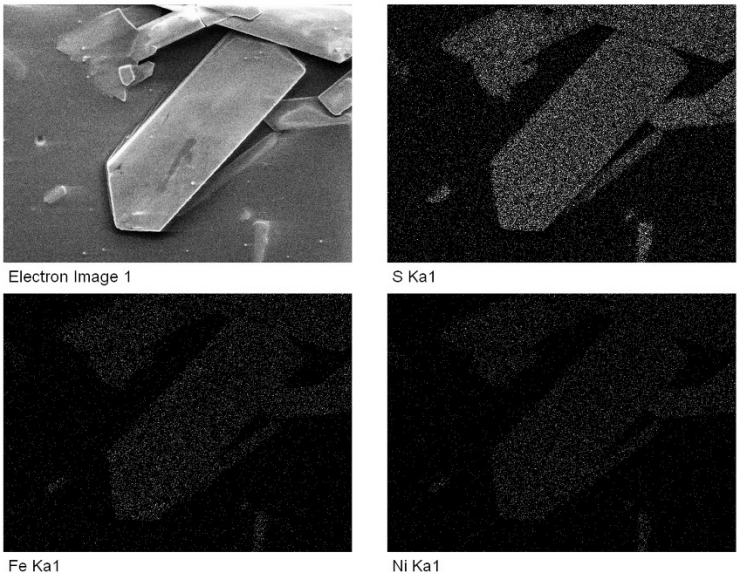

Figure S 11. SEM image of single crystals obtained by slow evaporation from MeCN/EtOH (top left) and EDX mapping of S, Ni and Fe; magnification 100x.

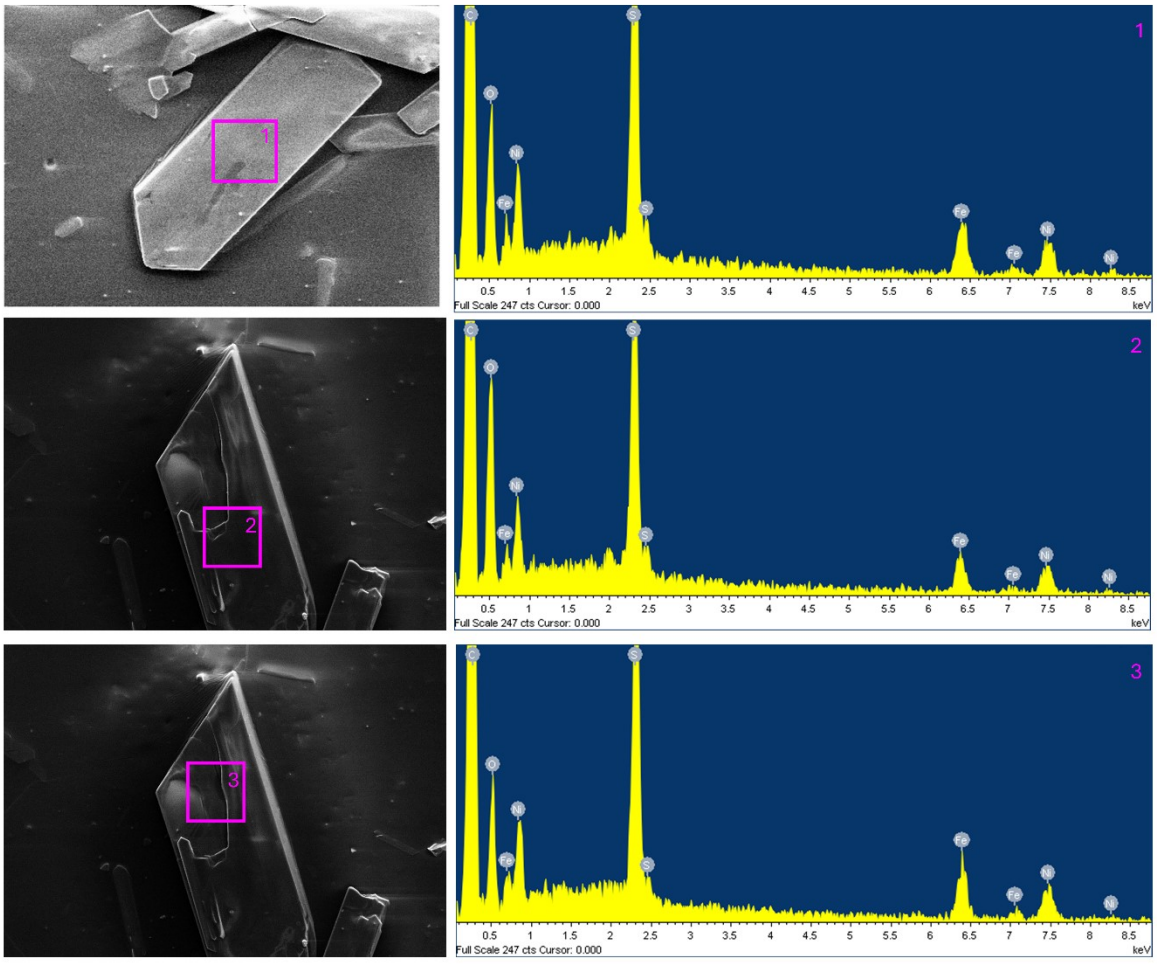

Table S 12. Representative EDX spectra from different regions of two single crystals obtained by evaporation from MeCN/EtOH; magnification 100x in inset 1, 75x in inset 2 and 3.

Table S 9. Elemental composition at position 1 – 3 (see Figure S 12).

Element	Corrected Conc.	Intensity Correction	Weight%	Weight% Sigma	Atom%	Atom% Sigma
Fe K (1)	1.67	1.0860	45.84	7.75	47.08	3.90
Ni K (1)	1.72	0.9416	54.16	7.75	52.92	3.32
Fe K (2)	1.37	1.0824	48.02	9.09	49.27	4.32
Ni K (2)	1.29	0.9389	51.98	9.09	50.73	4.02
Fe K (3)	1.16	1.0862	42.15	11.03	43.38	5.76
Ni K (3)	1.38	0.9417	57.85	11.03	56.62	4.24