Stabilisation of a paramagnetic BH_4^--bridged dinickel(II) complex by a macrodinucleating hexaaza-dithiophenolate ligand

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Supporting Information

Preparation of the compounds. Unless otherwise noted the preparations of the metal complexes were carried out under an argon atmosphere using Schlenk techniques. Compound **1**·ClO_4 was prepared as described in the literature (B. Kersting, G. Steinfeld, *Chem. Commun.* 2001, 1376). All compounds are hygroscopic and crystallize with solvent molecules of crystallization (see, for example, the crystal structure of **3**·BPh_4·$2CH_3CN$), but the compounds slowly lose their solvent molecules of crystallization upon standing in air. This is why the observed microanalytical data do not always fit exactly with the calculated values (for the solvent-free compounds).

Caution! *Perchlorate salts of transition metal complexes are hazardous and may explode. Only small quantities should be prepared and great care taken.*

Preparation of [(L)Ni$^{II}_2$(μ-ClO$_4$)]ClO$_4$ (2·ClO$_4$). To a solution of [(L)Ni$^{II}_2$(μ-Cl)]ClO$_4$ (**1**·ClO_4) (184 mg, 0.200 mmol) in MeCN (50 mL) was added solid $Pb(ClO_4)_2$ (44.7 mg, 0.110 mmol). The reaction mixture was stirred for 2 h before $PbCl_2$ was removed by filtration. To the dark yellow filtrate was added a solution of $LiClO_4$·$3H_2O$ (321 mg, 2.00 mol) in EtOH (100 mL). The solution was concentrated *in vacuo* to afford a dark green precipitate which was isolated by filtration and dried in air. Yield: 148 mg (75 %). M.p. 308–309 °C (decomp.). IR (KBr) ν / cm^{-1} = 3443(s) br, 3045(w), 3024(w), 2992(w), 2958(s), 2900(w), 2866(s),

2815(w), 1489(w), 1462(s), 1426(w), 1395(m), 1377(w), 1363(m), 1345(vw), 1326(w),

1310(m), 1293(w), 1262(m), 1236(m), 1200(w), 1170(m), 1156(s), 1111(vs) $[\nu_3(\mu\text{-}ClO_4^-)]$,

1100(vs) $[\nu_3(ClO_4^-)]$, 1019(m) $[\nu_4(\mu\text{-}ClO_4^-)]$, 1000(w), 981(w), 911(m), 932(m), 895(w),

882(m), 824(s), 818(s), 808(w), 754(w), 624(s), 603(w), 564(w), 544(w), 533(w), 494(w),

418(w). UV/vis (MeCN): λ_{max} / nm (ε / M^{-1} cm^{-1}) = 578 (129), 1066 (86). Elemental analysis

(%) calcd. for $C_{38}H_{64}Cl_2N_6Ni_2O_8S_2 \cdot EtOH \ H_2O$ (M = 985.37 + 64.08 g mol^{-1}): C 45.78, H

6.92, N 8.01, S 6.11; found C 46.06, H 6.82, N 8.06, S. 6.00.

[(L)Ni$^{II}_2$(μ-BH$_4$)](BPh$_4$) (3·BPh$_4$). To a solution of **2**·ClO$_4$ (220 mg, 0.223 mmol) in MeCN

(25 mL) was added a solution of N^{n}Bu$_4$BH$_4$ (100 mg, 0.387 mmol) in MeCN (2 mL). The

reaction mixture was stirred for 30 minutes during which time the colour turned from yellow

to pale green. Solid LiClO$_4$·3H$_2$O (20 mg) was added. The solution was concentrated to *ca.* 5–

7 mL. The resulting green solid of **3**·ClO$_4$ was filtered quickly and redissolved in 30 mL

MeCN. Solid NaBPh$_4$ 342 mg (1.00 mmol) was added. The solution was filtered and

concentrated to *ca.* 15 mL. The solution was kept at room temperature for 24 h. The resulting

green crystals were filtered and dried in air. The compound can be handled in air for ca 1-2 h

without noticeable deomposition, but for long term storage it should be stored under an argon

atmosphere. Yield: 136 mg (54 %). M.p. 208−210 °C (decomp). IR (KBr): ν / cm^{-1} =

3053(m), 3030(m), 2997(m), 2979(sh), 2962(s), 2953(sh), 2899(m), 2861(m), 2838(sh),

2809(w), 2390(m) (νBH_4^-), 2360(s) (νBH_4^-), 2153(s) (νBH_4^-), 2071(s) (νBH_4^-), 1602(w),

1579(w), 1460(s), 1424(m), 1393(m), 1375(w), 1361(w), 1350(vw), 1327(vw), 1304(w),

1293(w), 1263(w), 1235(w), 1200(w), 1169(w), 1153(m), 1131(w), 1110(w), 1091(m),

1075(s), 1056(s), 1036(s), 997(m), 982(m), 931(m), 910(m), 881(m), 843(m), 823(s),

808(shm), 748(sh), 733(vs), 704(vs) cm^{-1} (νBPh_4^-), 627(m), 612(s). UV/Vis (MeCN): λ_{max} /

nm (ε / M^{-1} cm^{-1}) = 650 (43), 1074 (77). Elemental analysis (%) calcd. (%) for

$C_{62}H_{88}B_2N_6Ni_2S_2 \cdot MeCN$ (M = 1120.54 + 41.05 g mol^{-1}): C 66.18, H 7.90, N 8.44, S 5.52;

found: C 65.73, H 7.73, N 8.13, S 5.72.

Reaction of 3·BPh$_4$ with protic reagents (H$_2$O, HCl, HClO$_4$, HCO$_2$H). General procedure:

To a solution of the borohydrido-bridged complex **3**·BPh$_4$ (112 mg, 0.100 mmol) in MeCN

(30 mL) was added a solution of 0.15 mmol of the respective reagent in MeCN (2 mL). The

reaction mixtures were stirred for 2 to 3 days under a protective argon atmosphere. The

solutions were then evaporated to dryness and redissolved in MeCN (10 mL). Small amounts

of an insoluble material were removed by filtration. Upon slow evaporation of the resulting

clear solutions, the products precipitated as microcrystalline solids.

[(L)Ni^{II}$_2$(μ-Cl)](BPh$_4$) (1·BPh$_4$): Yield: 87 mg (76 %). IR (KBr): ν / cm^{-1} = 733, 705 (BPh$_4^-$).

UV/Vis (MeCN): λ_{max} / nm (ε / M^{-1} cm^{-1}) = 658 (41), 919 (65), 998 (67); Elemental analysis

(%) calcd. for $C_{62}H_{84}BClN_6Ni_2S_2$ (M = 1141.51 g mol^{-1}): C 65.26, H 7.42, N 7.36, S 5.62;

found: C 65.12, H 7.32, N 7.14, S 5.33. These data are identical with those of **1**·BPh$_4$ reported

earlier (B. Kersting, G. Steinfeld, *Chem. Commun.* 2001, 1376).

[(L)Ni^{II}$_2$(μ-OH)](BPh$_4$) (4·BPh$_4$): Yield: 73 mg (65 %). IR (KBr) ν / cm^{-1} = 3546(m) (OH),

733, 705 (BPh$_4^-$). UV/vis (CH$_3$CN) λ_{max} / nm (ε / M^{-1} cm^{-1}) = 655 (52), 1056 (40). Elemental

analysis (%) calcd. for $C_{62}H_{85}BN_6Ni_2OS_2$ H$_2$O (M = 1122.71 + 18.02): C 65.28, H 7.69, N

7.37, S 5.62; found: C 65.24, H 7.44, N 7.38, S 5.68. These data are identical with those of

4·BPh$_4$ reported earlier (B. Kersting, G. Steinfeld, *Chem. Commun.* 2001, 1376).

[(L)Ni^{II}$_2$(μ-O$_2$CH)](BPh$_4$) (5·BPh$_4$): Yield: 106 mg (92 %). IR (KBr) ν / cm^{-1} = 1602

[ν_{as}(CO$_2$)], 1424 cm^{-1} [ν_s(CO$_2$)]. UV/Vis (MeCN): λ_{max} / (ε / M^{-1} cm^{-1} = 653 (35), 1112 (73).

Elemental analysis (%) calcd. for $C_{63}H_{85}BN_6Ni_2O_2S_2$ (M = 1150.72 g mol^{-1}): C 65.76, H 7.45, N 7.30, S 5.57; found: C 65.23, H 7.41, N 7.02, S 5.34. This compound was additionally characterized by X-ray crystal structure analysis (see below).

Complex 5·BPh$_4$ can also be prepared by the reaction of 3·BPh$_4$ with CO$_2$: A solution of the borohydrido-bridged complex **3**·BPh$_4$ (112 mg, 0.100 mmol) in MeCN (30 mL) was stirred for 12 h under a CO$_2$ atmosphere (1 bar). The solution was evaporated to dryness and redissolved in MeCN (10 mL). Upon slow evaporation, the formato-complex **5**·BPh$_4$ precipitated as a microcrystalline green solid. Yield: 110 mg (95 %). The analytical data are identical with those of **5**·BPh$_4$ prepared by the reaction described above.
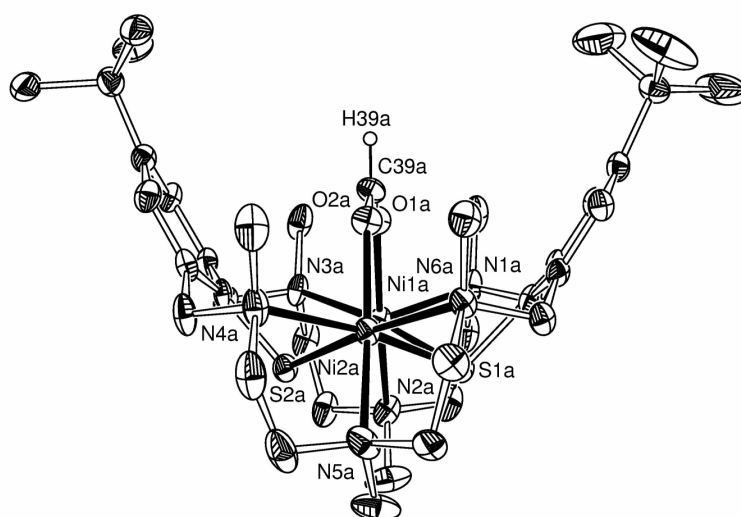
Fig. S1 ORTEP representation of the structure of the formato complex **5** with thermal ellipsoids drawn at the 50 % probability level. Only one molecule (A) of the two crystallographically independent molecules within the asymmetric unit is shown. *tert*-Butyl groups and hydrogen atoms, except that of the formato coligand, have been omitted for clarity. Selected bond lengths [Å] for molecule A [molecule B]: Ni(1A)–O(1A) 1.992(4) [2.000(4)], Ni(1A)–N(1A) 2.266(6) [2.238(6)], Ni(1A)–N(2A) 2.146(5) [2.167(5)], Ni(1A)–N(3A) 2.255(5) [2.313(6)], Ni(1A)–S(1A) 2.477(2) [2.501(2)], Ni(1A)–S(2A) 2.497(2) [2.466(2)], Ni(2A)–O(2A) 1.996(4) [2.000(4)], Ni(2A)–N(4A) 2.320(6) [2.250(6)],

Ni(2A)–N(5A) 2.136(6) [2.135(6)], Ni(2A)–N(6A) 2.243(6) [2.319(6)], Ni(2A)–S(1A)

2.478(2) [2.479(2)], Ni(2A)–S(2A) 2.487(2) [2.488(2)], Ni⋯Ni 3.481(1) [3.479(1)].

Magnetic susceptibility measurements. Temperature-dependent magnetic susceptibility

measurements of a powdered solid sample of **5**·BPh$_4$ were carried out on a SQUID

magnetometer (MPMS Quantum Design) over the temperature range 2.0–300 K. The

magnetic field applied was 0.2 T. The observed susceptibility data were corrected for the

underlying diamagnetism by using Pascals constants.

In order to determine the magnitude of the exchange interaction the $\chi_M T$ versus T

experimental data were analysed by using the spin Hamiltonian [Eq. (1)] for dinuclear

complexes, which includes two additional terms to account for Zeeman splitting and single-

ion zero-field interactions. The introduction of a D parameter is appropiate since for nickel(II)

ions, the non-cubic components of the ligand field may act on the $S = 1$ ground state to

produce a zero-field splitting which may be of the same order of magnitude as J.

$$H = -2J\, S_1 \cdot S_2 + D(S_{z1}^2 + S_{z2}^2 - 4/3) + g\beta(S_1 + S_2)B \qquad (1)$$

In order to reduce the number of the variables the D and g values were considered to be

identical for the two nickel(II) ions. The resulting Hamiltonian was diagonalised numerically

to obtain the magnetic susceptibility which was used to fit the $\chi_M T$ magnetic data for the

nickel(II) compounds. An excellent fit was obtained with $J = +27$ cm^{-1}, $g = 2.09$ and $D = 4.3$

cm^{-1} with an agreement factor $R = 5.94 \times 10^{-3}$. The solid line in Figure 2 (see main text)

represents this best fit. It should be noted that the inclusion of the D parameter improved the

low-temperature fit significantly, but it represents by no means an accurate value (temperature

dependent magnetic suscpetibility measurement are not very appropiate for the determination

of the sign and magnitude of D).

Table S1. Magnetic susceptibility data for $[(L)Ni^{II}_2(\mu\text{-}BH_4)](BPh_4)$ ($3\cdot BPh_4$) as a function of the temperature: Sample = 0.02184 [g]; M_r = 1120.54 [g/mol], diamagnetic correction = -0.0056027 [cm^3/mol], H = 0.2 Tesla.

T / K	$\chi_M T_{exp.}$ / cm^3 K mol^{-1}	$\chi_M T_{calcd.}$ / cm^3 K mol^{-1}
294.83	2.6930	2.6915
289.71	2.6981	2.6945
284.67	2.7011	2.6976
279.63	2.6995	2.7008
274.64	2.7067	2.7042
269.64	2.7103	2.7078
264.64	2.7135	2.7116
259.66	2.7179	2.7156
254.65	2.7197	2.7198
249.66	2.7220	2.7242
244.65	2.7272	2.7289
239.66	2.7311	2.7338
234.66	2.7375	2.7390
229.73	2.7450	2.7443
224.72	2.7498	2.7500
219.71	2.7589	2.7561
214.71	2.7642	2.7624
209.73	2.7708	2.7690
204.76	2.7790	2.7759
199.77	2.7840	2.7832
194.80	2.7918	2.7909
189.80	2.8006	2.7990
184.82	2.8090	2.8075
179.84	2.8195	2.8164
174.84	2.8280	2.8258
169.86	2.8360	2.8357

164.86	2.8457	2.8461
159.88	2.8590	2.8570
154.89	2.8699	2.8684
149.91	2.8810	2.8805
144.92	2.8934	2.8931
139.93	2.9090	2.9064
134.94	2.9221	2.9204
129.96	2.9364	2.9350
125.02	2.9403	2.9502
119.98	2.9678	2.9665
114.98	2.9846	2.9833
109.98	3.0037	3.0009
104.99	3.0223	3.0193
100.00	3.0425	3.0383
95.990	3.0512	3.0541
93.970	3.0618	3.0623
91.980	3.0711	3.0704
89.990	3.0797	3.0786
88.000	3.0870	3.0868
86.000	3.0958	3.0952
84.010	3.1037	3.1037
82.020	3.1121	3.1122
80.020	3.1188	3.1207
78.030	3.1269	3.1293
76.020	3.1353	3.1380
74.040	3.1446	3.1466
72.040	3.1530	3.1552
70.040	3.1610	3.1638
68.040	3.1700	3.1724
66.050	3.1780	3.1809
64.050	3.1853	3.1892
62.030	3.1877	3.1976
60.030	3.1959	3.2057
58.230	3.2155	3.2128

56.250	3.2253	3.2205
54.250	3.2322	3.2279
52.250	3.2391	3.2351
50.240	3.2465	3.2419
48.240	3.2542	3.2483
46.230	3.2620	3.2544
44.220	3.2685	3.2599
42.220	3.2736	3.2650
40.210	3.2782	3.2695
38.200	3.2826	3.2734
36.200	3.2853	3.2766
34.200	3.2877	3.2792
32.200	3.2891	3.2812
30.200	3.2902	3.2824
28.200	3.2913	3.2830
26.200	3.2903	3.2828
24.200	3.2889	3.2820
22.200	3.2860	3.2805
20.200	3.2826	3.2782
19.200	3.2805	3.2768
18.200	3.2773	3.2751
17.200	3.2750	3.2732
16.200	3.2727	3.2711
15.200	3.2701	3.2684
14.200	3.2672	3.2654
13.200	3.2638	3.2618
12.200	3.2608	3.2574
10.950	3.2336	3.2505
10.000	3.2372	3.2436
9.0100	3.2232	3.2345
8.0100	3.2072	3.2221
7.0000	3.1859	3.2047
6.0000	3.1501	3.1795
5.0000	3.1029	3.1406

4.0000	3.0649	3.0761
3.0000	2.9632	2.9580
2.0000	2.7360	2.7066