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

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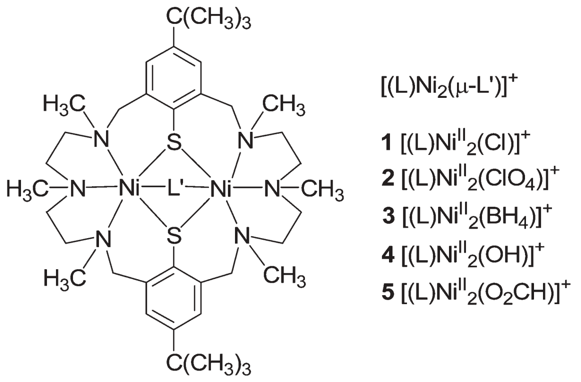
The first paramagnetic borohydrido-bridged dinuclear nickel(II) complex, $[(L)Ni^{II}_2(\mu_{1,3}\text{-}BH_4)]^+$, stabilised by a sterically demanding hexaaza-dithiophenolate macrocycle, has been obtained by the reaction of $[(L)Ni^{II}_2(\mu\text{-}ClO_4)]^+$ with $N^nBu_4BH_4$.

The search for dinuclear dithiolato-bridged complexes which model key features of the active site of hydrogenase enzymes is an active research area.[1,2] Two main strategies exist to access such compounds. One involves the addition of an electrophilic metal–carbonyl fragment to a nucleophilic metal complex with *cis*-oriented thiolate functions.[3] The resulting $[NiFeS_2]$, or $[Fe_2S_2]$, assemblies are co-ligated with CO and CN^- and represent good structural analogues of the proposed active site structures, as demonstrated recently by a number of research groups.[4–7] In the other strategy, macrocyclic dinucleating polyaza-dithiolate ligands are used for the cluster assembly.[8] Until now this strategy has only allowed for the production of homodinuclear nickel complexes, and it is unclear at present whether these more classical Werner-type coordination compounds will ever be able to bind the biologically relevant co-ligands CO, CN^- and H^-. Herein we provide the first evidence for nickel–hydrogen interactions in such compounds.

Our study was initiated by the recent discovery of Desrochers *et al.*[9] who demonstrated that the sterically encumbered hydrotris-(3,5-dimethyl-pyrazolyl)borate ligand (Tp^{*-}) can stabilize a hydrogen-rich nickel environment in $[Tp^*Ni^{II}(\mu_{1,3}\text{-}BH_4)]$. In order to test whether similar dinickel(II) complexes with a bridging borohydride co-ligand are supported by the dinucleating hexaaza-dithiophenolate ligand $(L)^{2-}$ (Scheme 1),[10] an acetonitrile solution of the chloro-bridged complex $[(L)Ni^{II}_2(\mu\text{-}Cl)]ClO_4$ (**1**·ClO_4) was treated with $N^nBu_4BH_4$ under an argon atmosphere at ambient temperature. Unlike $[Tp^*Ni^{II}Cl]$,[9] however, no reaction occurred. In a second approach, the reaction was carried out using the dark-green perchlorato-bridged complex $[(L)Ni^{II}_2(\mu\text{-}ClO_4)]ClO_4$ (**2**·ClO_4) which was prepared by Cl^- abstraction from **1**·ClO_4 with $Pb(ClO_4)_2$.† This gave a pale-green solution of the desired borohydrido-bridged complex **3**, which was isolated as its BPh_4^- salt in *ca.* 75% yield. In the absence of air and protic reagents this compound is stable for weeks, both in the solid state and in solution. This stability is quite remarkable given that nickel(II) complexes of sterically less demanding ligands are readily reduced to nickel boride.[11]



Scheme 1 Complexes **1**–**5**.

IR measurements of solid **3**·BPh_4 showed intense absorption bands at 2390, 2360, 2153 and 2071 cm^{-1} indicative of terminal B–H and bridging B–H···Ni functions.[12] The UV-Vis spectrum recorded in acetonitrile suggested the presence of octahedral Ni(II) ions [λ = 650 (ν_2) and 1074 nm (ν_1)].[13] Final confirmation came from an X-ray crystal structure determination of **3**·BPh_4·2MeCN (Fig. 1).§ As can be seen, the BH_4^- ion bridges the two Ni(II)

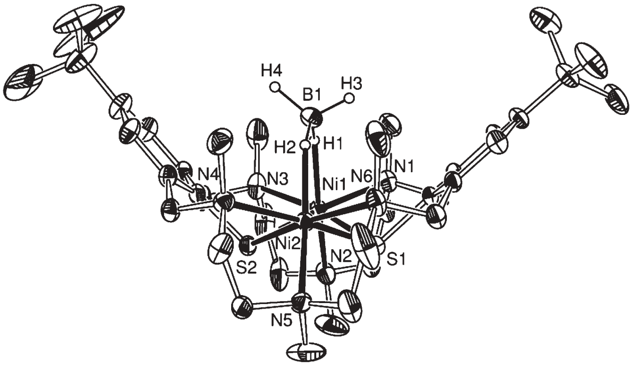


Fig. 1 ORTEP representation of the structure of complex **3** at 50% probability ellipsoids. Hydrogen atoms, except those of the BH_4^- co-ligand, have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–N1 2.219(4), Ni1–N2 2.152(4), Ni1–N3 2.284(4), Ni1–S1 2.437(2), Ni1–S2 2.459(1), Ni1–H1 1.93(4), Ni2–N4 2.271(4), Ni2–N5 2.135(4), Ni2–N6 2.260(4), Ni2–S1 2.439(2), Ni2–S2 2.457(2), Ni2–H2 1.84(4), B1–H1 1.25(4), B1–H2 1.24(4), B1–H3 1.12(4), B1–H4 1.12(4); Ni1···Ni2 3.458; Ni1–S1–Ni2 90.33(5), Ni2–S2–Ni1 89.41(5).

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† Electronic supplementary information (ESI) available: Preparation and characterisation data for complexes **2**–**5**. See DOI: 10.1039/b512744k

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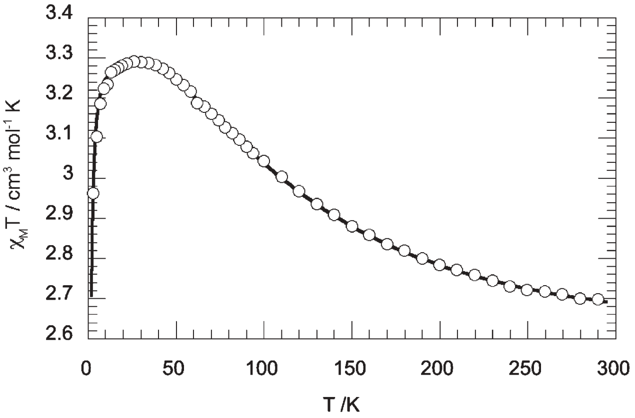

Fig. 2 Plot of χ_mT against T for **3**·BPh$_4$. The solid line represents the best theoretical fit of the magnetic susceptibility data by full-matrix diagonalization of the spin Hamiltonian $H = -2J\,S_1\cdot S_2 + D(S_{z1}{}^2 + S_{z2}{}^2 - 4/3) + g\beta(S_1 + S_2)B$. Experimental and calculated data are provided as ESI.†

centres in a symmetrical fashion to generate a bioctahedral N$_3$Ni^{II}(μ-S)$_2$(μ-BH$_4$)Ni^{II}N$_3$ core structure that has never been observed before in nickel–thiolate chemistry. There are no interactions between the MeCN of solvent of crystallization and the [(L)Ni$^{II}_2$(μ-BH$_4$)]$^+$ cations. The average Ni–H distance at 1.89(4) Å compares well with that in the mononuclear NiS$_4$H$_2$ complex [Ni^{II}(*bmp*)$_2$] (*bmp* = bis(2-mercapto-1-methylimidazolyl)-borate),[14] the only other sulfur-rich Ni(II) complex with B–H···Ni interactions that has been structurally characterised.

Magnetic susceptibility measurements have been carried out to see whether magnetic exchange interactions are present in **3**·BPh$_4$. As can be seen from Fig. 2, the product χ_mT (per dinuclear complex) gradually increases from 2.69 cm^3 K mol^{-1} at 295 K to a maximum of 3.29 cm^3 K mol^{-1} at 28 K, and then decreases rapidly to 2.74 μ_B at 2 K. This behaviour indicates an intramolecular ferromagnetic exchange interaction between the two Ni^{2+} ions in **3**.[15]

Least-squares fit of the magnetic susceptibility data by full-matrix diagonalization of the appropriate spin Hamiltonian $H = -2J\,S_1\cdot S_2 + D(S_{z1}{}^2 + S_{z2}{}^2 - 4/3) + g\beta(S_1 + S_2)B$ gave $J = 27$ cm^{-1}, $D = +4.3$ cm^{-1}, and $g = 2.09$ (or alternatively $J = 27.5$ cm^{-1}, $D = -3.9$ cm^{-1}, and $g = 2.09$). Interestingly, the J value of 27 cm^{-1} is by far the largest value that has ever been observed in dinuclear nickel(II) complexes supported by (L)$^{2-}$.[16] It indicates that the ferromagnetic magnetic exchange interactions are not only propagated *via* the bridging thiolate functions but also through the μ$_{1,3}$-bridging borohydride ion. To the best of our knowledge, this property of the BH$_4^-$ ion has not been documented previously in the literature. This suggests its use as a building block in the construction of molecular based magnetic materials.

Preliminary results show that **3** reacts with protic reagents HA, such as HCl, H$_2$O, or HCO$_2$H with liberation of H$_2$ and formation of the respective [(L)Ni$^{II}_2$(A)]$^+$ species (A = Cl$^-$ **1**, OH$^-$ **4** and HCO$_2^-$ **5**). Complexes **1** and **4** have been reported earlier. The new complex **5** is also readily produced by the reaction of **3** with CO$_2$. IR measurements of **5**·BPh$_4$ showed two absorption bands at 1602 and 1424 cm^{-1}, attributable to the symmetric and antisymmetric stretching frequencies of a μ$_{1,3}$-bridging formate ion. This was also confirmed by an X-ray crystal structure determination of **5**·BPh$_4$ (see ESI†).

In conclusion, we have prepared the first stable dinuclear nickel(II) borohydrido-bridged complex of a macrodinucleating hexaaza-dithiophenolate ligand. Work in progress is directed towards the synthesis of related compounds with bridging hydride ligands by taking advantage of the steric protection offered by the supporting ligand. Such compounds may also aid in understanding the electronic structures and the reactivities of the dinuclear active sites of the hydrogenase enzymes.

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Notes and references

§ *Crystal data for [(L)Ni$^{II}_2$(μ$_{1,3}$-BH$_4$)](BPh$_4$)·2MeCN* (**3**·BPh$_4$·2MeCN): C$_{66}$H$_{94}$B$_2$N$_8$Ni$_2$S$_2$, M = 1202.65. Triclinic, space group $P\bar{1}$, (no. 2), a = 15.992(3), b = 16.080(3), c = 16.515(3) Å, α = 63.82(3), β = 70.97(3), γ = 66.47(3)°, V = 3436(1) Å^3, Z = 2, $D_{\text{calcd.}}$ = 1.162 g cm^{-3}, μ(Mo-Kα) = 0.651 mm^{-1}, T = 210 K. Using Mo-Kα radiation (0.71073 Å), a total of 31051 reflections were collected of which 16023 were independent. Refinement converged to R_1 = 0.0749, wR_2 = 0.2053 [I > 2σ(I)]. Hydrogen atoms for the η^2-BH$_4$ ligand were located from the final difference map and were refined isotropically with U_{eq}(H) 1.2 times that of the boron to which they are attached. The MeCN solvate molecules were found to be disordered over two positions. CCDC 280004. *Crystal data for [(L)Ni$^{II}_2$(μ$_{1,3}$-O$_2$CH)](BPh$_4$)* (**5**·BPh$_4$): C$_{63}$H$_{85}$BN$_6$Ni$_2$O$_2$S$_2$, M = 1150.72. Monoclinic, space group $P2_1/n$, a = 18.452(4), b = 34.531(7), c = 18.452(4) Å, β = 92.22(3)°, V = 11748(4) Å^3, Z = 8, D_c = 1.301 g cm^{-3}, μ(Mo-Kα) = 0.761 mm^{-1}, T = 210 K. Using Mo-Kα radiation (0.71073 Å), a total of 74914 reflections were collected of which 28479 were independent. Refinement converged to R_1 = 0.0778, wR_2 = 0.1651 [I > 2σ(I)]. CCDC 280005. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512744k

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