An "Intermediate Spin" Nickel Hydride Complex Stemming from Delocalized $Ni_2(\mu\text{-H})_2$ Bonding

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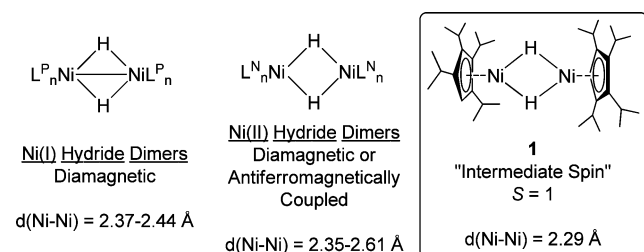[§]CNRS, CRPP, UPR 8641, F-33600 Pessac, France

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S *Supporting Information*

ABSTRACT: The nickel hydride complex $[Cp'Ni(\mu\text{-}H)]_2$ (**1**, Cp′ = 1,2,3,4-tetraisopropylcyclopentadienyl) is found to have a strikingly short Ni−Ni distance of 2.28638(3) Å. Variable temperature and field magnetic measurements indicate an unexpected triplet ground state for **1** with a large zero-field splitting of +90 K (63 cm^{-1}). Electronic structure calculations (DFT and CASSCF/CASPT2) explain this ground state as arising from half occupation of two nearly degenerate Ni−Ni π^* orbitals.

Nickel hydride compounds are prominent in synthetic[1] and biological[2] catalysis. The diamond-shaped $Ni_2(\mu\text{-H})_2$ core is an important structural motif (Chart 1),[3,4] and it can be supported by a variety of P- or N-donor ligands (denoted L^P or L^N, respectively) that strongly influence the electronic structure. Binuclear $[L^PNi(\mu\text{-H})]_2$ compounds, where L^P is a neutral chelating diphosphine, are diamagnetic due to the presence of a Ni(I)−Ni(I) bond with typical Ni−Ni bond lengths of 2.41 Å.[3] Here, the local Ni(I) spin states (i.e., $S_{Ni} = 1/2$) strongly couple together antiferromagnetically to yield a singlet $S_G = 0$ ground spin state for the complex ($\chi T = 0$ cm^3 K mol^{-1}; here χ is the molar magnetic susceptibility and T is temperature). In contrast, $Ni_2(\mu\text{-H})_2$ complexes supported by anionic or neutral L^N ligands contain Ni(II) ions that display either a local low-spin ($S_{Ni} = 0$) or high spin ($S_{Ni} = 1$) configuration depending on their geometry.[4] In complexes with $S_{Ni} = 1$, weak antiferromagnetic exchange coupling occurs between the two ions leading to an $S_G = 0$ 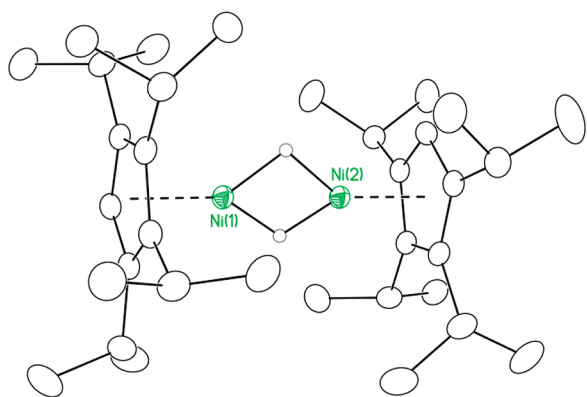ground spin state for the complex. However, as the exchange coupling is small, at room temperature (rt) the two Ni(II) ions appear uncoupled from each other, leading to a total χT value of ~ 2.0 cm^3 K mol^{-1}, i.e., the sum of the two metal ion site magnetic moments. We report here the first $Ni_2(\mu\text{-H})_2$ binuclear complex bearing cyclopentadienyl (Cp) type ligands. It has magnetic properties midway between those of known compounds ($\chi T \approx 1.0$ cm^3 K mol^{-1}), which indicates an unexpected "intermediate spin" $S_G = 1$ ground state and thus represents a new and unexpected electronic state available to $Ni_2(\mu\text{-H})_2$ compounds.

Known Ni hydride complexes supported by only Cp ligands are polynuclear clusters, e.g., $(CpNi)_4H_3$.[5] By utilizing the bulky 1,2,3,4-tetraisopropylcyclopentadienyl (Cp′) ligand, first reported by Sitzmann,[6] it was possible to synthesize the binuclear complex $[Cp'Ni(\mu\text{-H})]_2$, **1**, as a dark orange-red species prepared at −17 °C by mixing NaCp′ and NiBr$_2$·DME in THF, followed by addition of NaH, removal of solvent, and extraction into pentane. The first step of the reaction is identical to the method reported by Sitzmann et al. to prepare $[Cp'Ni(\mu\text{-}Br)]_2$ (**2**).[7] Thus, **2** is likely an intermediate in the formation of **1**. Compound **1** is soluble in THF, pentane, benzene, and toluene and is extremely sensitive to water, which causes a striking color change to dark forest green, attributable to an unidentified hydrolysis product.

In the crystal structure of **1**, the molecules initially appeared to be of Cp′Ni−NiCp′ having an unsupported Ni−Ni bond. We were, however, able to locate bridging hydride ligands in the positions shown in Figure 1, in agreement with mass spectral data that indicate that **1** is a dihydride ($m/z = 584.25$). The Ni···Ni distance in **1**, 2.28638(3) Å, is shorter than that in any other binuclear Ni(II) complex except for the Ni≡Ni distance of 2.28 Å in $[C(SiMe_3)(PMe_3)_2]Ni_2Cl_2$.[8] The Ni···Ni distance in **1** is significantly longer than the calculated Ni≡Ni distance of 2.06 Å for the hypothetical $[CpNi]_2$ molecule,[9] but similar to the Co−Co distance of 2.249(1) Å in $Cp*_2Co_2(\mu\text{-H})_3$.[10] Despite the inherent uncertainty of the H atom positions derived from X-ray data, we may infer a planar $Ni_2(\mu\text{-H})_2$ core from the C_5···Ni−Ni angles of ~178°, where C_5 denotes the Cp′ centroid. For the series of known $[Cp'Ni(\mu\text{-X})]_2$ compounds (X = Br, S, Se, Te,

Chart 1. $Ni_2(\mu\text{-H})_2$ Complexes

Ni(I) Hydride Dimers
Diamagnetic
d(Ni-Ni) = 2.37-2.44 Å

Ni(II) Hydride Dimers
Diamagnetic or
Antiferromagnetically
Coupled
d(Ni-Ni) = 2.35-2.61 Å

1
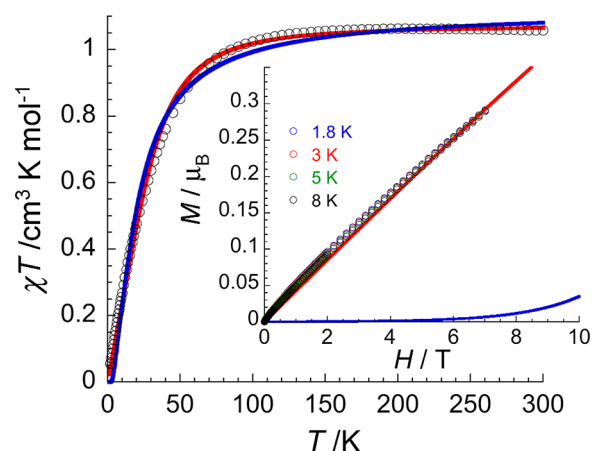"Intermediate Spin"
$S = 1$
d(Ni-Ni) = 2.29 Å

Figure 1. Crystal structure of **1** with thermal ellipsoids shown at the 50% probability level. All H atoms, except for the bridging hydride ligands, are omitted for clarity.

Figure 2. Temperature dependence of the χT product (χ is the magnetic susceptibility equal to M/H per mole of **1** at 1000 Oe) between 1.8 and 270 K for a polycrystalline sample of **1**. Solid lines are the fits using an S_{Ni} = 1 spin dimer model (see text, blue line) and the S_G = 1 ZFS model (see text, red line). Inset: M vs H data with numerical simulations using the parameters: (i) $S_1 = S_2 = 1$, $g = 1.50$ and $J/k_B = -8.4$ (blue line) and (ii) $S_G = 1$, $g = 2.07$ and $D/k_B = +90$ K (red line).

and OAr (Ar = 2,6-dimethylphenyl)), Ni···Ni separations > 3.0 Å indicate little direct Ni–Ni bonding.[7,11] The $[Cp'Ni(\mu\text{-}CO)]_2$ complex with Ni–Ni = 2.39 Å is proposed to have a Ni(I)–Ni(I) bond,[12] and therefore the possibility of direct Ni–Ni orbital overlap may also be considered for **1**.

The ^{1}H NMR spectrum of **1** shows four paramagnetically shifted signals at 10, 13, 14, and 20 ppm (Figure S1), attributed to the isopropyl methyl resonances as discussed in an NMR investigation of **2**.[13] Compound **1** displays an intense band in its absorption spectrum at 505 nm ($\varepsilon = 11\,000$ cm^{-1} M^{-1}, Figure S2), which is somewhat lower in energy than in the case of other $[Cp'Ni(\mu\text{-}X)]_2$ compounds.

Magnetic susceptibility measurements on **1** revealed a χT product of 1.08 cm^3 K mol^{-1} at 300 K that plummets below 50 K. We tested two possible causes for the observed magnetic behavior: intracomplex antiferromagnetic coupling between the two S_{Ni} = 1 Ni(II) spin centers, which would yield a singlet S_G = 0 ground spin state, or a large magnetic anisotropy of the system as a whole, with an unexpected triplet ground state (S_G = 1). The room temperature χT product is far from the expected value for two noninteracting S_{Ni} = 1 Ni(II) centers (2.0 cm^3 K mol^{-1} for g = 2), casting doubt on the antiferromagnetic coupling interpretation. The data were nevertheless fitted to a model using the isotropic S_{Ni} = 1 spin dimer Heisenberg Hamiltonian: $H = -2JS_1 \cdot S_2$, where J is the Ni–Ni magnetic interaction and $S_1 = S_2 = S_{Ni} = 1$.[14] Although the data fit this model well from a mathematical standpoint (Figure 2, blue line), giving $J/k_B = -8.4(7)$ K, the resulting $g = 1.50(5)$ makes little physical sense, as g values greater than 2.00 are seen in Ni(II)–Cp complexes.[7,15] Furthermore, a simulation[16] of an $S_1 = S_2 = 1$ dimer using the parameters found from the χT versus T fit is inconsistent with the field-dependent magnetization (M) data; the simulation only begins to show an increase in M at very high field (>6 T, Figure 2, inset, blue line).

We therefore tested the unprecedented possibility of an S_G = 1 ground spin state for the Ni$_2(\mu\text{-}H)_2$ core by fitting the χT data using a model that includes axial zero-field splitting (ZFS) based on the Hamiltonian: $\mathbf{H} = D \cdot S_z^2$, where D is the axial ZFS parameter and $S_z = 1$.[17] This model gave a more reasonable g value of 2.07(5) and $D/k_B = +90(5)$ K (+63(3) cm^{-1}) (Figure 2, red line). Moreover, the simulation of the M vs H data with these g and D/k_B values is in excellent agreement with the experimental data (Figure 2, inset, red line). Thus, the magnetic data clearly indicate a novel triplet ground state for **1**.

To examine the electronic basis for the unusual spin state of **1**, we utilized a molecular orbital analysis. Here we take the Ni–Ni vector as the z axis of the molecular coordinate system with the Ni$_2(\mu\text{-}H)_2$ core occupying the yz plane. The typical $[Cp'Ni]^+$ orbital ordering of d$_{xy}$, d$_{x^2-y^2}$ < d$_{z^2}$ ≪ d$_{xz}$, d$_{yz}$, shown in column (a) of Figure 3, is split by Ni–Ni orbital overlap to yield Ni$_2$ orbitals of σ, π, and δ symmetry in a $[Cp'Ni···NiCp']^{2+}$ pair (Figure 3b).

To consider bonding between the Ni$_2$ unit and the two hydride ligands (in D_{2h} symmetry), the a$_g$ H 1s combination (Figure 3d) is best suited to interact with the Ni–Ni σ bonding a$_g$ combination of Ni d$_{z^2}$ orbitals. This interaction will lead to a low-energy orbital that has bonding character between all four of the core atoms (1a$_g$) as well as a higher energy orbital that has Ni–Ni bonding character but Ni–H antibonding character (3a$_g$*). The H 1s combination of b$_{2u}$ symmetry can only interact with the Ni–Ni π-bonding b$_{2u}$ combination in which the d$_{yz}$ orbitals lie in the plane with the H atoms. Thus, a low energy Ni$_2(\mu\text{-}H)_2$ bonding orbital, 1b$_{2u}$, will be formed as well as a high-energy antibonding combination, 2b$_{2u}$*, which is raised in energy above the Ni$_2$ π* orbitals. Filling the resulting orbital manifold, given in column (c) of Figure 3, with the 20 electrons of the $[Ni_2H_2]^{2+}$ unit leads immediately to an explanation for the triplet ground state for **1** due to the filling of electrons up to the Ni–Ni π* orbitals of b$_{2g}$ and b$_{3g}$ symmetry. Since these b$_{2g}$ and b$_{3g}$ orbitals cannot interact with the H atoms, they remain quasi-degenerate. Thus, placing two electrons into these orbitals leads to the overall ^{3}B$_{1g}$ ground state.

The results of density functional theory (DFT) and *ab initio* CASSCF/CASPT2 calculations on **1** are consistent with the above orbital analysis. Of primary interest are the frontier orbitals: 1b$_{3u}$, 1b$_{2g}$, 1b$_{3g}$, and 2b$_{2u}$*. These orbitals are depicted in Figure 3e, where the occupied 1b$_{3u}$ orbital can be seen to have Ni–Ni π bonding character. The SOMOs 1b$_{2g}$ and 1b$_{3g}$ are Ni–Ni π* orbitals, and they are indeed quasi-degenerate, having a calculated splitting of only 57 cm^{-1} (82 K). The LUMO, 2b$_{2u}$*, is, as expected, the Ni$_2(\mu\text{-}H)_2$ antibonding orbital that would have Ni–Ni π bonding character if the hydride ligands were not present. The antibonding interaction with the hydride ligands has raised this orbital by roughly 1000 cm^{-1} above 1b$_{3u}$. The computed ground state wave function of **1** at the CASSCF/
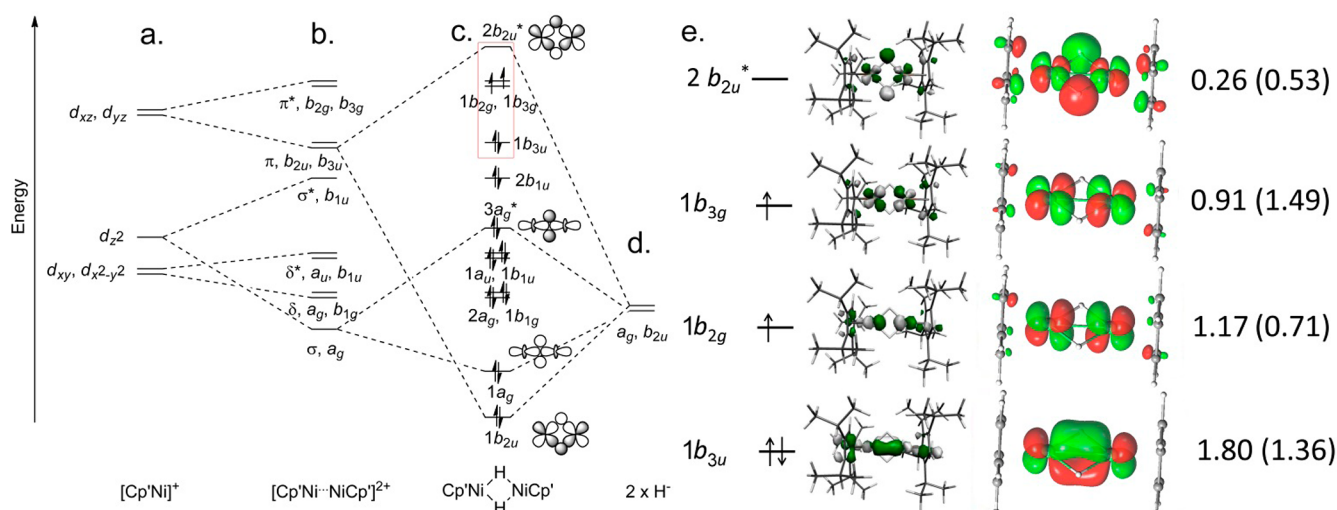
Figure 3. (a−d) Molecular orbital analysis of **1** assuming D_{2h} symmetry with the $Ni_2(\mu\text{-H})_2$ core occupying the yz plane. (e) Frontier orbitals of **1**, in detail from the red boxed region in (c). The green/gray orbitals are derived from DFT/B3LYP/TZVP calculations, and those in green/red derive from CASSCF calculations. The numbers listed next to each CASSCF orbital are the occupation numbers for the triplet (singlet) state.

CASPT2 level was found to be composed of 70% $|1b_{3u}^{2}1b_{2g}^{1}\text{-}1b_{3g}^{1}2b_{2u}^{0}\rangle$ and 12% $|1b_{3u}^{1}1b_{2g}^{1}1b_{3g}^{2}2b_{2u}^{0}\rangle$ character. This multireference character leads to the following occupation numbers $|1b_{3u}^{1.80}1b_{2g}^{1.17}1b_{3g}^{0.91}2b_{2u}^{0.26}\rangle$, which suggests significant static electron correlation among these four orbitals, in agreement with the near-degeneracy seen in the DFT results. This aspect is further reflected in the position of the corresponding singlet ^1A_g state lying at only 900 cm^{-1} above the ground state. The ^1A_g state has a stronger multireference character: 48% $|1b_{3u}^{2}1b_{2g}^{0}1b_{3g}^{2}2b_{2u}^{0}\rangle$ + 16% $|1b_{3u}^{0}1b_{2g}^{2}\text{-}1b_{3g}^{2}2b_{2u}^{0}\rangle$ + 8% $|1b_{3u}^{2}1b_{2g}^{2}1b_{3g}^{0}2b_{2u}^{0}\rangle$, plus other minor contributions; the occupation numbers are $|1b_{3u}^{1.36}1b_{2g}^{0.71}\text{-}1b_{3g}^{1.49}2b_{2u}^{0.53}\rangle$. Mulliken spin-density analysis of the $^3B_{1g}$ state shows that 0.98 electrons are localized on each Ni center, suggesting that the spin density is distributed equally across both Ni atoms as expected for the half-occupation of the two Ni−Ni π^* orbitals.

For the $1b_{3u}$ Ni−Ni π bonding orbital, the corresponding π antibonding orbitals ($1b_{2g}$ and $1b_{3g}$) are each half-filled. Therefore, there is a net 0.5 π bonding interaction in one plane that is counterbalanced by 0.5 π^* antibonding interaction in an orthogonal plane, and it makes little sense to discuss any localized Ni−Ni bonding in **1**. However, we note that the $Ni_2(\mu\text{-H})_2$ bonding orbital $1b_{2u}$ is doubly occupied, while its antibonding counterpart $2b_{2u}^*$ is nearly empty (occupancy of 0.27 electrons). Thus, we may describe a four-center bond that holds together the $Ni_2(\mu\text{-H})_2$ core, which is reflected in calculated Ni−Ni bond orders of 0.5−0.8.

In summary, we report the first example of a $Ni_2(\mu\text{-H})_2$ complex supported by cyclopentadienyl ligands. This complex displays a short Ni−Ni distance of 2.29 Å that results in the four frontier orbitals of the molecule being within 1000 cm^{-1} of each other. This near-degeneracy leads to a triplet ground spin state for the molecule and a low-lying singlet excited state. The two unpaired electrons in the d_{xz} and d_{yz} orbitals provide a strong, cylindrically symmetric spin distribution, leading to strong axial magnetic anisotropy manifested in axial ZFS on the order of 60 cm^{-1}. It is somewhat similar to the case of metal−metal bonded $Ru_2(II,II)$ compounds with two half-occupied π^* orbitals, which also have large (>100 cm^{-1}) axial ZFS.[18] These features could be useful design principles for preparing molecules with high magnetic anisotropy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and theoretical details; Figures S1−S4; Tables S1−S3; crystallographic information for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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