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Nickel(II) Chain with Alternating End-On/End-to-End Single Azido Bridges: A Combined Structural, Magnetic, and Theoretical Study

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The reaction of a tridentate Schiff base LH (L^-: 1,1,1-trifluoro-7-(dimethylamino)-4-methyl-5-aza-3-hepten-2-onato) with a Ni(II) salt in the presence of azide salt has led to a new alternating end-on (EO)/end-to-end (EE) azido-bridged Ni(II) chain of formula $\{[Ni_2(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)(L)_2(MeOH)_2]\}_n$. Its originality lies in the presence of single EE and EO coordination modes for the azide. It crystallizes in the $C2/c$ space group, $a = 21.570(7)$ Å, $b = 10.79(1)$ Å, $c = 16.154(5)$ Å, $\beta = 120.81(2)°$, $Z = 4$. The chain can be viewed as $\{Ni_2(N_3)(L)_2(MeOH)_2\}^+$ dimeric units linked to each other in a zigzag pattern by the other azide. Magnetic susceptibility and magnetization measurements have been performed and revealed that the chain can magnetically be depicted as isolated $\{Ni_2(N_3)\}$ units exhibiting antiferromagnetic interaction ($J_{AF} \sim -37$ cm^{-1}). Ab initio calculations confirmed the efficient magnetic coupling through the EE bridge and vanishingly small EO $\{Ni_2(\mu_{1,1}\text{-}N_3)\}$ interactions.

Introduction

The search for new functional molecular-based materials has led to tremendous developments in low-dimensional systems, in both chemistry and physics communities.[1,2] One of the main challenges in the synthesis of extended 1D-systems is to prevent the local magnetic moments from canceling out. Obviously, this condition is fulfilled as soon as ferromagnetic interactions dominate. However, in the presence of most frequent antiferromagnetic interactions, pioneer approaches were devoted to regular heterospin ferrimagnetic chains[2] holding alternating spin carriers, coupled through a unique exchange constant. Another strategy consists of varying the magnetic exchange constants between homospin carriers.[3] Finally, the use of strong anisotropic metal ions to reduce the magnetization relaxation has generated the promising field of single-chain magnets (SCMs).[4]

Pseudo-halide anions are known to be excellent ligands to obtain discrete three-dimensional materials. Among these, the azido ligand turned out to be extremely versatile in linking metal ions and a remarkable magnetic coupler for propagating interactions between paramagnetic ions. The structural variety of the azido complexes ranges from molecular clusters to extended 1D to 3D materials.[5,6] The main expression of the versatility of this ligand lies in the

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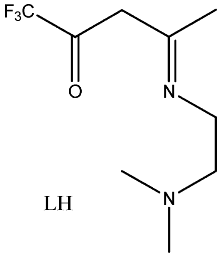
different coordination modes it can offer. The most common are the end-to-end ($\mu_{1,3}$-N_3, EE) and end-on ($\mu_{1,1}$-N_3, EO) modes, whereas triply ($\mu_{1,1,1}$,[7] $\mu_{1,1,3}$[8]) or quadruply ($\mu_{1,1,1,1}$,[9] $\mu_{1,1,3,3}$[10]) coordinated modes remain relatively rare. An additional interesting feature that illustrates the versatility of this ligand is in the number of azido ions involved in the coordination of the metal centers. One, two, or three azides can be encountered, both for the EE and EO modes.[5] Let us note that, when a single azide connects two metal centers in an EO fashion, it is always associated with another bridging moiety. To our best knowledge, only one exception has been reported for a Cu(II) chain.[11] Futhermore, different bridging modes of the azido ions may simultaneously exist in the same species, leading to original alternating topologies and magnetic behaviors exemplified by the reported $[\mathrm{EO-EE}]_n$, which is the most common, and $[\mathrm{EO-EE-EE}]_n$, $[\mathrm{EO-EO-EO-EE}]_n$, and $[\mathrm{EO-EO-EO-EO-EE}]_n$ sequences.[12]

From the magnetic point of view, depending on the bonding and symmetry modes of the azido bridge, the sign and amplitude of the magnetic exchange can be effectively tuned. In general, the EE mode favors antiferromagnetic interaction, whereas the EO one leads to ferromagnetic behavior.[5,13] It is also known that structural parameters greatly affect the nature and magnitude of the magnetic exchange in these systems.[5b,14] In that sense, we have recently demonstrated that a relatively small structural deformation of the EE coordination mode can switch the magnetic behavior from ferromagnetic to antiferromagnetic in Cu(II)-based complexes.[15] Apart from the tremendously abundant Cu(II) compounds, Ni(II), Mn(II), Fe(II), and Co(II) azido-bridged chains have been reported in the literature, some of them showing promising SCM behavior.[16]

Scheme 1. Schematic Drawing of the LH Ligand



As part of this work, we recently synthesized a new Cu(II) azide dinuclear complex, where each metal ion is coordinated by a tridentate Schiff base ligand and two azides in an EE mode.[15] Our aim was then to extend this study to a more anisotropic ion, such as Ni(II) holding $S = 1$ spin states. We here report the synthesis and magnetic characterization of an unprecedented alternating single end-on and end-to-end azido-bridged Ni(II) chain $\{[\mathrm{Ni_2}(\mu_{1,1}\text{-}\mathrm{N_3})(\mu_{1,3}\text{-}\mathrm{N_3})(\mathrm{L})_2(\mathrm{MeOH})_2]\}_n$. In the light of the resolved crystal structure, a detailed analysis of the underlying magnetic pathways through the azido bridges is proposed on the basis of correlated ab initio calculations. Such calculations allow us to evaluate the sensitivity of the EO interactions with respect to structural parameters.

Experimental Section

Caution! *Although we have not experienced any problem with the reported compound in this work, azide complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.*

All chemicals and solvents were used as received. All preparations and manipulations were performed under aerobic conditions.

Synthesis of the Ligand (LH). The synthesis of the ligand LH (L^-, 1,1,1-trifluoro-7-(dimethylamino)-4-methyl-5-aza-3-hepten-2-onato) has been previously reported (Scheme 1).[15] 1,1,1-Trifluoro-2,4-pentanedione (1 mL, 8.24 mmol) was dissolved in 20 mL of methanol cooled in an ice bath. Then, 0.95 mL (8.65 mmol) of *N,N*-dimethylethylendiamine was added under stirring. After 12 h of additional stirring at room temperature, the solvent was removed under vacuum. The oily yellow material collected was used without further purification.

Synthesis of the Complex $\{[\mathrm{Ni_2}(\mu_{1,1}\text{-}\mathrm{N_3})(\mu_{1,3}\text{-}\mathrm{N_3})(\mathrm{L})_2(\mathrm{MeOH})_2]\}_n$ (1). A solution of 0.238 g (1 mmol) of $\mathrm{NiCl_2{\cdot}6H_2O}$ with 0.224 g (1 mmol) of the ligand (LH) in 20 mL of methanol was added to

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Table 1. Crystal Data and Structural Refinement Parameters for **1**

	$\{[Ni_2(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)(L)_2(MeOH)_2]\}_n$
refined formula	$C_{20}H_{36}F_6N_{10}Ni_2O_4$
molecular weight (g·mol^{-1})	711.9
T (K)	293
λ (Mo Kα) (Å)	0.71073
crystal color	blue
crystal system	monoclinic
space group	$C2/c$ (no. 15)
a (Å)	21.570 (7)
b (Å)	10.79 (1)
c (Å)	16.154 (5)
β (deg)	120.81 (2)
V (Å^3)	3228 (4)
Z	4
ρ_{calc} (g cm^{-3})	1.465
μ (mm^{-1})	1.252
F(0000)	25536
$R(F)^a$ [$I > 3\sigma(I)$]	0.0521
$R_w(F)^b$ [$I > 3\sigma(I)$]	0.0601
S	1.13
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	−0.47/0.41
no. of reflections used	1934
no. of refined parameters	193

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = \sum[w((F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

a solution of 0.130 g (2 mmol) of the NaN_3 in 10 mL of methanol. Triethylamine (0.5 mL, 3.5 mmol) was added to the resulting green solution. The brown precipitate that formed was filtered off and the resulting brown solution was slowly evaporated. After 10 days, green plate shaped crystals suitable for single-crystal X-ray diffraction were isolated upon filtration. Yield: 28%. Anal. Calcd for $NiC_{10}H_{18}N_5O_2F_3$ (M = 318.0 g mol^{-1}): C, 37.8; H, 5.71; N, 22.0; Ni, 18.5. Found: C, 38.1; H, 5.52; N, 22.1; Ni, 18.0.

Crystallographic Data Collection and Refinement. Diffraction data were collected at room temperature using a Nonius Kappa CCD and the related analysis software:[17] Lorentz−polarization correction, peak integration, and background determination were carried out with the DENZO program; frame scaling and unit-cell parameters refinement were made through the SCALEPACK program. The lattice constants were refined by least-square refinement using 1934 reflections (0.99° < θ < 24.8°). No absorption correction was applied to the data sets. The structure was solved by direct methods using the SIR97 program[18] combined with Fourier difference synthesis and refined against F using reflections with [$I/\sigma(I) > 3$] via the program CRYSTALS.[19] All the thermal atomic displacements for non-hydrogen atoms have been refined with anisotropic terms. Hydrogen atoms have been located either theoretically or by Fourier difference. X-ray crystallographic data and refinement details are summarized in Table 1. Selected interatomic distances, bond lengths, and bond angles are listed in Table 2.

Magnetic Measurements. The magnetic measurements were carried out with a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from −7 to 7 T. Measurements were performed on a polycrystalline sample of 28.15 mg. The ac susceptibility was measured with an oscillating field of 3 Oe and frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for the sample holder and diamagnetic contribution.

Table 2. Selected Bond Lengths, Distances (Å), and Angles (deg) for **1**

Ni1−O1	2.035(3)	Ni1−N3−Ni1	133.3(2)
Ni1−N6	2.109(4)	Ni1−N6−N7	124.1(2)
Ni1−N3	2.091(2)		
Ni1−N2	2.175(4)	Ni1−N6−N6−Ni1^a	180.0(2)
Ni1−N1	2.035(3)		
Ni1−O2	2.138(3)		
Ni1−Ni1^b	3.8394(9)		
Ni1−Ni1^b	5.868(2)		

[a] Torsion angle. [b] Symmetry transformations used to generate equivalent atoms: −x, −y, −z.

Computational Details. Let us mention that all our calculations were performed using the crystal data and that no geometry optimizations were undertaken. Since the system we are interested in consists of open d-shell ions, we favored explicitly correlated ab initio calculations. Besides, the evaluation of magnetic coupling constants between two $S = 1$ Ni(II) ions calls for an accurate low-energy spectrum description (~10 cm^{-1}). Thus, rigorous multireference calculations were carried out including (i) first the leading physical configurations (complete active space self-consistent field, CASSCF) and then (ii) dynamical correlation effects using the dedicated difference configuration interaction (DDCI) method [20] implemented in the CASDI code.[21] Basis sets and pseudopotentials on the Ni atoms (9s6p6d)/[3s3p3d] and nearest-neighbor atoms (4s4p)/[3s2p] for N and (4s5p)/[3s3p] for O were used, whereas the rest of the molecule was described with smaller basis sets, i.e., (4s4p)/[2s2p] for C and (3s)/[1s] for H. Such a strategy has been successfully used in the study of magnetic properties of K_2NiF_4 perovskite.[22] Thus, CASSCF calculations implemented in the MOLCAS 5.4 package were performed, including six electrons in five MOs.[23] This enlarged CAS(6,5) includes two orbitals on each Ni(II) center and one doubly occupied ligand orbital. Along this scheme, one qualitatively introduces in a multireference wave function the leading physical configurations in the different states of interest. It has been shown that the use of an enlarged CAS allows one to reach accuracy with less demanding DDCI-2 calculations.[24] Therefore, we limited our calculations to the DDCI-2 level, using the singlet CASSCF wave function to evaluate the spin state energies.

Results and Discussion

Synthesis. The synthesis of the polymeric complex is based on the one-pot method using the LH ligand (Scheme 1) with metal and azide salts in the presence of a base to deprotonate the ligand. Such a synthetic procedure has already been conducted with Cu(II) salts in a Cu(II)/L/N_3 1/1/1 ratio and has led to a $[Cu_2L_2(N_3)_2]$ dinuclear complex.[15] However, the same procedure with Ni(II) ion has led to the crystallization of red crystals that have been identified as $[NiLN_3]$ monomers with the Ni(II) ion in a square plane

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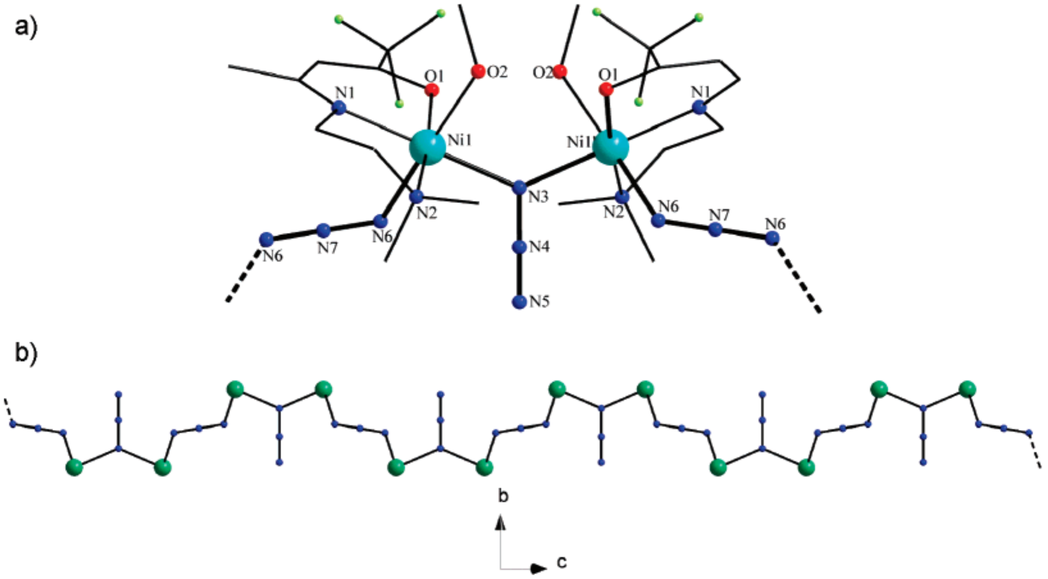

Figure 1. (a) View of the dimeric $\{Ni_2(\mu_{1,1}\text{-}N_3)(L)_2(MeOH)_2\}$ unit, with atomic labels. (b) View of the chain along the *b*-axis without the ligands. Hydrogen atoms have been omitted for clarity.

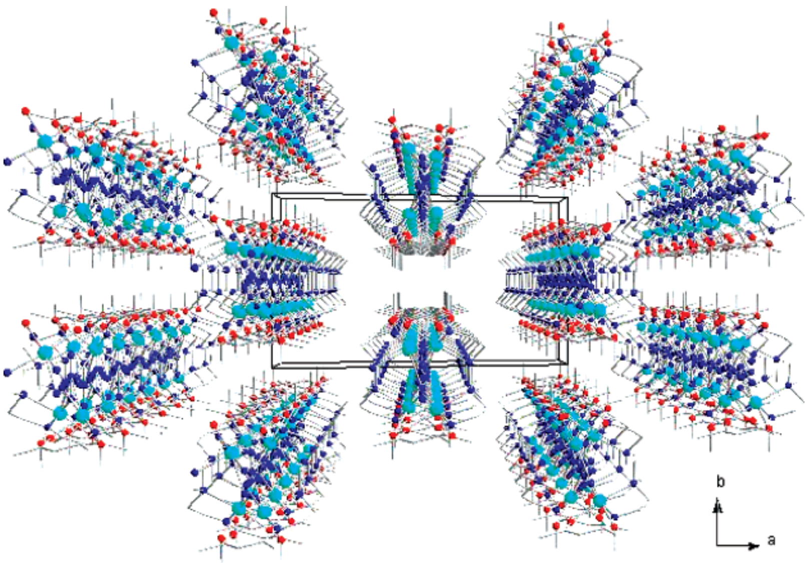

Figure 2. Perspective view of the chains along the *c*-axis. Hydrogen and fluorine atoms have been omitted for clarity.

configuration. It is only in the presence of an excess of azide that the extended $\{[Ni_2(\mu_{1,1}\text{-}N_3)(\mu_{1,3}\text{-}N_3)(L)_2(MeOH)_2]\}_n$ complex (**1**) is formed. The slow evaporation of the solvent allows the crystallization of well-defined crystals characterized by X-ray diffraction.

X-ray Single-Crystal Structure. Complex **1** crystallizes in the monoclinic *C*2/*c* space group. Its structure consists of Ni(II) cations surrounded by one protonated coordinated solvent molecule (MeOH) and one deprotonated ligand (L^-). The resulting {Ni(L)(MeOH)} units are bridged to each other by single azido ligands, giving a neutral monodimensional compound running along the *c*-axis of the unit cell (Figure 1). The chains are parallel and well-isolated from each other, as the shortest distances between the chains are 10.79 and 12.06 Å (Figure 2).

Two azide coordination modes are present in an alternating fashion along the chain. Each Ni(II) cation has one EO bridging mode with one of the neighboring Ni(II) ion, whereas the second is bridged by a single EE azido linkage. The chain can therefore also be viewed as $\{Ni_2(N_3)(L)_2(MeOH)_2\}^+$ dinuclear units linked to each other in a zigzag pattern by the other azide (Figure 1) with a center of symmetry lying in the middle of this EE azido bridge.

The Ni(II) ions are crystallographically equivalent and located in a distorted NiO_2N_4 octahedron. The two oxygen atoms come from a coordinated methanol with Ni−O bond length equal to 2.138(3) Å and from the L^- ligand with Ni−O equal to 2.035(3) Å. Two nitrogen atoms are part of the L^- ligand with Ni−N bond lengths equal to 2.035(3) and 2.175(4) Å and the two others from the N_3 ligands with Ni−N equal to 2.091(2) and 2.109(4) Å for EO and EE bridging modes, respectively (Table 2).

In the EO unit, the Ni1−N3−Ni1′ 133.3(2)° bond angle is higher than traditionally found in previous dimeric {Ni-

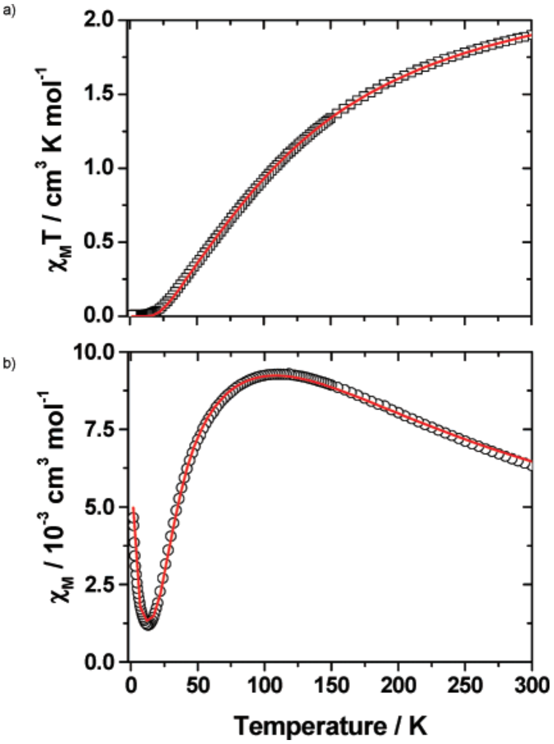

Figure 3. χ_MT (a) and χ_M (b) thermal evolution of compound **1** recorded at 1000 Oe (with $\chi_M = M/H$). Solid lines show the best fit obtained from the dimeric model.

($\mu_{1,1}$-N_3)$_2$Ni} entities (between 101° and 105°). Interestingly, though, on going from double to triple azido bridges between Ni(II) ions, a decrease in the reported Ni−N−Ni bond angles from ~103° to ~86° is observed.[5] Therefore, one may expect an increase of this parameter with only one EO azide link, in agreement with the 133.3° value. The EE azido bridge unit displays an expected Ni1−N6−N7 bond angle of 124.1(2)°, which falls within the usual bond angles values.[5] The EE azido coupler exhibits a symmetric coordination mode and a torsion angle, τ, of 180° (defined as the dihedral angle between the Ni1−N6−N7 and Ni1′−N6−N7 planes).[5] Due to the alternation of EE and EO bridging modes, two different Ni−Ni distances are observed, a short one at 3.839(1) Å and a long one at 5.868(2) Å along the EO and EE linkage, respectively (Table 2).

Magnetic Properties. The magnetic behavior of **1** is shown in Figure 3. At 300 K, the $\chi_M T$ product is 1.90 cm^3 K mol^{-1}. This value is slightly lower than the expected value for two Ni(II) metal ions ($S = 1$, $g = 2$). Decreasing the temperature, the $\chi_M T$ product continuously decreases to reach 0.008 cm^3 K mol^{-1} at 1.8 K, indicating dominant antiferromagnetic interactions between the Ni(II) ions and the presence of a diamagnetic ground state. The susceptibility shows a rounded maximum at 110 K at about 0.0093 cm^3 mol^{-1} and a strong decrease to 0.0012 cm^3 mol^{-1} at 13 K. The sharp increase in χ_M below 13 K can be attributed to paramagnetic impurities with Curie-type behavior. This is confirmed by the M vs H measurements at 1.85 K, which reveal the presence of a small paramagnetic residual contribution (impurity or chain defects).

The presence along the chain of two different kinds of Ni−Ni bridges is consistent with the presence of two kinds of magnetic exchanges. Therefore, two hypotheses are possible: (i) alternating ferro-/antiferromagnetic (F/AF) interactions, where the antiferromagnetic coupling is dominant as no maximum is observed on the χ_MT curve, and (ii) alternating antiferro-/antiferromagnetic (AF/AF) interactions. Data simulations performed either with the equation proposed for an alternating F/AF S = 1 Heisenberg chain[25] or considering the chain as an N-spin ring (with a $N = 8$) led to values of about -37 cm^{-1} for J and around zero for J'. The incertitude on J' is so large that even the sign of this parameter is undetermined. On the basis of the result that $|J| \gg |J'|$, the data were therefore simulated using a dinuclear approach described by the following Heisenberg spin Hamiltonian $\hat{H} = -2J\,\hat{S}_1\,\hat{S}_2$ including a single exchange constant (J). In addition, the paramagnetic impurity was taken into account as $\chi_M = (1 - \rho)\chi_{M(\mathrm{dimer})} + \rho g^2 S(S + 1)/8T$ (where 100ρ is the percentage of this impurity), as well as a temperature-independent paramagnetic (TIP) contribution. Very good agreement with experimental data was found with the refined parameters $g = 2.15$, $J = -37.1$ cm^{-1}, $\chi_{\mathrm{TIP}} =$ 6.3 10^{-4} cm^3 mol^{-1}, and 0.7% of paramagnetic impurity (Figure 3). Let us note that the χ_{TIP} value falls in the range of previously reported values in {Ni$_2$} dinuclears.[26] Such good agreement with this simple model indicates that the introduction of additional parameters is not relevant and would only lead to overparametrization of the fit. Therefore, the magnetic behavior of the chain **1** tends to be equivalent to that of {Ni$_2$} isolated entities. Hence, the singlet spin ground state rules out any chance to observe SCM behavior. As a matter a fact, we did not detect any out-of-phase ac signal.

Ab Initio Calculations. In order to support the analysis of the magnetic properties and to have some insight on the exchange mediated by the EO bridge, ab initio calculations were performed on **1**. The alternation of EO and EE units strongly suggests the presence of two magnetic exchange pathways that can be accessible through Ni$_2$ dimers spectroscopy analysis. Since the Ni(II) ion is formally d^8, one expects exchange interactions between $S = 1$ ions giving rise to three spin states in the Ni$_2$ units, namely singlet (S), triplet (T), and quintet (Q) states. Therefore, we looked into the spin state splitting in the two dinuclear moieties extracted from the crystal structure shown in Figure 4. This particular strategy has been successfully reported in the solid-state chemistry literature, and DDCI-2 calculations have already been performed on this type of dinuclear unit.[27] Our CASSCF calculations on the S state, based on enlarged CAS(6,5) space that includes two orbitals on each Ni(II) center and one doubly occupied ligand orbital, display the expected magnetic orbitals (Figure 4). These active MOs are very similar to the T and Q orbitals, while the three states are almost degenerate at this level of calculation in both dimers. However, the dynamical correlation effects are likely to change this

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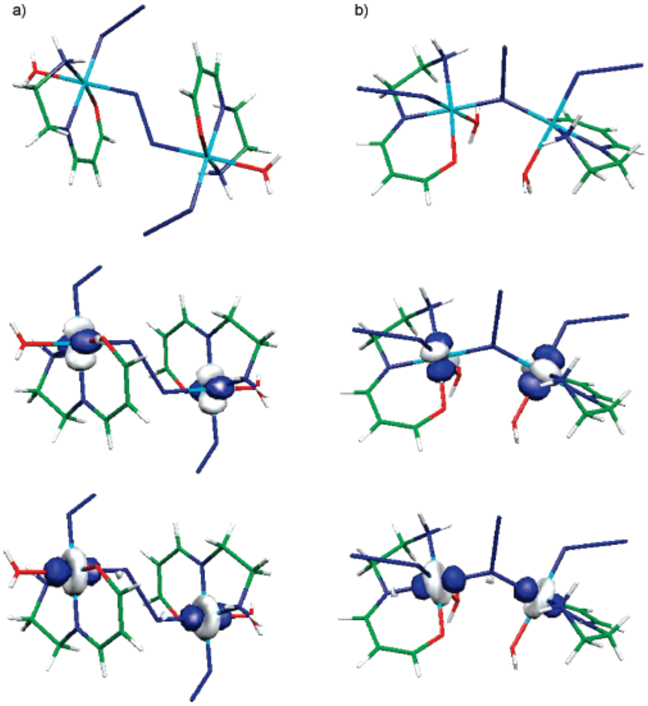

Figure 4. EE (a) and EO (b) dimeric units together with the *xy* (middle) and z^2 (bottom) MOs of the Ni(II) ions.

state of affair. The latter were included at a DDCI-2 level using the singlet MOs.

In a Heisenberg picture, $\hat{H} = -2J\,\hat{S}_1\,\hat{S}_2$, and the energy separations are $6|J|$ and $4|J|$ between the quintet and singlet and between the quintet and triplet states, respectively. Within the EE unit, a relatively large antiferromagnetic exchange constant ($J_{EE} = -53$ cm^{-1}) is calculated in relatively good agreement with the extracted value from experimental data.[28] This is to be contrasted with the EO Ni_2 unit, which exhibits a negligibly small magnetic interaction ($\alpha = J_{EO}/|J_{EE}|$ ratio ~ 0.02). Our ab initio calculations not only confirm the isolated dimers picture but also associate the leading antiferromagnetic exchange pathway to the EE bridging mode. In the light of the calculated $(E_Q - E_S)/(E_Q - E_T)$ ratio,[28] let us mention that the deviation from a pure Heisenberg picture is negligible (less than 2%), ruling out the speculated participation of quadratic terms.[22]

Discussion

The magnetic exchanges mediated through the EE and EO azido bridging modes have been extensively experimentally and theoretically studied. Concerning the EE coordination mode, a general observation of the reported studies reveals that the amplitude of the exchange interaction is smaller in single bridges than in double and triple ones.[5] The values of Ni1−N6−N7 angle equal to 124.1° and $J_{AF} = -37$ cm^{-1} are consistent with the values found in the literature.[5] Interestingly, single EO coordination modes are rather unusual as, to our knowledge, it has only been reported for a Cu(II) chain.[11] Previous DFT calculations performed on double and triple EO bridges have shown that the interaction is always ferromagnetic for Ni−N−Ni angles ranging from 80° to 110°.[14] Whereas calculations and experimental data agree well for double-bridged Ni(II) complexes, they notably differ for triple bridge systems, as the nature of the magnetic interaction (ferromagnetic[29] vs antiferromagnetic[30]) is very sensitive to small Ni−N−Ni angle variations. In **1**, the Ni1−N3−Ni1′ angle is 133°, much greater than the one usually encountered in other EO bridges associated with an almost null ferromagnetic coupling constant. One may therefore wonder whether a variation of this particular structural parameter may induce ferromagnetic character enhancement. The aim of this study is first to know if a chain picture can be recovered with such a single EO bridge. Besides, this ferromagnetic coupling can be used to generate $S = 2$ units. For $\alpha >> 1$, the system might be viewed as a combination of EO bridged $S = 2$ units, antiferromagnetically coupled through EE coordination mode of the azido bridge. Thus, a "Haldane-like" chain could be accessible. Indeed, the Haldane conjecture predicts that chains should be gapped in the case of integer spin quantum number, whereas the energy levels are gapless in the case of half-integer spins.[31] Such a "Haldane-like" picture could be extended to the already reported alternating EE/EO chains.

Therefore, similar ab initio calculations (i.e., CASSCF + DDCI-2) were performed to investigate the variation of the magnetic exchange constant J_{EO} with respect to the Ni1−N3−Ni1′ valence angle, θ, in the EO unit. The θ value was artificially modified from 120° to 140° by displacing the N_3 moieties perpendicular to the Ni−Ni direction, while the rest of the dimer was not altered. Let us mention that the Ni1−N3 and Ni1′−N3 distances were modified by less than 9% as θ is varied. From this magnetostructural inspection, the magnetic exchange constant variations are smaller than 1 cm^{-1}. Such values are not relevant from a computational point of view. Thus, even though our attempt to generate $S = 2$ "Haldane-like" chains was not successful, we believe that the combination of different local spin natures and magnetic interactions still deserves particular attention.

Concluding Remarks. Using the azido bridge versatility, we have prepared and characterized an unprecedented 1-D alternating EO/EE Ni(II) system. The magnetic data suggest that the chain behaves as isolated antiferromagnetic Ni_2 dimers with J_{AF} of -37 cm^{-1}. Our ab initio calculations confirmed this particular picture, and we attributed this antiferromagnetic exchange to the EE coordination mode of the azide ligand. As a matter of fact, the magnetic coupling through the EO azide bridge is negligibly small, $\alpha = J_{EO}/|J_{EE}| \sim 0.02$. Therefore, even if the system can be considered as an extended chain from the chemical point of view, it is magnetically described as isolated antiferromagnetic dimers. On the basis of magnetostructural correlations, our calculations suggest that the magnetic interaction on the EO unit is not sensitive to the Ni−N−Ni valence angle. In order to

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(28) At the CAS-DDCI-2 level, $E_Q - E_S = 320$ cm^{-1} and $E_Q - E_T = 216$ cm^{-1}.

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enhance this particular interaction, and generate synthetic models of $S = 2$ “Haldane-like” chains, we believe that one may consider different synthetic routes.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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