Two New μ-(1,3-Azido)-Bridged Polymers: Alternating Single and Double Bridges in a 1D Nickel(II) Complex and Uniform Bridge in a 2D Copper(II) Complex: Syntheses, Single-Crystal Structures and Magnetic Studies

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Two polymeric azido bridged complexes $[Ni_2L_2(N_3)_3]_n(ClO_4)_n$ (**1**) and $[Cu(bpds)_2(N_3)]_n(ClO_4)_n(H_2O)_{2.5n}$ (**2**) [L = Schiff base, obtained from the condensation of pyridine-2-aldehyde with *N*,*N*,2,2-tetramethyl-1,3-propanediamine; bpds = 4,4′-bipyridyl disulfide] have been synthesized and their crystal structures have been determined. Complex **1**, $C_{26}H_{42}ClN_{15}Ni_2O_4$, crystallizes in a triclinic system, space group $P\bar{1}$ with a = 8.089(13), b = 9.392(14), c = 12.267(18) Å, α = 107.28(1), β = 95.95(1), γ = 96.92(1)° and Z = 2; complex **2**, $C_{20}H_{21}ClCuN_7O_{6.5}S_4$, crystallizes in an orthorhombic system, space group *Pnna* with a = 10.839(14), b = 13.208(17), c = 19.75(2) Å and Z = 4. The crystal structure of **1** consists of 1D polymers of nickel(L) units, alternatively connected by single and double bridging μ-(1,3-N_3) ligand with isolated perchlorate anions. Variable temperature magnetic susceptibility data of the complex have been measured and the fitting of magnetic data was carried out applying the Borrás-Almenar formula for such types of alternating one-dimensional S = 1 systems, based on the Hamiltonian $H = -J\Sigma(S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1})$. The best-fit parameters obtained are J = –106.7 ± 2 cm^{-1}; α = 0.82 ± 0.02; g = 2.21 ± 0.02. Complex **2** is a 2D network of 4,4 topology with the nodes occupied by the Cu^{II} ions, and the edges formed by single azide and double bpds connectors. The perchlorate anions are located between pairs of bpds. The magnetic data have been fitted considering the complex as a pseudo-one-dimensional system, with all copper(II) atoms linked by μ(1,3-azido) bridging ligands at axial positions (long Cu···N_3 distances) since the coupling through long bpds is almost nil. The best-fit parameters obtained with this model are J = –1.21 ± 0.2 cm^{-1}, g = 2.14 ± 0.02.

Introduction

Azide represents an efficient superexchange pathway for propagating magnetic interaction between paramagnetic centers and along with its versatile coordination modes,[1] it is widely used for preparing magnetic materials of various dimensionality.[2,3] In general, the μ-(1,3-N_3) azide bridge creates an antiferromagnetic interaction while the μ-(1,1-N_3) connection mode shows a ferromagnetic interaction.[4] The M–N–M angle in μ-(1,1-N_3), and the M–N–N angle and the M–N_3–M dihedral angle in μ-(1,3-N_3) are the key factors in tuning the magnetic interaction.[5] It is well-established that the type and the connectivity of the coligand, i.e. monodentate, chelate, chelate-bridge, bridge, etc. (either neutral or ionic), dictate the binding modes of the azide ligand. It is also observed that different coligands of similar denticity with azide, in a particular bridging mode, i.e. μ-(1,1-N_3), μ-(1,3-N_3), etc. can affect the magnetic properties even in a same paramagnetic metal system. In fact the shape and size of coligands control the M–N–M angle in μ-(1,1-N_3), and the M–N–N angle and M–N_3–M dihedral angle in μ-(1,3-N_3).[6] In many cases spacers i.e. 4,4′-bipyridine, pyrazine, 1,2-bis(4-pyridyl)ethane, etc., are used in combination with azide to augment the ease of synthesizing multidimensional coordination polymers, leading to magnetic materials. Recently, the 4,4′-bipyridyl disulfide (bpds) ligand, characterized by the twisted –S–S– bridge, has been employed for the construction of coordination polymers showing topologically interesting assemblies.[7] It is worth noting that in most of the cases the bpds ligand coordinates metals in a double bridged fashion and, thanks to the flexible heterocyclic rings, sometimes stabilizes the structure through strong π–π interactions.[8] A literature survey revealed that molecular architecture obtained from the combination of bpds and azide is scarce.

Moreover, reports of alternate double and single μ-(1,3-N_3) bridges in transition metals is also rarely documented,

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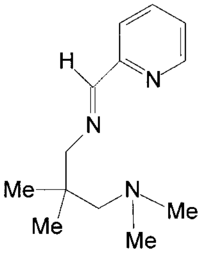
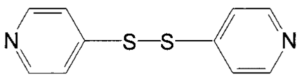
especially with nickel(II), and up to date only one system, with a triamine as coligand, has been reported.[9] The magnetism in such types of alternate bridging systems appears intriguing owing to the number of variable factors in these compounds.[6] The above facts prompted us to synthesize azide species using bpds as well as the tridentate ligand as a coligand. A Schiff base (L), derived from the condensation of pyridine-2-aldehyde with *N*,*N*,2,2-tetramethyl-1,3-propanediamine, has been chosen in the present work as the tridentate ligand. Previous attempts from our group to synthesize alternate single and double μ-(1,3-N_3) 1D chains of nickel using the mentioned Schiff base afforded 1D polymers comprising only single μ-(1,3-N_3) bridges which exhibited novel metamagnetic behavior.[10] In order to achieve alternating single and double azide bridges we have varied the relative molecular amount of the reagents.



L



bpds

The present contribution reports the syntheses, crystal structures and variable temperature magnetic behavior of two azido-bridged coordination polymeric networks, namely $[Ni_2L_2(N_3)_3]_n(ClO_4)_n$ (**1**) and $[Cu(bpds)_2(N_3)]_n(ClO_4)_n(H_2O)_{2.5n}$ (**2**). To the best of our knowledge complex **1** is the second example of a μ-(1,3-N_3) alternate single and double bridging Ni^{II} system. Complex **2** is a 2D grid of 4,4 topology with Cu^{II} ions occupying the nodes, where single azide and double bpds connectors take part in the formation of edges. Magnetic properties of complexes **1** and **2** have been interpreted indicating a very strong antiferromagnetic coupling and a weak antiferromagnetic one, respectively.

Results and Discussion

Description of the Structures

Complex 1

Crystal structure determination reveals that complex **1** consists of positively charged 1D polymers, $[Ni_2L_2(N_3)_3]_n^+$ counterbalanced by lattice perchlorate anions. The ORTEP drawing of the metal center with the atom numbering scheme is shown in Figure 1 while selected geometrical parameters are given in Table 1. The nickel(II) center, *meridionally* coordinated by the tridentate Schiff base, completes the distorted octahedral coordination sphere with three end-to-end bridging azide nitrogen atoms, resulting in a

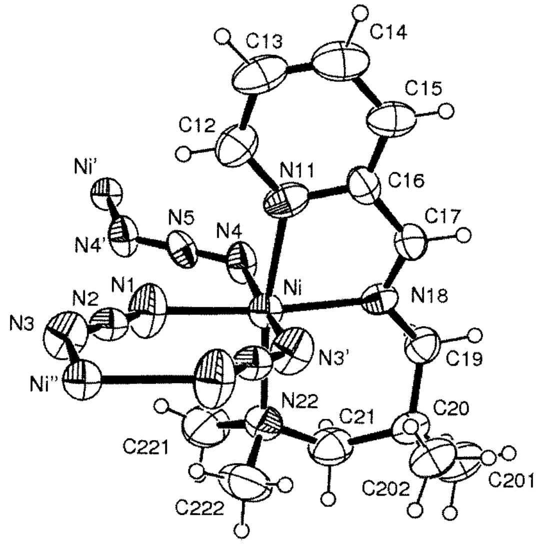


Figure 1. ORTEP plot of complex **1** with atom numbering scheme showing the alternating single and double connecting azide ligands.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1** and **2**.

Complex **1**[a]			
Ni–N(1)	2.096(7)	Ni–N(18)	2.062(6)
Ni–N(3′)	2.164(6)	Ni–N(22)	2.175(7)
Ni–N(4)	2.127(6)	Ni(′)–Ni	5.875(3)
Ni–N(11)	2.107(7)	Ni–Ni(′′)	5.304(3)
N(1)–Ni–N(3′)	90.2(2)	N(4)–Ni–N(18)	91.52(19)
N(1)–Ni–N(4)	88.8(2)	N(4)–Ni–N(22)	93.1(2)
N(1)–Ni–N(11)	95.0(3)	N(11)–Ni–N(18)	78.6(2)
N(1)–Ni–N(18)	173.5(3)	N(11)–Ni–N(22)	171.1(2)
N(1)–Ni–N(22)	93.5(3)	N(18)–Ni–N(22)	93.0(2)
N(3′)–Ni–N(4)	173.3(2)	N(2)–N(1)–Ni	132.9(5)
N(3′)–Ni–N(11)	83.5(2)	N(2′)–N(3′)–Ni	133.2(5)
N(3′)–Ni–N(18)	88.8(2)	N(5)–N(4)–Ni	122.5(3)
N(3′)–Ni–N(22)	93.5(3)	N(3)–N(2)–N(1)	176.1(7)
N(4)–Ni–N(11)	90.0(2)	N(4)–N(5)–N(4′)	180.0
Complex **2**[b]			
Cu(1)–N(11)	2.055(6)	Cu(1)–N(2)	2.447(7)
Cu(1)–N(22)	2.044(6)	S(17)–S(18)	2.027(4)
N(11′)–Cu–N(11)	89.1(3)	N(22)-Cu–N(22′′)	90.5(3)
N(11)–Cu–N(22)	90.3(2)	N(22)–Cu–N(2′)	90.6(2)
N(11)–Cu–N(22′′)	176.5(2)	N(22)–Cu–N(2)	86.3(2)
N(11)–Cu–N(2)	92.8(2)	N(2)–Cu–N(2′)	175.6(3)
N(11)–Cu–N(2′)	90.3(2)	N(1)–N(2)–Cu(1)	140.2(5)

[a] Symmetry operations: (′) at 1 – *x*, 2 – *y*, 2 – *z*; (′′) 1 – *x*, 1 – *y*, 2 – *z*. [b] Symmetry operations: (′) *x*, –*y* + 3/2, –*z* + 3/2; (′′) *x* – 1, –*y* + 3/2, –*z* + 3/2.

NiN_6 chromophore. The Schiff base N donors [N(11), N(18), N(22)] and the azide nitrogen atom N(1) define the equatorial plane around each pseudo octahedral nickel ion [Ni–N(1) 2.096(7), Ni–N(11) 2.107(7), Ni–N(18) 2.062(6), Ni–N(22) 2.175(7) Å]. The *trans* axial positions are occupied by the nitrogen atoms from the two different azides (Ni–N(3′) and Ni–N(4) of 2.164 and 2.127(6) Å, respectively) with a N(3′)–Ni–N(4) bond angle of 173.3(2)°. The slight distortion of each Ni^{II} is reflected on the *cisoid* angles [78.6(2)–95.0(8)°]. The equatorial mean plane is slightly tetrahedrally distorted (max deviation of ± 0.02 Å) with the metal displaced by 0.03 Å towards N(4).

The 1D chain developing along axis *b*, is formed by Ni(L) units connected alternatively by single and double bridging μ-(1,3-azide) ligands (Figure 2). The intermetallic separations between the single and double azide bridge are 5.875(3) and 5.304(3) Å, respectively. These values are comparable with those of 5.799 and 5.249 Å found in the closely related alternating system $[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$,[9] where the tridentate amine ligand, dpt is bis(3-aminopropyl)-amine. In contrast, the neutral polymer $[Ni(L)(N_3)_2]_n$[10] with single end-to-end azide junctions, the other N_3 being monocoordinated and pendant from the chain, shows an intermetallic distance of 5.662(1) Å, representing a mean value of the Ni···Ni distances for the present case. The N(2)–N(1)–Ni and N(2)–N(3)–Ni angles exhibited by the coordinated azide nitrogens are comparable, being 132.9(5) and 133.2(5)°, respectively, but somewhat larger than the N(5)–N(4)–Ni of 122.5(3)°. Correspondingly, the azide N(1)–N(2)–N(3) displays an angle of 176.1(7)° and the other [N(4)–N(5)–N(4′)] has a linear arrangement being located on a symmetry center. The pseudo torsion angles Ni–N(1)–N(3)–Ni′′ and Ni–N(4)–N(4′)–Ni′ are 180.0 and 5.3°, respectively.

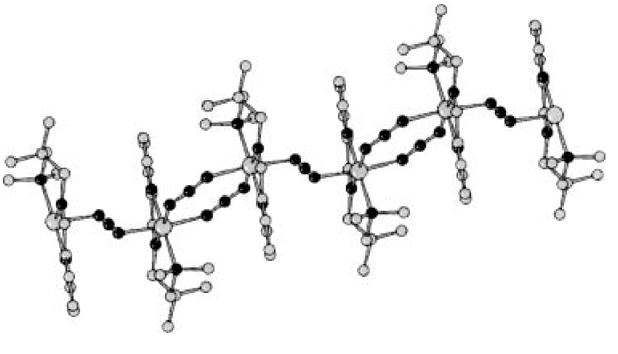


Figure 2. Polymeric structure of complex **1** (inversion centers are located at central nitrogen of the single bridging azide and in the midpoint of the double bridging azide).

Complex 2

The structure determination of **2** reveals that it is comprised of 2D undulated layers of $[Cu(N_3)(bpds)_2]^+{}_n$, where the charge is counterbalanced by perchlorate (ClO_4^-) anions with disordered water molecules in the crystal lattice. The ORTEP view of the coordination environment with the atom labeling scheme is shown in Figure 3 and a selection of bond lengths and angles is given in Table 1. The copper ion, located on a twofold axis, presents a hexacoordination geometry with four bpds nitrogen donors in the equatorial plane [Cu–N(11) 2.055(6), Cu–N(22) 2.044(6) Å, mean deviations of N donors ± 0.061(4) Å] and two azide nitrogens axially located at significantly longer distances [Cu–N(2), 2.447(7) Å]. The Cu–N(2)–N(1) bond angle presents a rather large value of 140.2(5)°. Taking into account the coordination linkages, the crystal structure can be envisaged as being formed by $–Cu–(bpds)_2–Cu–$ polymers of colinear Cu^{II} ions connected by μ-(1,3-N_3) ligands to build a 2D grid of 4,4 topology, with the nodes occupied by the copper ions, and the edges by the single μ-(1,3-N_3) and the double bpds connectors. Figure 4 shows a packing view down axis *c* indicating the perchlorate anions located inside the grid in between the double bpds connectors. The intermetallic distance along the azide is 6.703 Å and through the bpds ligands 10.839 Å (axis *a*). The zigzag arrangement of copper ions, in the $–Cu–(N_3)–Cu–$ array, displays a Cu–Cu–Cu angle of 160.31° and an ideal torsion angle Cu–N–N–Cu of 128.9°.

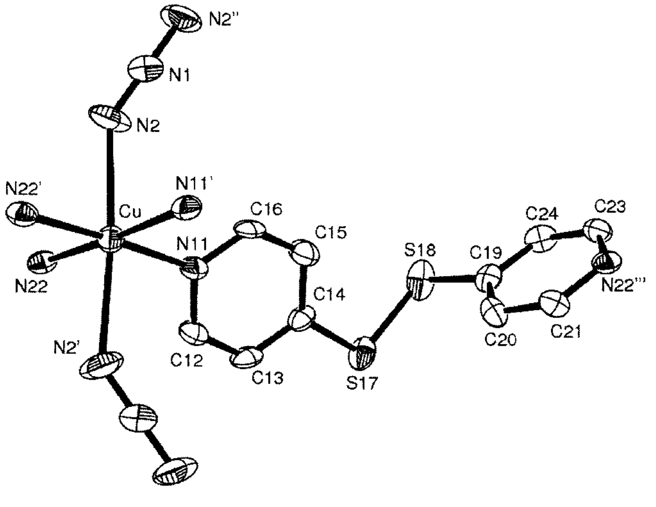


Figure 3. ORTEP plot of complex **2** with atom numbering scheme (symmetry operations: (′) *x*, –*y* + 3/2, –*z* + 3/2; (′′) *x* – 1, –*y* + 3/2, –*z* + 3/2; (′′′) 1 + *x*, *y*, *z*).

The crystal structure evidences a *gauche* conformation for the bpds spacer with a C–S–S–C torsion angle of 92.2(3)°, which is well in the range of 83.8(6)–95.5(8)°, found in a series of coordination polymers containing bpds ligands, in spite of the different coordination metal environment.[7e] However, it is interesting to note that the centrosymmetric space group furnishes both the possible enantiomeric conformers [± 92.2(3)°] for the acyclic disulfide[7c] and each 2D layer, piled parallel to the *ab* plane (Figure 5), contains only one of these.

Magnetic Properties

Complex 1

The magnetic properties of complex **1** in the form of χ_m and $\chi_m T$ (inset) vs. *T* plots (χ_m is the molar magnetic susceptibility for one Ni^{II} ion) are shown in Figure 6. The

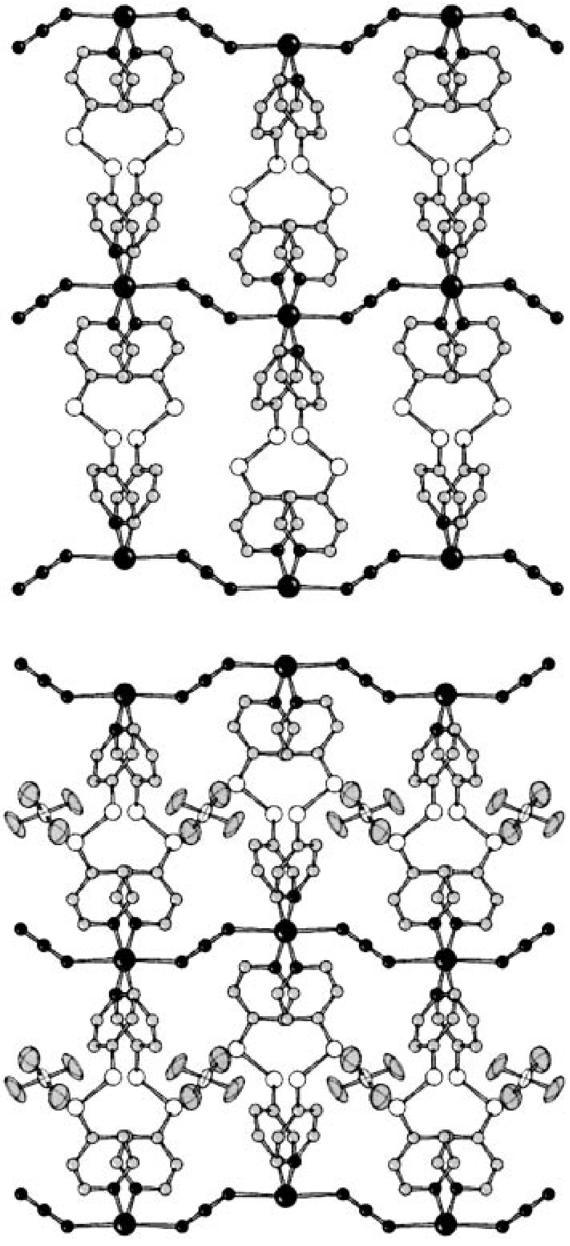


Figure 4. The 2D grid of complex **2** viewed down axis *c* indicating the location of perchlorate anions.

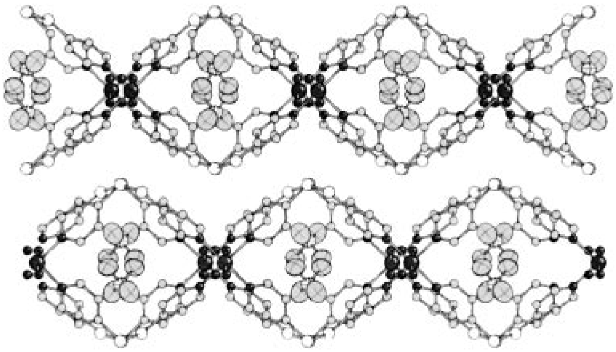


Figure 5. Side view (down axis *b*) of the 2D layers of complex **2** with perchlorate anions indicated as ellipsoids (disordered water molecules not shown).

value of χ_mT = 0.61 cm^3 mol^{-1} K at 300 K is smaller than the expected value for an isolated Ni^{II} ion with g > 2.00 (χ_mT close to 1.0 cm^3 mol^{-1} K). Starting from room temperature χ_mT values smoothly decrease down to 0.0 cm^3 mol^{-1} K at 2 K. At room temperature the χ_m value starts at 0.0022 cm^3 mol^{-1} and increases in a uniform manner to a maximum of 0.0023 cm^3 mol^{-1} around 190 K. Then χ_m values decrease to 0.0012 cm^3 mol^{-1} at 25 K and again increase at lower temperature (0.0014 cm^3 mol^{-1} at 2 K). The global feature is characteristic of very strong antiferromagnetic interactions, compensated at low temperature by the presence of small amounts of paramagnetic impurities (usually mononuclear ones following the Curie law) that originate from the increasing of χ_m at low temperatures.

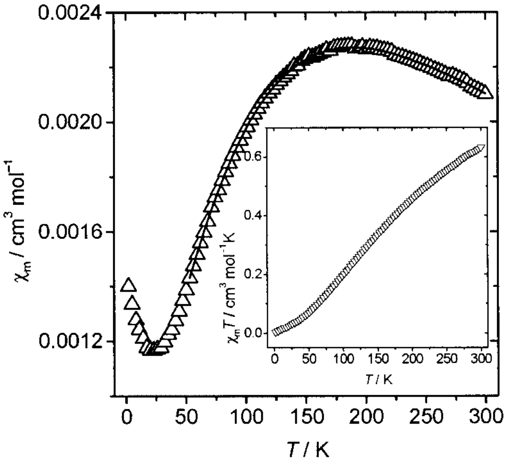


Figure 6. Plot of the χ_m vs. T for complex **1** (solid line represents the best-fit calculation; inset: plot of the χ_mT vs. T).

Complex **1** is actually an alternating 1D nickel(II) system with two kinds of alternate azide bridges: single and double end-to-end μ-(1,3-N_3). The fit of the magnetic data has been carried out applying the Borrás–Almenar formula for such types of alternating one-dimensional $S = 1$ systems,[11] based on the Hamiltonian $H = -J\Sigma(S_{2i}S_{21-1} + aS_{2i}S_{2i+1})$. In this Hamiltonian the single-ion anisotropy of Ni^{II} is not included. The work of Borrás–Almenar allows for the employment of two different formulae according to the alternation parameter (a between 0 and 0.5 or between 0.5 and 1). After some preliminary attempts, the best results corresponded to $a > 0.5$. Thus, the formula used in the fit was the following:

$$\chi_m = 0.25g^2/T\cdot(A + Bx + Cx^2):(1 + Dx + Ex^2 + Fx^3)$$

with $A = 1$; $B = 0.5$; $C = 0.1$; $D = 1.13693 + 0.748419a$; $E = 1.650652 - 1.4622193a + 1.668971a^2$; $F = 0.4447955 + 1.162769a$; $x = |J| / kT$.

Considering the shape of the experimental curve at low temperatures (Curie-law impurities) and that the Borrás–Almenar formula is not valid at low temperatures, mainly with a noticeable J value, we have removed all the experimental points from 50 to 2 K for the fit. With this condition, the best-fit parameters obtained are $J = -106.7 \pm 2$ cm^{-1}; $a = 0.82 \pm 0.02$; $g = 2.21 \pm 0.02$ and $R = 1.33 \times 10^{-5}$ (R is the agreement factor defined as

$\Sigma_i[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2 / \Sigma_i[(\chi_m T)_{obs}]^2$). These results indicate very strong antiferromagnetic coupling through the two kinds of azide bridging ligands. At this point, a question arises: which is which?

To the best of our knowledge only one similar complex has been reported by one of the authors.[9] The calculated J values were $J = -84.6$ cm^{-1} (for the double azido bridge) and $J' = -41.4$ cm^{-1} (for the single azido bridge). According to reported magneto-structural correlations,[6,9,12] the antiferromagnetic component of J is strongly dependent on the Ni–N–N and the Ni–N–N–N–Ni torsion angles, whereas only slightly from the Ni–N bond, with distances typically in the range, 2.12–2.17 Å.[6,9,12] For the mono-bridged fragment, the maximum coupling is expected for Ni–N–N angles close to 108°, while for greater values, the antiferromagnetic interactions must decrease. An accidentally orthogonal valley, centered at 164°, is found.[6] The values reported in the literature for similar systems range from $J = -100$ cm^{-1} (Ni–N–N angle of 120.9°) to -49 cm^{-1} (Ni–N–N angle of 137.2°). Thus, it seems that the sensitivity to this angle is very important. In complex **1**, the Ni–N–N of 122.52° implies strong antiferromagnetic coupling. Moreover, the Ni–N–N–N–Ni torsion angle is 180°, which allows the maximum AF coupling.[6]

The Ni-$(N_3)_2$-Ni fragment in complex **1** is not comparable to that previously reported.[9,12] In that case, a strong torsion between the two azide bridging ligands was detected, in contrast to parallel azide ligands in complex **1**. Thus, in the present case, the most important factor is only the δ angle, that represents the dihedral angle formed by the $(N_3)_2$ plane and the N–Ni–N plane.[6] For $\delta = 180°$ (0°) the AF coupling is at a maximum, whereas it is strongly reduced as this angle increases. The Ni–N–N is also important in this case. According to literature data, J values occur from -114.5 cm^{-1} for $\delta = 3.0$ to -4.6 cm^{-1} for $\delta = 45.0°$.[6] Thus, the small δ angle of 2.66° detected in **1** allows strong AF coupling. It seems to be logical that with the most favorable conditions of the double azide bridges, the J value is greater than that associated with a single azide bridging ligand.[6,9,12] Here these conditions are very favorable: thus the greatest J value may be assigned to the double azide bridging system while the smallest J to the single azide bridging ligand.

Complex 2

Magnetic properties of complex **2** are shown in Figure 7 as $\chi_m T$ vs. T plots (χ_m is the molar magnetic susceptibility for one Cu^{II} ion). The value of $\chi_m T$ at 300 K (0.43 cm^3 mol^{-1} K) is as expected for one magnetically quasi-isolated spin doublet ($g > 2.00$). Starting from room temperature the $\chi_m T$ values smoothly decrease down to 50 K, then quickly to 0.25 cm^3 mol^{-1} K at 2 K. The global feature is characteristic of very weak antiferromagnetic interactions. The reduced molar magnetization at 2 K (Figure 7, inset) also indicates that the antiferromagnetic coupling is very small. The $M/N\beta$ value at 5 T is close to one electron and the experimental curve lies slightly below the Brillouin function, assuming $g = 2.14$ (according to magnetic data and EPR measurements, see below).

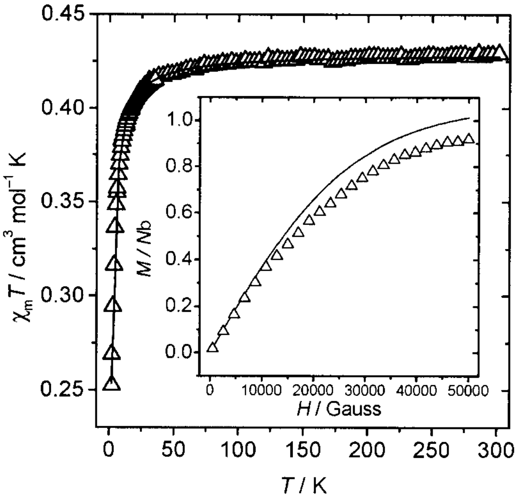


Figure 7. Temperature dependence of $\chi_m T$ vs. T for complex **2** (solid line indicates the best fit); inset: plot of the reduced magnetization ($M/N\beta$) at 2 K (solid line represents the Brillouin formula for the g value calculated from EPR spectra).

Actually complex **2** is a complicated two-dimensional copper(II) network with two kinds of bridging ligands: bpds and μ-(1,3-azide). Taking into consideration the long distances and the number of carbon atoms between adjacent copper(II) ions separated by the bpds, we may consider, from a magnetic point of view, a pseudo-one-dimensional structure. All copper(II) atoms are linked by μ-(1,3-N_3) bridging ligands in apical-apical positions (long-long distances). This gives a uniform $S = 1/2$ system. The fit of the magnetic data has been carried out using the formula given by Bonner and Fisher for this kind of uniform antiferromagnetic $S = 1/2$ chains.[13] The best-fit parameters obtained with this model are $J = -1.21 \pm 0.2$ cm^{-1}, $g = 2.14 \pm 0.02$ and $R = 2.1 \times 10^{-6}$ (R is the agreement factor defined as $\Sigma_i[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2 / \Sigma_i[(\chi_m T)_{obs}]^2$. This result indicates very small antiferromagnetic coupling through the μ-(1,3-azide) bridging ligands. The small J value can be interpreted as a consequence of the almost nil overlap between the copper(II) ions through the μ-(1,3-N_3) bridging ligands in the apical(long)-apical(long) coordination mode. Similar features have already been reported for other apical-apical polynuclear azide complexes, such as the dinuclear one reported by Drew et al., where the authors indicated "relatively weak antiferromagnetic interaction" without giving any value of J.[14] Taylor et al.,[15] reported an analogous complex where the lack of significant coupling between copper centers mediated by azide has been rationalized on the basis of the overlap. The major σ pathway for the interaction of two copper ions is via their d_{z^2} orbitals through the azide. The nearly square-pyramidal geometry of the d^9 copper atoms suggests that they have $d_{x^2-y^2}$ ground states:[13] therefore the unpaired electrons are localized in the basal plane and cannot effectively undergo coupling. Finally, one of us reported a similar complex with this kind of azide bridging in combination of bridging oxalate where the authors stated that "the coupling parameter corresponding to the apical bridge can reasonably be expected to be very small".[5f] On the other hand, the presence of the bpds bridging ligand which connects the one-dimensional –[μ-(1,3-N_3)Cu]$_n$– polymers can also contribute to the final J value. Thus, although the R value is very good, it must be considered carefully, owing to other possible magnetic interactions.

Let us remember that when the coordination mode is not apical(long)-apical(long) but equatorial(short)-equatorial(short) the coupling is normally strongly antiferromagnetic.[16] However, the most usual coordination mode is neither equatorial(short)-equatorial(short) nor apical(long)-apical(long) but equatorial(short)-apical(long) for the most current five-coordination mode. In this case both weak ferro- or antiferromagnetic coupling can be found, depending mainly on the distortion of the copper(II) ions.

The EPR spectra show the same shape at different temperatures (Figure 8), which is the typical pattern corresponding to an elongated octahedral copper(II) center with $g_{||}$ = 2.28 and $g_{\perp}$ = 2.07 (g_{av} = 2.14), in perfect agreement with the value obtained by magnetic measurements.

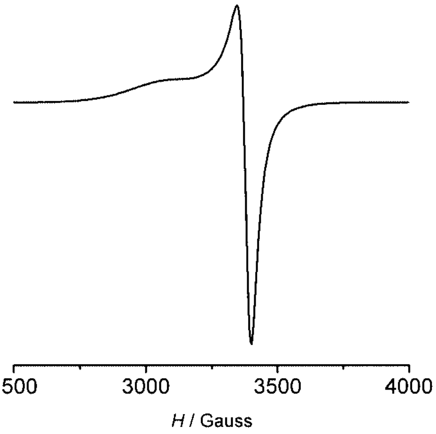


Figure 8. The EPR spectrum of complex **2** at room temperature (same shape was obtained at different temperatures).

Conclusion

We have presented here the syntheses, single-crystal structures and magnetic behaviors of two new azide complexes of nickel(II) (**1**) and copper(II) (**2**) using a Schiff base and 4,4′-bipyridyl disulfide, respectively, as coligands. Complex **1** is a 1D chain of nickel(II) with alternating single and double μ-(1,3-N_3) bridges. Complex **2** is a 2D grid of 4,4 topology comprising single μ-(1,3-N_3) and double bridging 4,4′-bipyridyl disulfide. Magnetic susceptibility data have been fitted using the Borrás–Almenar formula of alternating one-dimensional $S = 1$ system based on the Hamiltonian $H = -J\Sigma(S_{2i}S_{21-1} + \alpha S_{2i}S_{2i+1})$ for complex **1**. Whereas for complex **2**, susceptibility data were fitted by using the typical formula for a uniform antiferromagnetic $S = 1/2$ chain. The best-fit parameters for complex **1** indicate very strong antiferromagnetic coupling through the two kinds of azide bridging and for complex **2** reflect very small antiferromagnetic coupling through the μ-(1,3-azide). The magnetic interactions are compared to those of closely related complexes taking into account all the coordination angles involving azide bridging ligands as well as the coordination metal environment.

Experimental Section

Materials: High purity 4,4′-bipyridyl disulfide (Aldrithiol-4; 98%) and *N*,*N*,2,2-tetramethyl-1,3-propanediamine of Aldrich Chemical Co. Inc. were used and all other chemicals were of AR grade.

Physical Measurements: Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer. Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants. EPR spectra were recorded on powder samples at the X-band frequency with a BRUKER 300E automatic spectrometer, varying the temperature between 4–300 K.

Crystallographic Data Collection and Refinement: Data collections of the complexes reported were carried out at 293(2) K on a diffractometer equipped with a Mar-research image plate and Mo-K_α radiation (λ = 0.71073 Å). 95 frames were measured at 2° intervals with a counting time of 2 min, and the crystal positioned at 70 mm from the image plate. The crystallographic data, the condition for the intensity data collection and some features of the structure refinements are listed in Table 2. Data analysis was carried out with the XDS program[17] and the structures were solved by direct methods with the SHELX97 program.[18] An empirical absorption correction was applied using DIFABS.[19] The structures were anisotropically refined on F^2 using the SHELXL program[18] with the contribution of hydrogen atoms at calculated positions. The perchlorate anion of complex **2** was found to be disordered over two positions (refined occupancies of 0.78(2):0.28(2)). Three residuals on the ΔF map of complex **2** were interpreted as disordered water oxygens that account for a total of 1.25 molecules (2.50 per metal unit). All the calculations were performed using the Wingx System Ver. 1.64.5.[20]

Synthesis

Caution! Perchlorate as well as azide salts were used in small quantities and handled with care since explosion may occur.

[$Ni_2L_2(N_3)_3$]$_n$(ClO_4)$_n$ (1): The tridentate Schiff base (L) was prepared by refluxing pyridine-2-aldehyde (1 mmol; 0.107 g) and *N*,*N*,2,2-tetramethyl-1,3-propanediamine (1 mmol; 0.130 g) in methanol (10 mL) according to literature method.[21] A methanolic solution (10 mL) of nickel(II) perchlorate hexahydrate (1 mmol; 0.365 g) was added to the hot (ca. 40 °C) methanolic solution (10 mL) of tridentate Schiff-base ligand (1 mmol). The resulting solution was cooled to room temperature. An aqueous solution (5 mL) of sodium azide (1.5 mmol; 0.0975 g) was added dropwise to it with continuous stirring and the resulting reaction mixture was filtered and the filtrate was allowed to evaporate in a refrigerator. Suitable green single crystals for structure determination were obtained from the filtrate after a few days. Yield: 72%. $C_{26}H_{42}ClN_{15}Ni_2O_4$ (781.62): calcd. C 39.91, H, 5.37, N 26.86; found C 39.80, H 5.41, N 26.75. IR (cm^{-1}): 3443 (w), 3378 (w),

Table 2. Crystal data and refinement details of complexes **1** and **2**.

	1	**2**
Formula	$C_{26}H_{42}ClN_{15}Ni_2O_4$	$C_{20}H_{21}ClCuN_7O_{6.5}S_4$
M_r [g mol^{-1}]	781.62	690.67
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pnna*
a [Å]	8.089(13)	10.839(14)
b [Å]	9.392(14)	13.208(17)
c [Å]	12.267(18)	19.75(2)
α [°]	107.28(1)	90.0
β [°]	95.95(1)	90.0
γ [°]	96.92(1)	90.0
Volume [Å^3]	874(2)	2827(6)
Z	2	4
$D_{calcd.}$ [g cm^{-3}]	1.485	1.623
μ Mo-K_α [mm^{-1}]	1.209	1.213
F(000)	408	1408
θ_{max} [°]	26.10	25.02
Reflect. collected	6707	15554
Unique reflections	3107	2502
*R*int	0.0565	0.0684
Observed $I > 2\sigma(I)$	1879	2254
Parameters	246	188
Goodness of fit (F^2)	1.045	1.261
R_1 [$I > 2\sigma(I)$][a]	0.0702	0.0876
wR_2[a]	0.2091	0.1825
$\Delta\rho$ [e Å^{-3}]	0.574, –0.774	1.273, –0.504

[a] $R_1 = \Sigma \|F_o| - |F_c\| / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

2964 (m), 2901 (m), 2090 (vs), 2061 (vs), 1598 (m), 1093 (vs), 624 (w).

$[Cu(bpds)_2(N_3)]_n(ClO_4)_n(H_2O)_{2.5n}$ (2): An aqueous solution (10 mL) of copper perchlorate hexahydrate (1 mmol; 0.370 g) was added to a methanolic solution(10 mL) of bpds (2 mmol; 0.440 g). An aqueous solution (10 mL) of sodium azide (1 mmol; 0.065 g) was slowly poured into the resulting greenish solution while stirring. A deep green colored compound separated out. The whole reaction mixture was stirred for 30 min and filtered. The separated solid was washed several times with water-methanol (1:1) and dissolved in a minimum amount of 4(N) ammonia solution resulting in a deep blue solution. Green single crystals suitable for X-ray diffraction quality were obtained after a few days on keeping the solution in a refrigerator. Yield: 75%. $C_{20}H_{21}ClCuN_7O_{6.5}S_4$ (690.67): calcd. C 34.74, H 3.05 N 14.18; found C 34.98, H 3.05, N 14.09. IR: $\tilde{\nu}$ = 3544–3190 (s, v br), 3086 (vw), 2042 (vs), 1591 (vs), 1416 (s), 1099 (vs), 1059 (s), 812 (m), 718 (s), 500 (w)cm^{-1}.

Further details of the crystal structure determination have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC-251930 and -251931 for complexes **1** and **2,** respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) *Molecular-Based Magnetic Materials: Theory, Technique and Applications* (Eds.: M. M. Turnbull, T. Sugimoto, L. K. Thomson), ACS Symposium Series 644, American Chemical Society: Washington DC, **1996**; b) S. Sikorav, I. Bkouche-Waksman, O. Kahn, *Inorg. Chem.* **1984**, *23*, 490; c) D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio, *Magnetic Molecular Materials*; NATO ASI, Kluwer: Dordrecht, **1991**; d) J. Ribas, M. Monfort, I. Resino, X. Solans, P. Rabu, F. Maingot, M. Drillon, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2671.

[2] a) J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* **1993**, *32*, 3557; b) J. Ribas, M. Monfort, R. Costa, X. Solans, *Inorg. Chem.* **1993**, *32*, 695; c) M. A. Halcrow, J. C. Huffman, G. Christou, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 889; d) A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1994**, *33*, 1842; e) R. Vicente, A. Escuer, J. Ribas, M. S. El Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1995**, *34*, 1278; f) J. Ribas, M. Monfort, B. K. Ghosh, R. Cortes, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1996**, *35*, 864; g) M. Monfort, J. Ribas, X. Solans, *J. Chem. Soc. Chem. Commun.* **1993**, 350; h) M. Monfort, I. Resino, J. Ribas, H. Stoeckli-Evans, *Angew. Chem. Int. Ed.* **2000**, *39*, 191; i) F. A. Mautner, R. Cortes, L. Lezama, T. Rojo, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 96.

[3] a) J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385; b) A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, *Acc. Chem. Res.* **1989**, *22*, 392; c) P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah, N. Ray Chaudhuri, *Inorg. Chem.* **2000**, *39*, 5147; d) P. S. Mukherjee, T. K. Maji, G. Mostafa, J. Ribas, M. S. El Fallah, N. Ray Chaudhuri, *Inorg. Chem.* **2001**, *40*, 928; e) P. S. Mukherjee, T. K. Maji, T. Mallah, E. Zangrando, L. Randaccio, N. Ray Chaudhuri, *Inorg. Chim. Acta* **2001**, *315*, 247; f) T. K. Maji, P. S. Mukherjee, S. Konar, G. Mostafa, J. P. Tuchagues, N. Ray Chaudhuri, *Inorg. Chim. Acta* **2001**, *314*, 211; g) D. Gatteschi, *Adv. Mater.* **1994**, *6*, 635.

[4] a) M. I. Arriortua, A. R. Cortes, L. Lezama, T. Rojo, X. Solans, *Inorg. Chim. Acta* **1990**, *174*, 263; b) A. Escuer, R. Vicente, J. Ribas. *J. Magn. Mater.* **1992**, *110*, 181; c) A. Escuer, R. Vicente, J. Ribas, X. Solans. *Inorg. Chem.* **1995**, *34*, 1793.

[5] a) J. Comarmond, P. Plumere, J. M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, I. Morgersten-Badarau, *J. Am. Chem. Soc.* **1982**, *104*, 6330; b) O. Khan, S. Sikorav, J. Gouteron, Y. Jeannin, *Inorg. Chem.* **1983**, *22*, 2877; c) S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.* **1994**, *33*, 5555; d) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, *120*, 11122; e) M. A. Aebersold, M. Gillon, O. Plantevin, L. Pardi, O. Kahn, I. Bergeret, V. Seggern, L. Ohrstrom, A. Grand, E. Lelievre-Berna, *J. Am. Chem. Soc.* **1998**, *120*, 5238; f) P. S. Mukherjee, T. K. Maji, G. Mostafa, W. Hibbs, N. Ray Chaudhuri, *New J. Chem.* **2001**, *25*, 760; g) T. K. Maji, P. S. Mukherjee, G. Mostafa, T. Mallah, J. Cano-Boquera, N. Ray Chaudhuri, *Chem. Commun.* **2001**, 1012; h) P. S. Mukherjee, S. Dalai, G. Mostafa, T.-H. Lu, E. Rentschler, N. Ray Chaudhuri, *New J. Chem.* **2001**, *25*, 1203; i) P. S. Mukherjee, T. K. Maji, A. Escuer, R. Vicente, J. Ribas, G. Rosair, F. A. Mautner, N. Ray Chaudhuri, *Eur. J. Inorg. Chem.* **2002**, 943; j) S. Dalai, P. S. Mukherjee, T. Mallah, M. G. B. Drew, N. Ray Chaudhuri, *Inorg. Chem. Commun.* **2002**, *5*, 472; k) S. Konar, E. Zangrando, M. G. B. Drew, T. Mallah, J. Ribas, N. Ray Chaudhuri, *Inorg. Chem.* **2003**, *42*, 5966; l) D. Ghoshal, T. K. Maji, E. Zangrando, T. Mallah, E. Riviére, N. Ray Chaudhuri, *Inorg. Chim. Acta* **2004**, *357*, 1031.

[6] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–195*, 1027.

[7] a) A. J. Blake, N. R. Brooks, N. R. Champness, M. Crew, A. Deveson, D. Fenske, D. H. Gregory, L. R. Hanton, P. Hubberstey, M. Schroder, *Chem. Commun.* **2001**, 1432; b) R. Horikoshi, T. Mochida, H. Moriyama, *Inorg. Chem.* **2001**, *40*, 2430; c) F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2001**, *123*, 7740; d) M. Hong, W. Su, R.Cao, M.

Fujita, J. Lu, *Chem. Eur. J.* **2000**, *6*, 427; e) R. Horikoshi, T. Mochida, N. Maki, S. Yamada, H. Moriyama, *J. Chem. Soc. Dalton Trans.* **2002**, *28*.

[8] A. K. Ghosh, D. Ghoshal, T.-H. Lu, G. Mostafa, N. Ray Chaudhuri *Cryst. Growth Des.* **2004**, *4*, 851.

[9] R. Vicente, A. Escuer, J. Ribas, X. Solans, *Inorg. Chem.* **1992**, *31*, 1726.

[10] P. S. Mukherjee, S. Dalai, E. Zangrando, F. Lloret, N. Ray Chaudhuri, *Chem. Commun.* **2001**, 1444.

[11] a) J. J. Borrás-Almenar, Ph. D. Thesis, Valencia, Spain, **1992**; b) J. J. Borrás-Almenar, E. Coronado, J. Curély, R. Georges, *Inorg. Chem.* **1995**, *34*, 2699.

[12] R. Vicente, A. Escuer, *Polyhedron* **1995**, *14*, 2133.

[13] J. C. Bonner, M. E. Fisher, *Phys. Rev. A* **1964**, *135*, 640.

[14] M. G. B. Drew, M. McCann, S. M. Nelson, *J. Chem. Soc. Chem. Commun.* **1979**, 481.

[15] J. H. Satcher, M. W. Droege, T. J. R. Weakley, R. T. Taylor, *Inorg. Chem.* **1995**, *34*, 3317.

[16] a) I. Bkouche-Waksman, M.-L. Boillot, O. Kahn, S. Sikorav, *Inorg. Chem.* **1984**, *23*, 4454; b) P. Chaudhuri, K. Oder, K. Wieghardt, B. Nuber, J. Weiss, *Inorg. Chem.* **1986**, *25*, 2818.

[17] W. Kabsch, *J. Appl. Crystallogr.* **1988**, *21*, 916.

[18] G. M. Sheldrick, *SHELX97, Programs for Crystal Structure Analysis (Release 97–2)*, University of Göttingen, Germany, **1998**.

[19] N. Walker, D. Stuart, *Acta Crystallogr., Sect.* A **1983**, *39*, 158.

[20] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[21] a) G. Zakrzewski, L. Sacconi, *Inorg. Chem.* **1968**, *7*, 1034; b) P. Bamfield, R. Price, R. G. J. Miller, *J. Chem. Soc. (A)* **1969**, 1447.

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