DOI: 10.1002/ejic.200900575

Single End-to-End Azidocopper(II) Chain Based on an Electroactive Ligand: A Structural, Electrochemical, Magnetic and Ab Initio Study

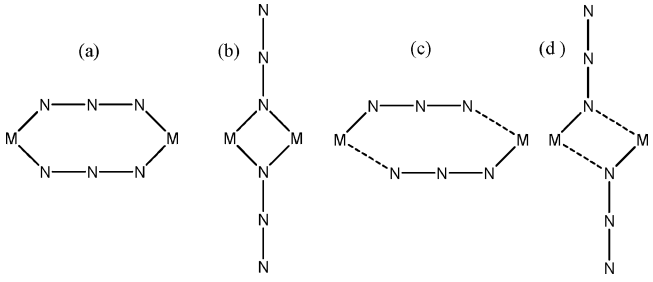
Guillaume Pilet,*[a] Maurice Médebielle,[b] Jean-Bernard Tommasino,[a] Guillaume Chastanet,*[a,c] Boris Le Guennic,[c] and Cyrille Train[d]

Keywords: Magnetic properties / Chain structures / Azides / Copper

By combining azide and the (Z)-1,1,1-trifluoro-4-(quinolin-8-ylamino)but-3-en-2-one enaminone ligand, HL, an azido-bridged copper(II) one dimensional polymer was synthesized in a one-pot reaction. The solved and refined crystal structure evidenced the unusual single and asymmetric end-to-end coordination mode of the azide ion. The redox properties of this complex were studied by cyclic voltammetry, and oxidation of the azido bridge was evidenced. Magnetic measurements, combined with magnetostructural-driven analysis revealed a weak ferromagnetic interaction between the copper(II) ions within the N_3^--bridged chains, complemented by an antiferromagnetic interaction between the chains mediated by π–π interactions. A survey of the scarce literature of single end-to-end azido bridges, associated with quantum chemical ab initio calculations, was carried out to tentatively identify the relevant parameters driving the weak intrachain exchange interaction.

Introduction

Research on hybrid organic–inorganic metallic clusters exhibiting local magnetic moments has led to important progress in both the chemistry and physics communities.[1,2] The design of such clusters should imply ligands able to aggregate metal centres and mediate exchange interactions between them. In that sense, the pseudohalide azido ion, N_3^-, turns out to be a very versatile candidate.[2b,3–5] The most frequently encountered coordination modes of the azido bridges are end-to-end ($\mu_{1,3}$-N_3, EE) and end-on ($\mu_{1,1}$-N_3, EO; Scheme 1).[2b,3] Besides, triple $\mu_{1,1,1}$[6] and $\mu_{1,1,3}$[7] or quadruple $\mu_{1,1,1,1}$[8] and $\mu_{1,1,3,3}$[9] connection modes remain relatively rare. One or several azido bridges may be involved in the coordination of metal centres with double EE and EO bridges being the most common (Scheme 1). An additional feature lies in the coordination pattern, which may either be symmetric, with all equivalent metal–azide bond lengths, or deviate from such perfect picture (Scheme 1). As a result of the large panel of coordination abilities, the structural variety of azido complexes ranges from molecular clusters[5] to multidimensional materials (1D,[2b,10] 2D[11] and 3D[12]).[13] Furthermore, different bridging modes of the azido ions may simultaneously exist in the same species, leading to original alternating topologies and magnetic behaviours exemplified by the widespread $\{EO–EE\}_n$ sequence[3,10] and the less common, $\{EO–EE–EE\}_n$, $\{EO–EO–EO–EE\}_n$, $\{EO–EO–EO–EO–EE\}_n$ chain assemblies.[14]



Scheme 1. Symmetric EE (a) and EO (b) and asymmetric EE (c) and EO (d) coordination modes for the azido bridge.

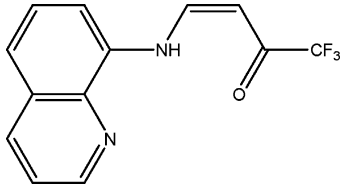
The sign and magnitude of the exchange coupling constant, *J*, may be drastically tuned. From magnetostructural correlations, based on both experimental[15] and theoretical[16] studies, some general trends have been evidenced for double-bridged species: the EE mode favours antiferromag-

[a] Laboratoire des Multimatériaux et Interfaces (LMI, UMR 5615) Groupe de Cristallographie et Ingénierie Moléculaire, Université de Lyon and Université Claude Bernard Lyon 1, Bâtiment Raulin,
43 bd du 11 Novembre 1918, 69622 Villeurbanne, France
E-mail: guillaume.pilet@univ-lyon1.fr
guillaume.chastanet@univ-lyon1.fr
[b] Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS, UMR 5246) Synthèse de Molécules d'Intérêt Thérapeutique, Université de Lyon and Université Claude Bernard Lyon 1,
43 bd du 11 Novembre 1918, 69622 Villeurbanne, France
[c] Laboratoire de Chimie (UMR 5182), Ecole Normale Supérieure de Lyon, Université de Lyon,
46 allée d'Italie, 69364 Lyon Cedex 07, France
[d] Institut Parisien de Chimie Moléculaire (UMR 7201), Matériaux Magnétiques Moléculaires et Absorption X, UPMC Univ. Paris 06, case 42,
4 place Jussieu, 75252 Paris Cedex 05, France

netic interactions, whereas the EO one generally leads to ferromagnetic behaviour. These studies have also highlighted the great sensibility of the magnetic exchange coupling with specific structural parameters such as the metal–azido–metal angles or asymmetry in the coordination mode of the azido bridges.[17] Similarly to the richness of azido-based material topologies, the magnetic properties are extremely wide, giving rise to single molecule magnets (SMMs)[5] and single-chain magnets (SCMs)[18] materials.

To complete the coordination sphere of the metal centres, azide ions are often associated with other ligands. Among those, multidentate Schiff base molecules are widely used. In that sense, we have reported recently the ability of such a ligand class to generate various molecular architectures[19] involving azido coupler[4,17,20] or exhibiting SMM properties.[21] Our attention is currently focused on the design of multidentate ligands that may hold redox properties in order to tune the magnetic behaviour either in the oxidized or reduced forms. Enaminones and their trifluoromethylated analogues would possess such potentialities. Indeed, they are possible redox-noninnocent ligands,[22] as they can either be N,O-coordinated to transition-metal ions as closed-shell anions, radical–anions or dianions. Recently, we studied their coordination ability to form polynuclear assemblies.[23] Such systems deserve particular attention, as the electrochemistry of only two other fluorinated enaminone complexes [with Cu^{II} and Ni^{II}] have been reported to date.[24] Such ligands have been involved also in the preparation of metallomesogens with liquid crystal properties[25] or highly active catalysts in olefin polymerization.[26]

We report here the thorough investigation, including synthesis, structural analysis, redox properties and magnetic characterizations, as well as quantum chemical calculations, of a 1D azido-bridged copper(II) chelated by the HL enaminone ligand [HL = (*Z*)-1,1,1-trifluoro-4-(quinolin-8-ylamino)but-3-en-2-one; Scheme 2] polymer. This complex is one of the scarce examples of neutral chains based on single EE-N_3 bridge.



Scheme 2. Schematic representation of the HL ligand.

Results

In our previous studies, the HL ligand was evidenced to coordinate copper(II) ions, giving rise to the mononuclear species [CuL_2] in a 2:1 ligand/ion ratio.[23] The electrochemical study of this complex in dichloromethane and in *N*,*N*-dimethylformamide revealed two distinct monoelectronic reduction processes, that is, $Cu^{II} \rightarrow Cu^{I}$ and $Cu^{I} \rightarrow Cu^{0}$. In addition, the Cu^{I} species generated from the reduction of the [$Cu^{II}L_2$] complex is stable and exhibits a quasireversible redox process, opening the possibility to modulate the exchange interaction between copper ions within polynuclear architectures. Indeed, this process converts paramagnetic Cu^{II} into diamagnetic Cu^{I} ions, switching off the exchange coupling between copper centres.

A common strategy to generate polynuclear assemblies involves bridging ligands such as the azide N_3^- ion. In that sense, the concomitant use of tridentate Schiff base ligands, copper ion and azide salt may give rise to extended networks.[4,10–14,20,27,28] Therefore, we applied this strategy in a one-pot method to build such extended architecture.

Crystal Structure Description

The $\{CuL(N_3)\}_n$ complex crystallizes in the monoclinic system. According to the observed systematic extinctions, its structure was solved and refined in the $P2_1/c$ space group (see the Experimental Section). It consists of neutral chains running along the *b* axis of the unit cell (Figure 1a) and built from the [$CuL(N_3)$] neutral asymmetric unit (Figure 1b). Each copper atom is connected to its Cu^{II} neighbours by a single azido bridge in an EE mode ($\mu_{1,3}$-N_3). Let us note that only few examples of singly bridged compounds are known.[27,28]

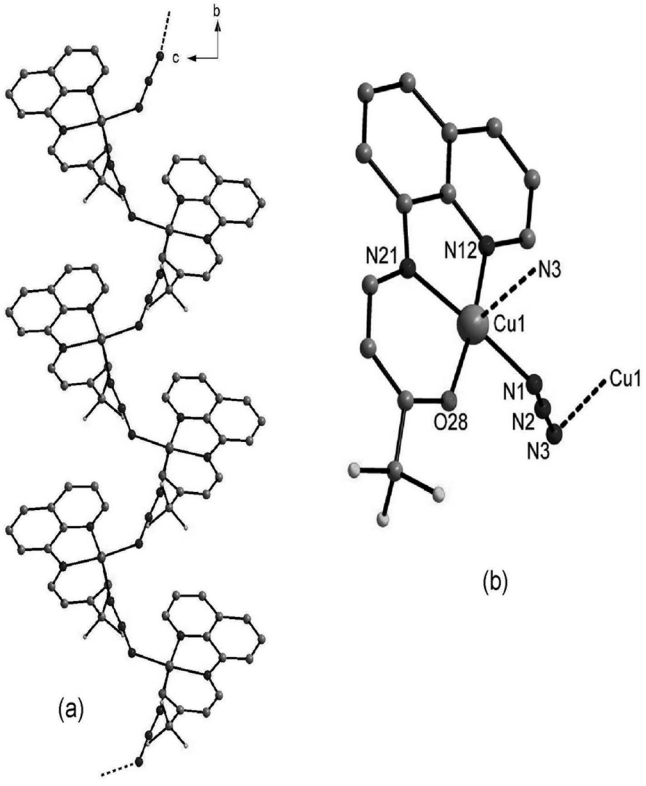


Figure 1. (a) Infinite neutral chain $\{CuL(N_3)\}_n$ running along the *b* axis of the unit cell; (b) asymmetric unit. H atoms are omitted for clarity.

Each Cu^{II} cation is five-coordinate and located in a regular square pyramid with an Addison parameter of 0.03.[29] The basal square plane is composed of two nitrogen atoms [N12 and N21 with Cu–N bond lengths equal to 1.995(3)

and 1.965(3) Å, respectively], one oxygen atom [O28, Cu–O bond length equals to 1.953(3) Å] belonging to the deprotonated L^- ligand and a third nitrogen atom (N1) brought by an azido bridge (Figure 1b) with a Cu–N bond length of 1.973(3) Å. The apical position is occupied by the terminal nitrogen atom (N3) of a second azido bridge with a Cu–N bond length of 2.446(3) Å. The presence of long and short Cu–N(azido) bond lengths induces an asymmetric EE coordination mode of this single $\mu_{1,3}$-N_3 bridge. The metal ions are separated by 5.6910(5) Å, in agreement with the usual metal–metal distances observed for simple or double EE N_3 bridges.[4]

The crystal packing can be described by parallel chains stacked by π interactions. Indeed, the shortest distance between adjacent aromatic rings is 3.43 Å (Figure 2). This leads to intermolecular Cu···Cu distances of 5.925 Å, slightly larger than the intrachain one.

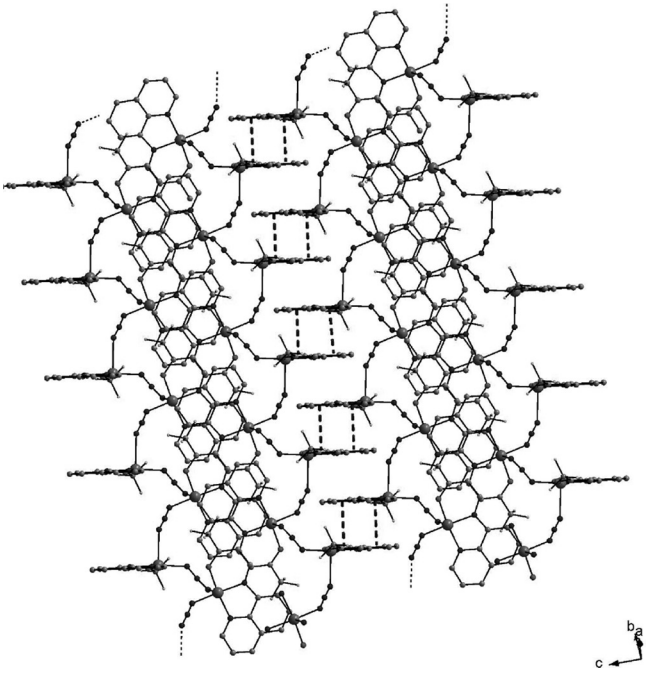


Figure 2. View of two parallel $\{CuL(N_3)\}_n$ chains with the close contact between ligands. H atoms are omitted for clarity.

Electrochemical Studies

This 1D polymer complex described above is a derivative of one of our previous compounds $[CuL_2]$[23] and synthesized from the same enaminone ligand. The redox properties of the HL and azide ligands as well as the $\{CuL(N_3)\}_n$ complex were studied by cyclic voltammetry in acetonitrile (CH_3CN) and *N*,*N*-dimethylformamide (DMF). Moreover, to help the assignment of the peaks observed in the polymeric $\{CuL(N_3)\}_n$ voltammogram, a comparison with the monomeric $[CuL_2]$ electrochemical behaviour was made.[30]

The HL ligand involved in the title compound was first studied in acetonitrile. The voltammogram reveals one reduction step at –1.40 V (Figure 3, dark grey curve) and one oxidation step at 1.40 V. Both processes are irreversible, demonstrating that the radical–anion and radical–cation are unstable and give rise to follow-up chemical reactions. Moreover, the NaN_3 salt in this solvent (containing 6% of H_2O to ensure better solubility) gives a single irreversible oxidation step at 0.9 V (Figure 3, black curve).[31] In addition, cyclic voltammetry analysis of the ligand in CH_3CN/H_2O (6%) in presence of NaN_3 gave the corresponding oxidation steps at 0.9 and 1.4 V (Figure 3, light grey curve); the absence of new electroactive species demonstrates that no chemical reaction between these two reactants occurs.

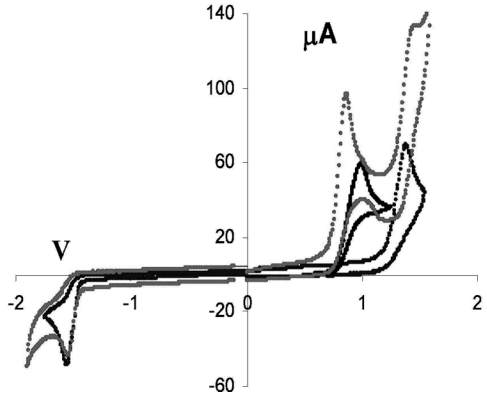


Figure 3. Cyclic voltammetry of HL (dark grey), NaN_3 (black) and a mixture of NaN_3/HL (2 mM < *C* < 4 mM, light grey) in CH_3CN/H_2O (6%) with 0.1 M nBu_4NPF_6 as supporting electrolyte.

{CuL(N₃)}ₙ Complex in Acetonitrile

No peak corresponding to the reduction of the free ligands was observed. The voltammogram shows two irreversible reduction processes, with similar intensities, at –0.58 and –0.77 V (Table 1). The first reduction step is connected to an oxidation wave at 0.10 V of weak intensity, whereas the second reduction step is associated with a typical redissolution peak of Cu^0 at –0.37 V. Exhaustive electrolysis at a potential corresponding to the second reduction step gives an electron apparent number value equal to 1.7 F mol^{-1}. Then, the working electrode is covered by a Cu^0 mirror. The reduction mechanism can be summarized as follows:

$$\{Cu^{II}L(N_3)\}_n + e^- \rightarrow \{Cu^{I}L(N_3)\}_n$$

$$\{Cu^{I}L(N_3)\}_n + e^- \rightarrow n\ Cu^0 + nL^- + nN_3^-$$

Table 1. Electrochemical data[a] for the Cu^{II} complex.

Solvent	E_{pc}[b] [V]	E_{pa}[c] [V]
DMF	–0.60	–0.10[d]/0.10[d]/0.90
CH_3CN	–0.58/–0.77	–0.37[d]/0.10[d]/0.90/1.40

[a] Peak potential recorded at 293 K with a glassy carbon electrode with 0.1 M nBu_4NPF_6 as supporting electrolyte; all potential are vs. SCE, scan rate 0.05 V s^{-1}. [b] Cathodic peak potential. [c] Anodic peak potential. [d] Anodic peak potential only appears after reduction.

The complex can also be oxidized at 0.9 and 1.4 V. Let us mention that the oxidation peak at 0.9 V was not observed in $[CuL_2]$[23] (Table 2), whereas it appeared at this

potential for the free azide salt (Figure 3). Therefore, this process was associated to the oxidation of the azido bridge.

Table 2. Electrochemical data[a] of the complexes in DMF.

Complexes	E_{pc}[b] [V]	E_{pa}[c] [V]
$\{Cu^{II}L(N_3)\}_n$	–0.60	–0.10[d]/0.10[d]/0.90
$[Cu^{II}L_2]$	–0.80/–1.10	–0.25[d]

[a] Peak potential recorded at 293 K with a glassy carbon electrode with 0.1 M nBu_4NPF_6 as supporting electrolyte; all potential are vs. SCE, scan rate 0.05 V s^{-1}. [b] Cathodic peak potential. [c] Anodic peak potential. [d] Anodic peak potential only appears after reduction. The potential of the redissolution peak is not mentioned here.

The fact that the azido bridge in the $\{CuL(N_3)\}_n$ complex may be oxidized at the same potential as the free azide anion suggests similar redox properties. The assignment of the 1.4 V oxidation step is more tricky, as it may correspond to the oxidation of L^- or residual HL ligand or to the one-electron oxidation of Cu^{II}. Indeed, the latter phenomenon was suggested in a recent study for a N,N,N,O-coordinating tripodal ligand.[32]

{CuL(N$_3$)}$_n$ Complex in N,N-Dimethylformamide

In this solvent, a first monoelectronic reduction step (determined by coulometry) is observed at –0.6 V and remains irreversible up to 1 V s^{-1} (Figure 4, peak C1). This reduced complex, $\{Cu^{I}L(N_3)\}_n$, is not stable and upon oxidation gives rise to two new species at –0.1 and 0.1 V (Figure 4, peaks A1 and A2, respectively). In addition, a second irreversible reduction step was evidenced at a more negative potential close to –2.2 V, which has not yet been assigned. Moreover, no redissolution peak could be observed (Tables 1 and 2).

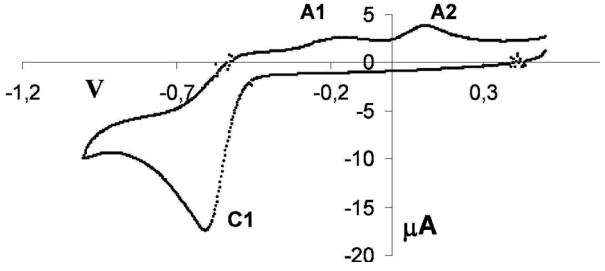


Figure 4. Reduction process of the complex (1 mM) in DMF with 0.1 M nBu_4NPF_6 as supporting electrolyte.

Then, a strong solvent effect was evidenced, because the electrochemical studies of $\{Cu^{II}L(N_3)\}_n$ revealed only one monoelectronic process in DMF instead of two in acetonitrile. In addition, comparison with the electrochemical behaviour of $[Cu^{II}L_2]$[23] allowed us to assign voltammogram peaks and highlight the role of the azido ligand. Moreover, the observed oxidation steps in DMF around –0.1 and 0.1 V are irreversible for the $\{Cu^{II}L(N_3)\}_n$ complex. This contrasts with the $[Cu^{II}L_2]$ behaviour, as its reduction into Cu^0 gives rise to a quasireversible peak around –0.25 V. This quasireversibility was even more pronounced when only one monoelectronic process [$Cu^{II} \rightarrow Cu^{I}$] was performed, with an estimated standard potential E^0 of –0.23 V. Thus, this suggests that the presence of the azido bridge in $\{Cu^{II}L(N_3)\}_n$ strongly affects the redox behaviour of the whole complex in a manner that still has to be clarified. The difference of stability between the two reduced forms of the chain and the monomer are currently under study.

Magnetic Studies

Figure 5 reports the magnetic properties of the $\{Cu^{II}L(N_3)\}_n$ chain. At room temperature, the χT value of 0.400 cm^3 K mol^{-1} corresponds to the expected value for one copper(II) ion (0.375 cm^3 K mol^{-1}) with a slight anisotropy of the g factor (2.08). Upon cooling, χT is almost constant down to 50 K and then slightly increases to 12 K, where it reaches a maximum value of 0.407 cm^3 K mol^{-1}. Below 12 K, χT decreases down to 0.384 cm^3 K mol^{-1} at 2 K.

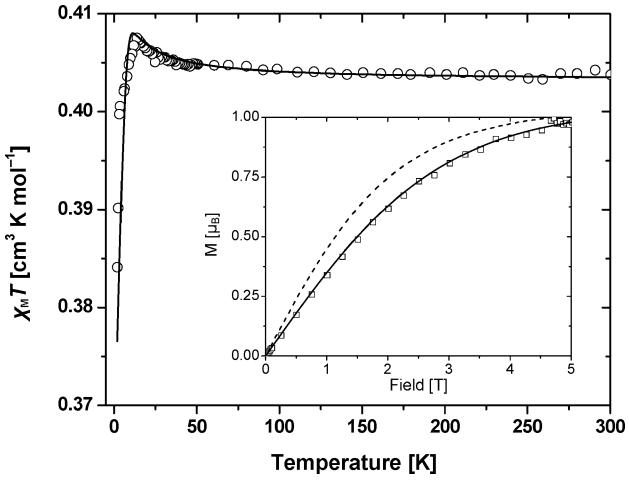


Figure 5. Thermal dependence of the molar magnetic susceptibility. The insert presents the magnetization curve at 2 K. The lines stand for the fit discussed in the text.

This behaviour indicates the coexistence of weak ferromagnetic (F) and antiferromagnetic (AF) exchange interactions between the copper(II) ions. The experiment was reproduced to avoid any artefact of measurement. The competition between F and AF interactions is also evidenced by the magnetic field dependence of the magnetization at 2 K (Figure 5, inset) that reaches 0.98 μ_B at 5 T, without a clear saturation, instead of the expected 1 μ_B for one spin ½. The magnetization curve is well reproduced by a Brillouin function for one spin ½ with g = 2.08 (solid line), whereas the curve calculated for one spin 1 (g = 2.08) coming from a ferromagnetic coupling between two copper(II) ions deviates from the experiment (dashed line).

An estimation of the magnetic exchange constants was obtained by using high-temperature series expansion[2a,33] based on the $H = -J\Sigma\hat{S}_i\hat{S}_{i+1}$ spin Hamiltonian. This estimation is complicated by the presence of the interchain coupling, J', which was introduced through the molecular field approximation. Figure 5 presents one fitted curve with $J_{intra} \approx +1.5$ cm^{-1}, with an intermolecular interaction $J' \approx$

$-1.2\ cm^{-1}$ ($z = 2$). The similar intensities observed for the intra- and interchain interactions may be correlated with the Cu···Cu distances that are almost equivalent within and between the chains. Obviously, the relevance of such values is questionable.

Ab Initio Calculations

CAS(2,2) calculations were performed to evaluate the intra- and interchain exchange interactions. The intrachain behaviour was estimated on a $[Cu_2L_2(N_3)_3]^-$ dimer. As expected, the magnetic orbitals are mainly Cu-$d_{x^2-y^2}$ type with a small delocalization on the coordinated atoms of the square pyramid base (Figure 6). At the highest level of calculations (DDCI-3),[41] a small F exchange constant was calculated ($2.7\ cm^{-1}$), in agreement with the values extracted from the experimental fit. Then the intermolecular contribution between two adjacent $[CuL(N_3)_2]^-$ entities stacked together by π interactions (Figure 2) were estimated at the same level of calculations ($J' = -0.4\ cm^{-1}$). Even if these results lie within the limits of accuracy of such a method, the calculated exchange constants qualitatively reproduces the experimentally observed behaviour.

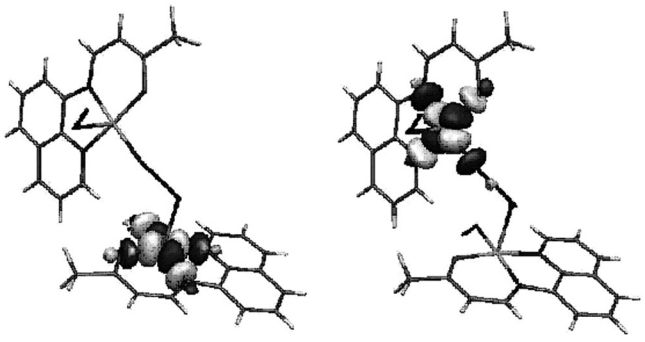


Figure 6. Magnetic molecular orbitals of the $[Cu_2L_2(N_3)_3^-]$ dimer.

Discussion

Traditional studies of double azido-bridged metal complexes have evidenced ferromagnetic interactions mediated by an end-on coordination mode, whereas end-to-end coordination modes generally lead to antiferromagnetic coupling.[2a,3] However, in copper systems, the magnitude of the AF component of the superexchange constant J is strongly dependent on structural parameters.

The coupling may be strongly AF when the end-to-end azido ligands are bonded to the equatorial coordination sites of the two copper atoms (symmetric coordination mode, Scheme 1a), in which case the atomic orbitals involved in the superexchange mechanism are the $d_{x^2-y^2}$ orbitals. In contrast, very low coupling interactions and even F exchange could be encountered when the copper ions are bound by axial and equatorial azido ligands (asymmetric coordination mode, Scheme 1c). In the latter situation, the metallic atomic orbitals involved in the coordination are of $d_{x^2-y^2}$ and d_{z^2} type. In a perfect square pyramid coordination polyhedron of the copper ions (Addison parameter $\tau = 0$), the overlap between the $d_{x^2-y^2}$ and the ligand orbitals is expected to be small, leading to a weak exchange interaction. Deviation from the square pyramid is often encountered when the copper ion is out of the basal plane (Addison parameter $\tau > 0$), with the limit geometry being a trigonal bipyramid polyhedron (Addison parameter $\tau = 1$), leading to a greater mixing of $d_{x^2-y^2}$ and d_{z^2} atomic orbitals. Therefore, a greater AF coupling is observed in such cases.[16b] Let us note that, for highly asymmetric double azido-bridged copper ions, this interaction could become F.[17]

Several other structural parameters have been shown to strongly affect the exchange interaction between the copper ions, as the null overlap between the axial ligand orbitals and the $d_{x^2-y^2}$ magnetic orbitals are ruled out. Indeed, when the Cu–N–N angle with the axial ligand is 90°, a zero spin density delocalization towards the σ ligands orbitals should be theoretically observed, whereas it should be at a maximum for 180°. Moreover, the Cu–$\mu_{1,3}$-N_3–Cu torsion angle (θ) affects the contribution of the σ ligand orbitals in the delocalization and therefore in the exchange interaction, as it was observed that large torsion angles θ enhance the F behaviour.[15g,15h,16b]

In our case, the copper ion lies on a square pyramidal polyhedron with one nitrogen atom of the bridging azido linked to the equatorial position, whereas the other end nitrogen of the same azido is linked to the axial site of the neighbouring copper(II) centre, indicating that the spin unpaired electron is mainly located in the basal $d_{x^2-y^2}$ orbital, as confirmed by the theoretical calculations (Figure 6). The consequence is that the delocalization is mainly towards the equatorial π ligand orbitals, whereas it is very poorly of σ-type towards the axial ligand, leading to a weak interaction, as observed experimentally. The nature of this low interaction may be F or AF, as a function of the bond parameters in the bridging region. The AF component of the superexchange may be drastically reduced for large M–N–N bond angles or large θ angles.[10b] Then, the F nature may be explained tentatively by the quasiorthogonal arrangement of the magnetic orbitals,[2a] because the angle α between the two basal planes of the square pyramid coordination polyhedron of the Cu^{II} ions is 81°.[28i] However, inspection of the literature rules out such a naïve picture. Indeed, the title complex is a scarce example of a single end-to-end azido bridge. With the objective of drawing some trends for a single end-to-end azido-bridging mode, Table 3 reports similar complexes structural and magnetic data usually used in magnetostructural correlations. Except for one 2D architecture, all complexes are arranged in either alternated or uniform polymeric chains.

A first look at the exchange parameters J indicates a preference for weak F interactions in such single azido-bridged systems. In that sense, with $J = 1.5\ cm^{-1}$, the title complex is relevant with the other values. Let us notice that several magnetic models were used to extract these exchange constants. Therefore, a strict comparison of the absolute values may be difficult, especially for the one obtained from inter-

Table 3. Structural and magnetic parameters for single EE bridges.

Type of complex	Cu–N[a] [Å]	δ[b] [Å]	d_{Cu-Cu} [Å]	θ[c] [°]	Cu–N–N [°]	τ[d]	α[e] [°]	J [cm^{-1}]	Magnetic model	Ref.
Alternated chain	2.46	0.48	5.32	75.9	122.3/123.9	0.24/0.16	63	–22.5	Fisher model	[28a]
Alternated chain	2.36	0.39	5.59	69.8	120.5/143.4	0.21/0.097	20.6	0.45	interdimer interaction	[28b]
Alternated 2D	2.33	0.35	5.81	101.7	121.5/144.7	0.01	65.7	0.4	interdimer interaction	[28c]
Alternated chain	2.29	0.28	5.63	55.1	122.2/151.4	0.1/0.022	24.9	–2.7	alternated chain	[28d]
Uniform chain	2.47	0.51	5.06	87.4	108.2/124.1	0.07	0	–3.8	Hall model	[28e]
Uniform chain	2.36	0.37	6.12	124.1	123.6/161.3	0.18	56.4	1.84	HTSE[f]	[28f]
Uniform chain	2.36	0.41	5.69	97.8	126.5/131.2	0.083	35.9	2.15	HTSE[f]	[27a]
Uniform chain	2.31	0.35	5.63	49.9	131.2/139.1	0.17	15.8	3.61	HTSE[f]	[27a]
Uniform chain	2.27	0.32	5.54	40.4	132.2/139.0	0.15	14	2.06	HTSE[f]	[27a]
Uniform chain	2.27	–	5.59	31.4	134.4/136.7	0.12	–	2.69	HTSE[f]	[28g]
Uniform chain	2.4	–	5.74	102.8	122.5/135.1	0.13	33.8	2.02	HTSE[f]	[28g]
Uniform chain	2.49	0.55	5.77	91.6	125.6/135.7	0.15	29.7	1.36	HTSE[f]	[28i]
Uniform chain	2.45	0.47	5.69	86.3	127.8/130.5	0.03	81	1.5	HTSE[f]	this work

[a] The longest Cu–N(azide) bond length. [b] δ is the difference between the longest and the shortest Cu–N(azide) bond lengths and is related to the "shearing-like" distortion.[17] [c] θ is the Cu–N1···N3–Cu torsion angle, assuming the linearity of the azide bridge. [d] τ is the Addison parameter.[29] [e] α is the angle between the two basal planes of the square pyramid coordination polyhedron of two adjacent Cu^{II} ions. [f] High-temperature series expansion model.[2a,33]

dimer interactions. Among these systems, only three complexes are reported with AF exchange. One of them even exhibits a strong AF behaviour with $J = -22.5$ cm^{-1}.

Nevertheless, none of the usual geometrical parameters used in magnetostructural correlations allow a clear trend in the evolution of J for single EE azido-bridged complexes to be drawn. A closer look at other structural data such as the Cu···Cu distance or the α angle between the two basal planes of the square pyramid coordination polyhedron of the Cu^{II} ions failed to draw convincing correlations. Therefore, one may postulate that a single structural parameter is not sufficient to correctly depict such a system. The greater flexibility allowed by single bridges, with respect to double ones, may explain the need of a multiparameter description. However, both a tentative combination of several parameters and a restriction to uniform chains described by the same magnetic model, that is, the high-temperature series expansion (HTSE),[2a,33] do not raise any tendency.

Finally, let us note that the weakness of the magnetic exchange constants in the single EE coordination mode of the azido ligand does not facilitate any detailed magnetostructural analysis. In addition, the large AF value $J = -22.5$ cm^{-1} observed in $\{Cu^{II}L'(N_3)\}_n$ [with HL′ = 1-(dimethylamino)-2-(salicylideneamino)ethane][28a] deserves particular attention, as its magnetic behaviour strongly differs from the other complexes.

Conclusions

The structural, magnetic and electrochemical study of one of the scarce examples of a single end-to-end azidocopper(II) chain was achieved. The redox activity of the enaminone electroactive ligand involved in this architecture was checked, as well as the electrochemical behaviour of the complex in acetonitrile and *N*,*N*-dimethylformamide. Whereas the new species (with a new Cu^{II}/Cu^{I} redox couple) generated from the reduction of the $[CuL_2]$ complex is stable and exhibits a quasireversible redox process, no such stable species was observed from the reduction of the $\{Cu^{II}L(N_3)\}_n$ polymeric chain. The role of the azide ligand on the absence of reversibility remains to be clarified.

The magnetic inspection, supported by state-of-the-art ab initio quantum calculations has evidenced very weak ferromagnetic interactions between the metallic centres through single end-to-end asymmetric azido bridges. Whereas magnetostructural trends are known for double azido-bridged complexes, no correlation emerged from our analysis for singly bridged species. Therefore, further magnetostructural investigations, mainly based on high-level theoretical calculations, are currently in progress to fully rationalize the experimental observations collected for this class of systems.

Experimental Section

General Comments: *Caution!* Although we did not experience any problems, azido complexes are potentially explosive. Small amounts of material should be prepared and handled with care. The synthesis of the HL ligand was previously reported.[23]

Synthesis of the $\{CuL(N_3)\}_n$ Complex: A solution of $CuCl_2{\cdot}2H_2O$ (73.2 mg, 0.56 mmol) dissolved in methanol (5 mL) was added drop by drop to a solution of HL (150 mg, 0.56 mmol) in methanol (15 mL). After 10 min of stirring, NaN_3 (10 mL, 183 mg, 2.8 mmol) dissolved in methanol was added dropwise. The solvent of the resulting dark green solution was removed by slow evaporation for 10 d, giving crystals (plates) suitable for X-ray analyzes and isolated upon filtration. Yield: 128 mg (62%). $C_{13}H_8CuF_3N_5O$ (370.78): calcd. C 42.11, H 2.17, N 18.88, F 15.37, Cu 17.14; found C 42.9, H 2.2, N 19.1, F 15.0, Cu 16.8.

Electrochemical Measurements: Electrochemical measurements were performed by using an EG & G-Princeton Applied Research 263A all-in one potentiostat by using a standard three-electrode setup with a glassy carbon electrode, platinum wire auxiliary electrode and SCE (saturated calomel electrode) as the reference electrode. CH_3CN and DMF solutions of the compound under study were 1 mM and 0.1 M in the supporting electrolyte nBu$_4$NPF$_6$ with the voltage scan rate equals to 0.05 V s^{-1}. Under these experimental

conditions, the ferrocene/ferricinium couple, used as internal reference for peak potential measurements, was located at 0.416 V in CH_3CN and 0.445 V in DMF.

Single-Crystal X-ray Diffraction Studies: Data collection was performed at 293 K by using the KappaCCD analysis programs.[34] The lattice constants were refined by least-squares refinements. No absorption correction was applied to the data sets. The structure was solved by direct methods by using the SIR97 program[35] combined with Fourier difference syntheses and refined against F by using the CRYSTALS program.[36] Hydrogen atoms were found either by Fourier difference or located theoretically based on the conformation and environment of the supporting atom and then refined. All the atomic displacement parameters for non-hydrogen atoms were refined anisotropically.[37] Results of the refinement can be found in Table 4.

Table 4. Crystal data and structure refinement parameters.

Formula	$C_{13}H_8CuF_3N_5O$
Fw [g mol^{-1}]	370.8
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
T [K]	293
Z	4
a [Å]	9.6555(6)
b [Å]	8.7154(3)
c [Å]	16.450(1)
β [°]	99.868(2)
V [Å^3]	1363.8(1)
Independent reflections	3223
R_{int}	0.035
D [g cm^{-3}]	1.806
μ [mm^{-1}]	1.648
R [$I/\sigma(I) > 2$]	0.0375
R_w [$I/\sigma(I) > 2$]	0.0378
S	1.13
No. reflections used	1864
No. parameters refined	232
$\Delta\rho_{max}$ [e$^-$ Å^{-3}]	0.38
$\Delta\rho_{min}$ [e$^-$ Å^{-3}]	–0.31

Magnetic Measurements: Magnetic measurements were performed on polycrystalline samples by using a Quantum Design SQUID magnetometer MPMS-XL that works between 1.8 and 300 K for DC applied fields ranging from –5 to 5 T. The magnetic susceptibility was measured at 0.5 and 1 T. The magnetic data were corrected for the sample holder and diamagnetic contributions.

Computational Details: Calculations were performed on a molecular dimer unit $[Cu_2(N_3)_3L_2]^-$ extracted from the crystal data, without any geometry optimization. Because the system we are interested in consists of an open d-shell ion (Cu^{II}, d^9), we favoured explicitly correlated ab initio calculations. Besides, the evaluation of magnetic coupling constants calls for an accurate low-energy spectrum description (≈ 10 cm^{-1}). Thus, rigorous multireference calculations were carried out to take advantage of the relevant information conveyed by the wavefunction. Firstly, complete active space self-consistent field (CASSCF)[38] calculations, including *n* electrons in *m* MOs, were performed by using the MOLCAS 7.2 package[39] to generate a reference space [CAS(*n*,*m*)], which consists in the configurations that qualitatively describe the problem. Caballol et al.[40] showed that a CAS(2,2) including two electrons in two orbitals (one on each metal centre) is recommended for the EE azido-bridged copper(II) complexes, whilst a CAS including π and π* azido orbitals is required to describe EO analogues.[16d] The dynamical correlation effects were then incorporated on top of the triplet CASSCF wavefunction by using the dedicated difference configuration interaction (DDCI)[41] method implemented in the CASDI code.[42] With this approach, one concentrates on the differential effects rather than on the evaluation of the absolute energies. Such a strategy was successfully used to study the magnetic properties of various molecular and extended materials.[4,17,43] Basis sets and pseudopotentials on the Cu atoms (9s6p6d)/[3s3p4d][44] as well as (4s4p)/[2s2p] for C and N, and (4s5p)/[2s3p] for O[45] were used, whereas the H atoms were described with (3s)/[1s].[46]

Acknowledgments

We would like to thank the Centre National de la Recherche Sscientifique for financial support as well as the fdp-magnets Agence Nationale de la Recherche program (ANR-07-JCJC-0045-0) and in part the Région Rhône-Alpes (CIBLE 2009 ENAMBRIMOLE project). Single-crystal X-ray diffraction studies were performed at the "Centre de Diffractométrie Henri Longchambon", Université Claude Bernard Lyon 1. B. L. G. thanks the "Institut de Développement et de Ressources en Informatique" (IDRIS) for computing facilities. Rita Matrak and Fabrice Fenain are thanked for some preliminary syntheses.

[1] D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, **2006**.
[2] a) O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, **1993**; b) J. S. Miller, M. Drillon (Eds.), *Magnetism: Molecules to Materials II: Molecule-Based Materials*, Wiley-VCH, Weinheim, **2002**.
[3] J. Ribas, A. Escuer, M. Montfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193*, 1027.
[4] G. Chastanet, B. Le Guennic, C. Aronica, G. Pilet, D. Luneau, M.-L. Bonnet, V. Robert, *Inorg. Chim. Acta* **2008**, *361*, 3847.
[5] A. Escuer, G. Aromi, *Eur. J. Inorg. Chem.* **2006**, 4721 and references cited therein.
[6] a) M. A. Halcrow, J. C. Huffman, G. Christou, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 889; b) M. A. Halcrow, J.-S. Sun, J. C. Huffman, G. Christou, *Inorg. Chem.* **1995**, *34*, 4167; c) M. W. Wemple, D. M. Adams, K. S. Hagen, K. Folting, D. N. Hendrickson, G. Christou, *J. Chem. Soc., Chem. Commun.* **1995**, 1591; d) D. Ma, S. Hikichi, M. Akita, Y. Morooka, *J. Chem. Soc., Dalton Trans.* **2000**, 1123; e) M. A. S. Goher, J. Cano, Y. Journaux, M. A. M. Abu-Yussef, F. A. Mautner, A. Escuer, R. Vicente, *Chem. Eur. J.* **2000**, *6*, 778.
[7] F. Meyer, S. Demeshko, G. Leibeling, B. Kersting, E. Kaifer, *Chem. Eur. J.* **2005**, *11*, 1518.
[8] G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia, *Angew. Chem. Int. Ed.* **2001**, *40*, 884.
[9] a) F. Meyer, P. Kircher, H. Pritzhow, *Chem. Commun.* **2003**, 774; b) S. Demeshko, G. Leibeling, W. Maringgele, F. Meyer, C. Mennerich, H.-H. Klaus, H. Pritzhow, *Inorg. Chem.* **2005**, *44*, 519; c) C. Golze, A. Alfonsov, R. Klingeler, B. Büchner, V. Kataev, C. Mennerich, H.-H. Klaus, M. Goiran, J.-M. Broto, H. Rakoto, S. Demeshko, G. Leibeling, F. Meyer, *Phys. Rev. B* **2006**, *73*, 2244031.
[10] For example, see: a) E.-Q. Gao, S.-Q. Bai, Y.-F. Yue, Z.-M. Wang, C.-H. Yan, *Inorg. Chem.* **2003**, *42*, 3642; b) A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1993**, *32*, 3727; c) G. Viau, M. G. Lombardi, G. D. Munno, M. Julve, F. Lloret, J. Faus, A. Caneschi, G. M. Clemente-Juan, *Chem. Commun.* **1997**, 1195; d) F. Meyer, H. Pritzkow, *Inorg. Chem. Commun.* **2001**, *4*, 305; e) T.-F. Liu, J.-L. Zuo, Z. Yu, Y. Zhong, H.-L. Sun, G. Su, Y.-J. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 13976; f) Z. Shen, J.-L. Zuo, Z. Yu, Y. Zhong, J.-F. Bai, C.-M. Che, H.-K. Fun, J. J. Vittal, X.-Z. You, *J. Chem. Soc., Dalton Trans.* **1999**, 3393; g) A. Escuer, R.

Vicente, F. A. Mautner, M. A. S. Goher, *Inorg. Chem.* **1997**, *36*, 1233; h) A. Escuer, R. Vicente, M. S. El Fallah, S. B. Kumar, F. A. Mautner, D. Gatteschi, *J. Chem. Soc., Dalton Trans.* **1998**, 3905; i) U. B. K. Gosh, M. Montfort, J. Ribas, G. Mostafa, T. H. Lu, C. Sinha, *Eur. J. Inorg. Chem.* **2004**, 250.

[11] a) J. L. Manson, A. M. Arif, J. S. Miller, *Chem. Commun.* **1999**, 1479; b) M. Montfort, I. Resino, J. Ribas, H. Stoecki-Evans, *Angew. Chem. Int. Ed.* **2000**, *39*, 191; c) Z. Shen, J.-L. Zuo, S. Gao, Y. Song, C.-M. Che, H.-K. Fun, X.-Z. You, *Angew. Chem. Int. Ed.* **2000**, *39*, 3633; d) M. Monfort, J. Ribas, X. Solans, *J. Chem. Soc., Chem. Commun.* **1993**, 350; e) J. Ribas, M. Montfort, X. Solans, M. Drillon, *Inorg. Chem.* **1994**, *33*, 742; f) R. Cortès, L. Lezama, T. Rojo, J. L. Pizarro, I. Arriortua, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1810.

[12] a) F. A. Mautner, R. Cortès, L. Leama, T. Rojo, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1810; b) F.-C. Liu, Y.-F. Zeng, J. Jiao, X.-H. Bu, J. Ribas, S. R. Batten, *Inorg. Chem.* **2006**, *45*, 2776; c) F.-C. Liu, Y.-F. Zng, J.-R. Li, H.-J. Zhang, X.-H. Bu, *Inorg. Chem.* **2005**, *44*, 7298.

[13] Y.-F. Zeng, X. Hu, F.-C. Liu, X.-H. Bu, *Chem. Soc. Rev.* **2009**, *38*, 469.

[14] For recent examples, see: a) M. A. M. Abu-Youssef, M. Drillon, A. Escuer, M. A. S. Goher, F. A. Mautner, R. Vicente, *Inorg. Chem.* **2000**, *39*, 5022; b) F.-C. Liu, Y.-F. Zeng, J.-P. Zhao, B.-W. Hu, X.-H. Bu, J. Ribas, J. Cano, *Inorg. Chem.* **2007**, *46*, 1520; c) M. A. M. Abu-Youssef, A. Escuer, M. A. S. Goher, F. A. Mautner, G. J. Reiss, R. Vicente, *Angew. Chem. Int. Ed.* **2000**, *39*, 1624; d) F.-C. Liu, Y.-F. Zeng, J.-P. Zhao, B.-W. Hu, X.-H. Bu, J. Ribas, J. Cano, *Inorg. Chem.* **2007**, *46*, 1520.

[15] a) J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* **1993**, *32*, 3557; b) R. Vicente, A. Escuer, *Polyhedron* **1995**, *14*, 2133; c) A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1998**, *37*, 782; d) R. J. Butcher, C. J. O'Connor, E. Sinn, *Inorg. Chem.* **1981**, *20*, 3486; e) S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.* **1994**, *33*, 5555; f) T. K. Karmakar, B. K. Ghosh, A. Usman, H. K. Fun, E. Riviere, T. Mallah, G. Aromí, S. K. Chandra, *Inorg. Chem.* **2005**, *44*, 2391; g) S. Triki, C. J. Gomez-Garcia, E. Ruiz, J. Sala-Pala, *Inorg. Chem.* **2005**, *44*, 5501; h) A. Escuer, M. Font-Bardia, S. S. Massoud, F. A. Mautner, E. Penalba, X. Solans, R. Vicente, *New J. Chem.* **2004**, *28*, 681.

[16] a) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, *120*, 11122; b) F. Fabrizi di Biani, E. Ruiz, J. Cano, J. J. Novoa, S. Alvarez, *Inorg. Chem.* **2000**, *39*, 3221; c) C. Adamo, V. Barone, A. Bencini, F. Totti, I. Ciofini, *Inorg. Chem.* **1999**, *38*, 1996; d) J. Cabrero, C. de Graaf, E. Bordas, R. Caballol, J.-P. Malrieu, *Chem. Eur. J.* **2003**, *9*, 2307.

[17] a) C. Aronica, E. Jeanneau, H. El Moll, D. Luneau, B. Gillon, A. Goujon, A. Cousson, M. A. Carvajal, V. Robert, *Chem. Eur. J.* **2007**, *13*, 3666; b) M. A. Carvajal, C. Aronica, D. Luneau, V. Robert, *Eur. J. Inorg. Chem.* **2007**, *28*, 4434.

[18] a) H.-L. Sun, Z.-M. Wang, S. Gao, *Chem. Eur. J.* **2009**, *15*, 1757; b) T. F. Liu, D. Fu, S. Gao, Y. Z. Zhang, H. L. Sun, G. Su, Y. J. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 13976; c) X.-T. Liu, X. Y. Wang, W. X. Zhang, P. Cui, S. Gao, *Adv. Mater.* **2006**, *18*, 2852.

[19] a) B. Le Guennic, S. Petit, G. Chastanet, G. Pilet, D. Luneau, N. Ben Amor, V. Robert, *Inorg. Chem.* **2008**, *47*, 572; b) L. F. Chibotaru, L. Ungur, C. Aronica, H. El Moll, G. Pilet, D. Luneau, *J. Am. Chem. Soc.* **2008**, *130*, 12445.

[20] M.-L. Bonnet, C. Aronica, G. Chastanet, G. Pilet, D. Luneau, C. Mathonière, R. Clérac, V. Robert, *Inorg. Chem.* **2008**, *47*, 1127.

[21] a) C. Aronica, G. Pilet, G. Chastanet, W. Wernsdorfer, J.-F. Jacquot, D. Luneau, *Angew. Chem. Int. Ed.* **2006**, *45*, 4659; b) C. Aronia, G. Chastanet, G. Pilet, B. Le Guennic, V. Robert, W. Wernsdorfer, D. Luneau, *Inorg. Chem.* **2007**, *46*, 572.

[22] a) C. C. Lu, B. Eckhard, T. Weyhermüller, E. Bothe, K. Wieghardt, *J. Am. Chem. Soc.* **2008**, *130*, 3181; b) C. C. Lu, B. Eckhard, T. Weyhermüller, E. Bothe, K. Wieghardt, *Inorg. Chem.* **2007**, *46*, 7880; c) S. Messaoudi, V. Robert, N. Guihéry, D. Maynau, *Inorg. Chem.* **2006**, *45*, 3212; d) K. Chlopek, B. Eckhard, T. Weyhermüller, K. Wiegardt, *Inorg. Chem.* **2005**, *44*, 7087; e) P. Ghosh, B. Eckhard, T. Weyhermüller, F. Neese, K. Wieghardt, *J. Am. Chem. Soc.* **2003**, *125*, 1293.

[23] G. Pilet, J.-B. Tommasino, F. Fenain, R. Matrak, M. Médebielle, *Dalton Trans.* **2008**, 5621.

[24] a) H. C. Budnikov, O. Yu. Kargina, *J. Electroanal. Chem.* **1984**, *169*, 195; b) G. K. Budnikov, O. Yu. Kargina, V. I. Morozov, Ya. A. Aizikovoch, K. I. Pashkevich, *Zh. Obshch. Khim.* **1982**, *52*, 1008.

[25] a) U. M. Kauhanka, M. M. Kauhanka, *Liq. Cryst.* **2006**, *33*, 213; b) C. P. Roll, A. G. Martin, H. Görls, G. Leibeling, D. Guillon, B. Donnio, W. Weigand, *J. Mater. Chem.* **2004**, *14*, 1722; c) U. Pietrasik, J. Szydlowska, D. Piociecha, J. Przedmojski, E. Gorecka, *Liq. Cryst.* **1998**, *25*, 177.

[26] a) L. Zhang, M. Brookhar, P. S. White, *Organometallics* **2006**, *25*, 1868; b) H.-Y. Wang, J. Zhang, X. Meng, G.-X. Jin, *J. Organomet. Chem.* **2006**, *691*, 1275; c) X.-F. Li, K. Dai, W.-P. Ye, L. Pan, Y.-S. Li, *Organometallics* **2004**, *23*, 1223.

[27] a) P. S. Mukherjee, T. K. Maji, A. Escuer, R. Vicente, J. Ribas, G. Rosair, F. A. Mautner, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* **2002**, 943; b) Z. N. Chen, J. Qiu, Z. K. Wu, D. G. Fu, K. B. Yu, W. X. Tang, *J. Chem. Soc., Dalton Trans.* **1994**, 1923.

[28] a) C. Adhikary, D. Mal, K.-I. Okamoto, S. Chaudhuri, S. Koner, *Polyhedron* **2006**, *25*, 2191; b) E.-Q. Gao, S.-Q. Bai, C.-F. Wang, Y.-F. Yue, C.-H. Yan, *Inorg. Chem.* **2003**, *42*, 8456; c) Z. Shen, J.-L. Zuo, S. Gao, Y. Song, C.-M. Che, H.-K. Fun, X.-Z. You, *Angew. Chem. Int. Ed.* **2000**, *39*, 3633; d) P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah, N. R. Chaudhuri, *Inorg. Chem.* **2000**, *39*, 5147; e) G. De Munno, M. G. Lombardi, P. Paoli, F. Lloret, M. Julve, *Inorg. Chim. Acta* **1998**, *282*, 252; f) M. A. S. Goher, A. Escuer, F. A. Mautner, N. A. Al-Salem, *Polyhedron* **2001**, *20*, 2971; g) S. Dalai, P. S. Mukherjee, M. G. B. Drew, T.-H. Lu, N. R. Chaudhuri, *Inorg. Chim. Acta* **2002**, *335*, 85; h) A. M. Madalan, M. Noltemeyer, M. Neculai, H. W. Roesky, M. Schmidtmann, A. Müller, Y. Journaux, M. Andruh, *Inorg. Chim. Acta* **2006**, *359*, 459; i) T. K. Maji, P. S. Mukherjee, G. Mostafa, T. Mallah, J. Cano-Boquera, N. R. Chaudury, *Chem. Commun.* **2001**, 1012.

[29] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, *7*, 1349.

[30] The $[CuL_2]$ complex has been studied in dichloromethane and DMF. However, as a result of the insolubility of $\{CuL(N_3)\}_n$ in CH_2Cl_2, this latter was replaced by CH_3CN (also as a result of the insolubility of NaN_3 and the nonmiscibility of water with this solvent). The comparison of the monomeric and the polymeric behaviours was then carried out by using DMF data.

[31] a) M. R. DeFelippis, M. Faraggi, M. H. Klapper, *J. Phys. Chem.* **1990**, *94*, 2420; b) Z. B. Alfassi, A. Harriman, R. E. Huie, S. Mosseri, P. Neta, *J. Phys. Chem.* **1987**, *91*, 2120.

[32] S. Sarkar, A. Mondal, J. Ribas, M. G. B. Drew, K. Pramanik, K. K. Rajak, *Eur. J. Inorg. Chem.* **2004**, 4633.

[33] G. A. Baker Jr., G. S. Rushbrooke, H. E. Gilbert, *Phys. Rev.* **1964**, *135*, A1272.

[34] B. V. Nonius, *Nonius COLLECT, DENZO, SCALEPACK, SORTAV*, KappaCCD program package, Delft, The Netherlands, **1999**.

[35] G. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Siliqi, M. C. Burla, G. Polidori, M. Camalli, *Acta Crystallogr., Sect. C* **1996**, *52*, C79.

[36] D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *CRYSTALS*, Issue 11; Chemical Crystallography Laboratory, Oxford, UK, **1999**.

[37] CCDC -706499 [for $\{CuL(N_3)\}_n$] contains 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.

[38] B. O. Roos, *Adv. Chem. Phys.* **1987**, *69*, 399.

[39] G. Karlström, R. Lindh, P. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, *28*, 222.
[40] a) C. J. Calzado, J. Cabredo, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **2002**, *116*, 2728; b) C. J. Calzado, J. Cabredo, J. P. Malrieu, R. Caballol, *J. Chem. Phys.* **2002**, *116*, 3985.
[41] a) J. Miralles, J.-P. Daudey, R. Caballol, *Chem. Phys. Lett.* **1992**, *198*, 555; b) J. Miralles, O. Castell, R. Caballol, J.-P. Malrieu, *Chem. Phys.* **1993**, *172*, 33.
[42] N. Ben Amor, D. Maynau, *Chem. Phys. Lett.* **1998**, *286*, 211.
[43] For instance: a) I. P. R. Moreira, N. Suaud, N. Guihéry, J.-P. Malrieu, R. Caballol, J. M. Bofill, F. Illas, *Phys. Rev. B* **2002**, *66*, 134430; b) D. Herebian, K. E. Wieghardt, F. Neese, *J. Am. Chem. Soc.* **2003**, *125*, 10997; c) S. Messaoudi, V. Robert, N. Guihéry, D. Maynau, *Inorg. Chem.* **2006**, *45*, 3212; d) B. Le Guennic, V. Robert, *C. R. Chim.* **2008**, *11*, 650; e) C. de Graaf, F. Illas, *Phys. Rev. B* **2001**, *63*, 014404.
[44] Z. Barandiaran, L. Seijo, *Can. J. Chem.* **1992**, *70*, 409.
[45] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431.
[46] W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.* **1969**, *51*, 2657.

Received: June 23, 2009
Published Online: October 1, 2009

