Three Novel End-to-End Single Azido-Bridged Ferromagnetic Copper(II) Chains: Synthesis, Crystal Structure, and Magnetic Behavior

Partha Sarathi Mukherjee,[a] Tapas Kumar Maji,[a] Albert Escuer,*[b] Ramon Vicente,[b] Joan Ribas,[b] Georgina Rosair,[c] Franz A. Mautner,[d] and Nirmalendu Ray Chaudhuri*[a]

Keywords: Copper / N ligands / Azido bridge / Magnetic properties

Three new single end-to-end azido-bridged copper(II) chains $[Cu(L1)(N_3)]_n(ClO_4)_n$ (**1**), $[Cu(L2)(N_3)]_n(ClO_4)_n$ (**2**), and $[Cu(L3)(N_3)]_n(ClO_4)_n$ (**3**) using three different tridentate Schiff bases L1, L2, and L3, obtained from condensation of pyridine-2-carbaldehyde with *N*,*N*-dimethylethane-1,2-diamine, *N*,*N*-diethylethane-1,2-diamine, and 4-(2-aminoethyl)morpholine, respectively, have been synthesized, and their crystal structures have been determined by X-ray diffraction methods. Complex **1**, $C_{10}H_{15}CuN_6ClO_4$, crystallizes in an orthorhombic system, space group $P2_12_12_1$, with a = 7.434(3), b = 12.047(4), c = 17.404(6) Å, and Z = 4; complex **2**, $C_{12}H_{19}CuN_6ClO_4$, crystallizes in an orthorhombic system, space group $Pna2_1$, with a = 14.723(5), b = 13.829(5), c = 8.002(5) Å, and Z = 4 and complex **3**, $C_{12}H_{17}CuN_6ClO_5$, crystallizes in an orthorhombic system, space group $Pna2_1$, with a = 13.837(15), b = 14.804(2), c = 8.050(4) Å, and Z = 4. Each structure consists of a single end-to-end azido-bridged copper(II) 1D chain where each copper(II) center possesses a square pyramidal geometry. Magnetic susceptibility data, measured from 4 to 300 K, show weak ferromagnetic interaction through the end-to-end bridging azido pathway in all the complexes. The magnetic data were fitted to a high temperature series-expansion for a one-dimensional system with $S = {}^1/_2$ local spin based on the Hamiltonian $H = -J\Sigma S_i{\cdot}S_{i+1}$ for all the complexes, giving the parameters $J = +2.15\ \mathrm{cm}^{-1}$, g = 2.23 for **1**, $J = +3.61\ \mathrm{cm}^{-1}$, g = 2.16 for **2**, and $J = +2.06\ \mathrm{cm}^{-1}$, g = 2.17 for **3**. This unusual magnetic behavior through the end-to-end bridging azido pathway has been correlated to the structural parameters.

Introduction

Recently, chemists as well as physicists have concentrated their efforts on the study of multinuclear molecular-based magnetic materials from the need to understand the fundamental science associated with magnetic interactions between the paramagnetic metal ions and the bridging ligands to develop the magneto-structural correlation enabling the design synthesis of interesting magnetic materials.[1−4] These molecular-based magnets can be designed to yield dimer, tetramer, mono-, bi-, and three-dimensional extended structures[5−8] with the paramagnetic metal ions using suitable bridging ligands which act as a superexchange pathway between paramagnetic centers and determine the strength of magnetic interactions i.e., the coupling parameter (J). The construction of molecular-based magnetic materials with ferromagnetic ordering is one of the major challenges in magneto-chemistry. The proper choice of the bridging ligand, which determines the magnetic behavior of the molecule, is an important task to the chemist for synthesizing such type of materials.

The azido ligand is an efficient superexchange pathway for propagating magnetic interaction between the paramagnetic centers such as copper(II), giving dimeric, tetranuclear, cubane, 1D, 2D, and 3D complexes.[9−17] The versatility of this ligand is due to its diverse binding modes leading to a variation in the magnetic properties that depend on its orientation with respect to the magnetic centers.[18] In general, the bridging modes observed for the azido group are end-to-end with anti-ferromagnetic interaction[19,20] and end-on with ferromagnetic interaction.[21] However, the magnetism of the latter is dependent on the M−N−M angle.[22−27] For copper(II) systems, ferromagnetic interaction is observed for complexes having Cu−N−Cu angles less than 108°. For angles above this value, molecules show antiferromagnetic interaction.[27] Hoffmann et al.[28] and later Ribas et al.[29] showed the possibility of even ferro-

---

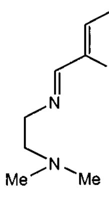
[a] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Kolkata-700032, India
E-mail: icnrc@mahendra.iacs.res.in
Fax: (internat.) + 91-33/473-2805

[b] Departament de Química Inorgànica, Universitat de Barcelona,
Diagonal 647, 08028 Barcelona, Spain

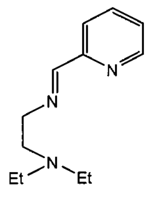
[c] Department of Chemistry, Heriot Watt University,
Edinburgh EH 144AS, UK

[d] Institut für Physikalische und Theoretische Chemie, Technische Universität Graz,
8010 Graz, Austria

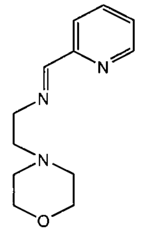
magnetic interaction through an end-to-end azido pathway on the basis of theoretical calculations. This theory has been successfully tested in a scarce number of complexes. Only a few structurally solved M^{II} systems, showing weak ferromagnetic interaction through the end-to-end bridging azido pathway have recently been reported in the literature.[30−33] One of them is a 1D chain of Ni^{II} with an end-to-end azido-bridge using a nonchelating capping co-ligand[30] and the second one is a dimer of Ni^{II} using a chelating co-ligand.[31] Recently this laboratory reported the first observation of a ferromagnetic interaction through end-to-end azido pathways in a copper(II) system.[32,33] This unusual result prompted us to synthesize more and more such complexes types. In the present paper we report on the synthesis, X-ray crystal structures of three new 1D single azido-bridged copper(II) chains, $[Cu(L1)(N_3)]_n(ClO_4)_n$ (**1**), $[Cu(L2)(N_3)]_n(ClO_4)_n$ (**2**), and $[Cu(L3)(N_3)]_n(ClO_4)_n$ (**3**) where L1, L2, and L3 are three different Schiff bases obtained from the condensation of pyridine-2-carbaldehyde with *N*,*N*-dimethylethane-1,2-diamine, *N*,*N*-diethylethane-1,2-diamine, and 4-(2-aminoethyl)morpholine, respectively, and observation of unusual ferromagnetic interaction through the end-to-end azido pathway.



L1



L2



L3

Results and Discussion

IR Spectroscopy

The presence of strong bands at 2062, 2075, and 2070 cm^{-1} in the IR spectrum of complexes **1**, **2**, and **3**, respectively, are due to asymmetric stretching of azide. Peaks at 1662, 1659, and 1674 cm^{-1} in the IR spectrum of **1**, **2**, and **3**, respectively, are due to the stretching of the C=N group in these complexes.

Description of the Structures

All the structures consist of 1D copper(II)-azido chain isolated by a ClO_4^- anion. In the chain structures, each copper(II) atom is coordinated by one tridentate (NNN donor) Schiff base ligand and two bridging azido ligands in a square pyramidal geometry.

$[Cu(L1)(N_3)]_n(ClO_4)_n$ (1)

A labeled scheme of **1** is shown in Figure 1. The main bond lengths and angles are listed in Table 1. Other distances and angles may be found in the deposited information (Cambridge database; see reference at the end of the Exp. Sect.). The structure of **1** consists of copper Cu(L1)(N_3) units bridged by an end-to-end azido resulting in a chain system with perchlorate counter anions. The basal plane of each copper atom consists of one tridentate L1 ligand, Cu(1)−N(1) 2.051(4), Cu(1)−N(2) 1.953(4), Cu(1)−N(3) 2.058(3) Å, and one nitrogen atom N(11) of the azido ligand *trans* to N(2) with a Cu(1)−N(11) distance of 1.947(3) Å and the apical coordination site occupied by the N(13)* atom from another azido-bridging ligand, Cu(1)−N(13)* 2.355(4) Å. One oxygen atom from the perchlorate counter anion weakly interacts with the copper atom, Cu(1)−O(1) 2.914(4) Å in a *trans* position to N(13)*. The L1 ligand is roughly planar, with N(2) and N(3) displaced 0.120(1) and 0.036(4) Å from the mean plane defined by the aromatic ring. Bond angles between N(2)−Cu(1)−N(11) and N(1)−Cu(1)−N(3) are 168.2(2)° and 163.3(2)° and the bond angles between the apical equatorial coordination sites are greater than 90°, suggesting a square pyramidal arrangement. Azido ligand acts as a single end-to-end bridge between the copper atoms, showing the Cu(1)−N(11)−N(12) and Cu(1)−N(13)*−N(12)* bond angles of 126.5(3)° and 131.2(4)°. The torsion angle Cu(1)−N(11)−N(12)−N(13)−Cu(1)* has a value of 97.8(4)° and the CuN_4 neighboring mean planes an angle of 34.6(1)°.

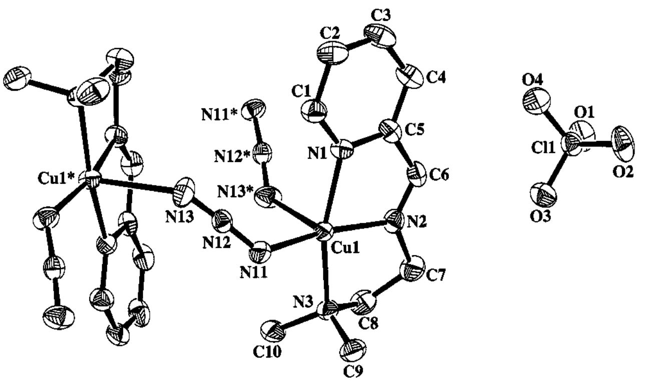


Figure 1. View of the $[Cu(L1)(N_3)]_n(ClO_4)_n$ (**1**) with atom labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms

$[Cu(L2)(N_3)]_n(ClO_4)_n$ (2) and $[Cu(L3)(N_3)]_n(ClO_4)_n$ (3)

The labeled scheme of complexes **2** and **3** are shown in Figures 2 and 3, respectively. The main bond lengths and angles of complexes **2** and **3** are listed in Tables 2 and 3, respectively. Other distances and angles may be found in the deposited information (Cambridge database). The structures of **2** and **3** consist of Cu(L2)(N_3) and Cu(L3)(N_3) units, respectively, bridged by end-to-end azido resulting in a 1D coordination chain and perchlorate counter anions. Each copper atom in the polymeric chain is in a square pyramidal geometry. The local environment of the copper atoms in both the complexes consists of one tridentate Schiff base ligand and the two azido-bridging ligand. In both the complexes all three nitrogen atoms of the tridentate ligands (L2 and L3) are occupied in the basal plane of

Table 1. Selected bond lengths [Å] and angles [°] for $[Cu(L1)(N_3)]_n(ClO_4)_n$ (**1**) (symmetry codes: *i* = $x + 1/2, -y + 1/2, -z$; *ii* = $x - 1/2, -y + 1/2, -z$)

Cu(1)−N(11)	1.947(3)	Cu(1)−N(2)	1.953(4)
Cu(1)−N(1)	2.051(4)	Cu(1)−N(3)	2.058(3)
Cu(1)−N(13)*_*i*	2.355(4)	N(11)−N(12)	1.181(5)
N(12)−N(13)	1.158(5)		
N(11)−Cu(1)−N(2)	168.2(2)	N(11)−Cu(1)−N(1)	102.7(2)
N(2)−Cu(1)−N(1)	80.4(2)	N(11)−Cu(1)−N(3)	93.4(2)
N(2)−Cu(1)−N(3)	83.0(2)	N(1)−Cu(1)−N(3)	163.3(2)
N(11)−Cu(1)−N(13)*_*i*	95.7(2)	N(2)−Cu(1)−N(13)*_*i*	95.8(2)
N(1)−Cu(1)−N(13)*_*i*	89.3(2)	N(3)−Cu(1)−N(13)*_*i*	93.4(2)
Cu(1)−N(11)−N(12)	126.5(3)	N(13)−N(12)−N(11)	176.0(4)
Cu(1)*_*ii*−N(13)−N(12)	131.2(4)		

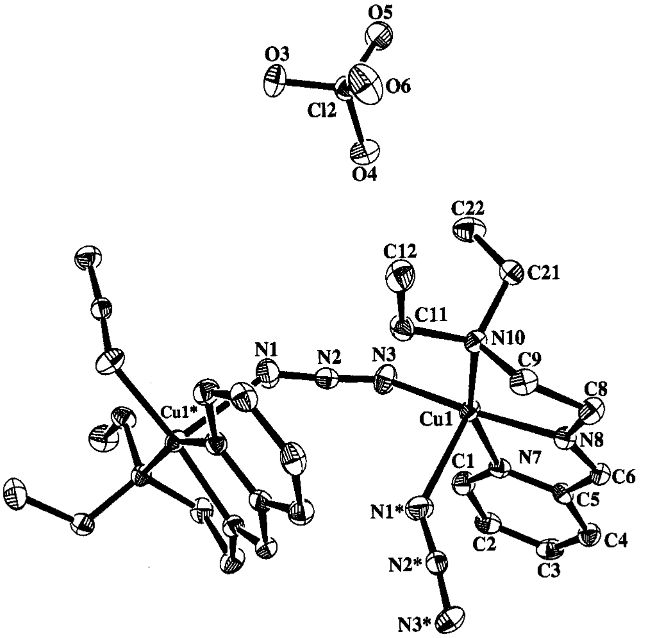


Figure 2. View of the $[Cu(L2)(N_3)]_n(ClO_4)_n$ (**2**) chain with atom labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms

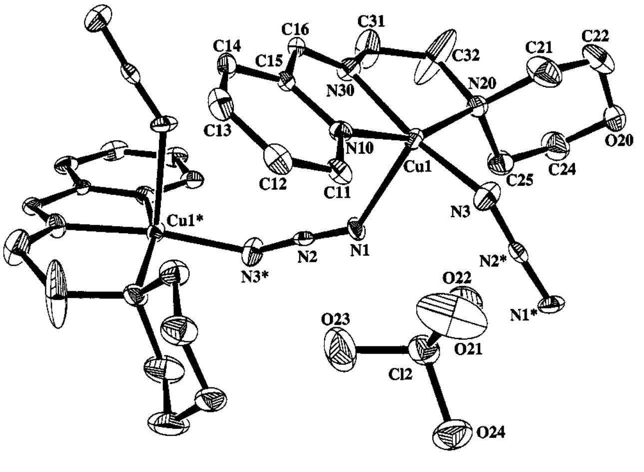


Figure 3. View of the $[Cu(L3)(N_3)]_n(ClO_4)_n$ (**3**) chain with atom labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms

the square pyramid. In the case of complex **2** the bond lengths in the basal plane are Cu(1)−N(8) 1.961(3), Cu(1)−N(7) 2.039(3), Cu(1)−N(10) 2.068(3), and Cu(1)−N(3) 1.965(3) Å. The axial position of Cu(1) is occupied by N(1)* of the azido of the neighboring $[Cu(L2)(N_3)](ClO_4)$ moiety with a Cu(1)−N(1)* distance of 2.311(3) Å for **2**. While for complex **3** the basal plane bond lengths are Cu(1)−N(30) 1.939(7), Cu(1)−N(20) 2.064(6), Cu(1)−N(10) 2.030(6), and Cu(1)−N(3) 1.951(7) Å which is in a *trans* position to N(30) and the axial position of Cu(1) is occupied by N(1) of the azido of the neighboring $[Cu(L3)(N_3)](ClO_4)$ moiety with a Cu(1)−N(1) distance of 2.270(5) Å. The Cu(1)−N(3)−N(2)−N(1)−Cu(1)* torsion angle is 50.0(4)° and the normals to the two copper equatorial coordination planes are inclined at 15.9(1)° for **2**. For complex **3** the Cu(1)−N(1)−N(2)−N(3)*−Cu(1)* torsion angle is 40.4(8)° and the normals to the two copper equatorial coordination planes are inclined at 14.2(2)°. The intrachain copper−copper distance is 5.630(2) and 5.540(2) Å for complexes **2** and **3,** respectively, and each copper(II) in the chain has square pyramidal geometry with the Cu atom displaced towards the axial azide ligand by 0.1681(15) and 0.241(3) Å out of the equatorial plane. One of the perchlorate oxygen atoms has an intermolecular contact to copper approximately *trans* to N(1)* with a Cu(1)−O(3) distance of 3.405(5) Å in **2** and the similar contact distance in **3** is 3.398(6) Å. Such long Cu−O contact distances are beyond the bonding region.

Magnetic Results

The variable temperature magnetic susceptibility data for complexes **1−3** were recorded between 300 and 4 K. Plots of $\chi_M T$ versus T for compounds **1−3** are similar (Figure 4), showing a constant increase of the $\chi_M T$ when the temperature decreases, reaching $\chi_M T$ values between 0.68 and 0.86 $cm^3 \cdot K \cdot mol^{-1}$ per copper atom respectively, suggesting ferromagnetic interactions. On the basis of structural features of complexes **1−3** the magnetic data were fitted as chains using the one-dimensional $S = {}^1/_2$ expression based on the Hamiltonian $H = -J\Sigma S_i \cdot S_{i+1}$. A high-temperature series-

Table 2. Selected bond lengths [Å] and angles [°] for $[Cu(L2)(N_3)]_n(ClO_4)_n$ (**2**) (symmetry codes: $i = -x + 1, -y + 2, z + 1/2$, $ii = -x + 1, -y + 2, z - 1/2$)

Cu(1)−N(8)	1.961(3)	Cu(1)−N(1)*_*i*	2.311(3)
Cu(1)−N(10)	2.068(3)	Cu(1)−N(7)	2.039(3)
Cu(1)−N(3)	1.965(3)	N(2)−N(3)	1.161(4)
N(1)−N(2)	1.181(4)		
N(8)−Cu(1)−N(1)*_*i*	91.43(11)	N(8)−Cu(1)−N(7)	79.94(11)
N(1)*_*i*−Cu(1)−N(7)	92.04(11)	N(8)−Cu(1)−N(10)	82.90(10)
N(1)*_*i*−Cu(1)−N(10)	101.62(12)	N(7)−Cu(1)−N(10)	160.11(11)
N(8)−Cu(1)−N(3)	170.40(12)	N(1)*_*i*−Cu(1)−N(3))	96.24(11)
N(7)−Cu(1)−N(3)	93.99(11)	N(10)−Cu(1)−N(3)	101.60(11)
Cu(1)−N(3)−N(2)	131.2(3)	Cu(1)*_*ii*−N(1)−N(2)	139.1(3)
N(1)−N(2)−N(3)	175.0(3)		

Table 3. Selected bond lengths [Å] and angles [°] for $[Cu(L3)(N_3)]_n(ClO_4)_n$ (**3**) (symmetry codes: $i = -x, -y, z - 1/2$, $ii = -x, -y, z + 1/2$)

Cu(1)−N(30)	1.939(7)	Cu(1)−N(3)	1.951(7)
Cu(1)−N(10)	2.030(6)	Cu(1)−N(1)	2.270(5)
Cu(1)−N(20)	2.064(6)	N(1)−N(2)	1.144(9)
N(2)−N(3)*_*i*	1.193(9)		
N(30)−Cu(1)−N(3)	167.5(2)	N(30)−Cu(1)−N(10)	80.4(2)
N(3)−Cu(1)−N(10)	93.6(3)	N(30)−Cu(1)−N(20)	83.6(3)
N(3)−Cu(1)−N(20)	99.1(3)	N(10)−Cu(1)−N(20)	158.4(2)
N(30)−Cu(1)−N(1)	91.6(3)	N(10)−Cu(1)−N(1)	95.3(2)
N(3)−Cu(1)−N(1)	99.9(3)	Cu(1)−N(1)−N(2)	139.0(5)
N(20)−Cu(1)−N(1)	99.6(2)	Cu(1)−N(3)−N(2)*_*ii*	132.2(5)
N(1)−N(2)−N(3)*_*i*	176.1(7)		

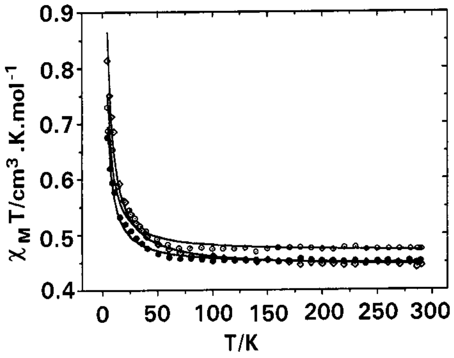


Figure 4. Plots of $\chi_M T$ vs. T (K) data for **1** (open circles), **2** (open rhombus), and **3** (filled circles); the solid lines correspond to the best fit obtained

expansion, valid for both positive and negative J values, has been proposed.[41−42] The results of the best fit, shown as the solid lines in Figure 4, were $J = +2.15$ cm^{-1}, $g = 2.23$, $R = 1.5 \cdot 10^{-4}$ for complex **1**; $J = +3.61$ cm^{-1}, $g = 2.16$, $R = 1.3 \cdot 10^{-4}$ for complex **2**; and $J = +2.06$ cm^{-1}, $g = 2.17$, $R = 1.3 \cdot 10^{-4}$ for complex **3**. These J values are of the same order as that of previously reported results for a similar compound with a tridentate Schiff base.[32]

From the EPR spectra, the g values for complexes **1−3** are (at 4 K): $g_{\parallel} = 2, 19, 2.22, 2.22$ and $g_{\perp} = 2.08, 2.12, 2.07$, respectively. The three spectra are very similar as may be expected from structural data. On cooling from room temperature down to 4 K the g values are practically constant, but the line-width becomes larger due to dipolar effects along the ferromagnetic chain for all of them.

Superexchange Mechanism

Ferromagnetic interactions for azido-bridged metal complexes are generally associated with an end-on coordination mode whereas end-to-end coordination modes of the azido bridge generally allows antiferromagnetic coupling for a large number of Cu^{II}, Ni^{II}, Co^{II}, or Mn^{II} systems reported to date.[41,43] For copper systems, the magnitude of the antiferromagnetic component of the superexchange parameter J is strongly dependent on two main factors, i.e. the atomic orbitals of the copper atoms involved in the superexchange pathway and on the M−N−N angle α and on the $M-N_3-M$ torsion angle θ in the bridging region.

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, in which case the atomic orbitals involved in the superexchange mechanism are the two $d_{x^2-y^2}$ orbitals. In contrast, very low coupling interactions should be expected when the interaction is between axial-equatorial coordination sites and the atomic orbitals involved are the $d_{x^2-y^2}$ and d_{z^2} respectively. The different magnetic behavior is related to the low unpaired electronic density found in the d_{z^2} atomic orbital in the square pyramidal or octahedrally coordinated copper atoms. Classical attempts to relate the magnitude of the superexchange coupling and the structural data for the axial-equatorial case conclude a greater anti-ferromagnetic coupling for the trigonal bipyramidal arrangement in agreement with the greater mixing of the $d_{x^2-y^2}$ and d_{z^2} atomic orbitals.[44] In our case, complexes **1−3** exhibit a square pyramidal geometry of the copper(II) with one nitrogen of the bridging azido linked to the equatorial position of one copper(II) whereas the other end nitrogen of the same azide is linked to the axial site of the neighboring copper(II) center, indicating that the spin unpaired electron is mainly located in the basal $d_{x^2-y^2}$ orbital whereas the d_{z^2} orbital contains spin paired electrons. The consequence is that there is a good delocalization of the electron density of one of the copper(II) atoms towards the bridging azido, while the delocalization from the second copper is poor because azide

Table 4. Crystal data and structure refinement for $[Cu(L1)(N_3)]_n(ClO_4)_n$ (**1**), $[Cu(L2)(N_3)]_n(ClO_4)_n$ (**2**), and $[Cu(L3)(N_3)]_n(ClO_4)_n$ (**3**)

	1	**2**	**3**
Empirical formula	$C_{10}H_{15}ClCuN_6O_4$	$C_{12}H_{19}ClCuN_6O_4$	$C_{12}H_{17}ClCuN_6O_5$
Formula mass	382.27	410.32	424.31
Space group	$P2_12_12_1$	$Pna2_1$	$Pna2_1$
a [Å]	7.434(3)	14.723(5)	13.837(15)
b [Å]	12.047(4)	13.829(5)	14.804(2)
c [Å]	17.404(6)	8.002(5)	8.050(4)
α, β, γ [°]	90, 90, 90	90, 90, 90	90, 90, 90
V [$Å^3$]	1558.7(10)	1629.2(13)	1649.0(8)
Z	4	4	4
T [°C]	20(2)	20(2)	20(2)
λ(Mo-K_α) [Å]	0.71069	0.71069	0.71069
$\rho_{calcd.}$, g cm^{-1}	1.629	1.673	1.709
μ(Mo-K_α) [mm^{-1}]	1.599	1.536	1.525
R[a]	0.0426	0.0341	0.0469
$R^2\omega$[b]	0.0862	0.0770	0.1200

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

occupies an apical position with a longer distance and so, a weak interaction should be expected, which is also observed experimentally.[8]

The nature of this low interaction may be ferro or antiferromagnetic, 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 $M-N_3-M$ torsion angles.[29] The effect of the M−N−N bond angle is not determinant in our case because the Cu−N−N bond angles, in all cases, lie below 140°, but the effect of the θ torsion angles should be considered. The maximum antiferromagnetic component is found for $\theta = 180$ or 0° and quickly diminishes with an increase in θ and becomes zero (accidental orthogonality) for $\theta = 90°$.[29] In compound **1** the Cu−N−N angles are 126.6 and 131.3° and the torsion angle defined by the Cu(1)−N(11)−N(12)−N(13) and the N(11)−N(12)−N(13)−Cu(1)* mean planes is 97.8°. In compound **2** the Cu−N−N angles are 131.2(3) and 139.1(3)° and the $Cu-N_3-Cu$ torsion angle is 50.4(4)°. In compound **3** the Cu−N−N angles are 132.2(5) and 139.0(5)° and the $Cu-N_3-Cu$ torsion angle θ is 40.4(8)°. The large $Cu-N_3-Cu$ torsion angles, along with the axial-equatorial bridging mode of the azido ligand and the square-pyramid geometry in all these complexes orient the magnetic orbitals in almost orthogonal fashion to nullify the antiferromagnetic component of the superexchange resulting in a net weak ferromagnetic interaction.

Conclusions

We have presented here the synthesis, single crystal structure and magneto-structural correlation of three novel end-to-end single azido-bridged 1D copper(II) chains, using three different tridentate (NNN-donor) Schiff base ligands and the observation of unusual ferromagnetic interaction through end-to-end azido pathways in a copper(II) system. Fitting of the $\chi_M T$ versus T data in the temperature range between 300 and 4 K using a high temperature series-expansion for $S = {}^1/_2$ local spin lead to the coupling parameters, $J = +2.15\ cm^{-1}$ for **1**, $J = +3.61\ cm^{-1}$ for **2**, and $J = +2.06\ cm^{-1}$ for **3**. Positive J values as well as the nature of $\chi_M T$ versus T plot clearly indicate the existence of an intrachain ferromagnetic interaction in all of the complexes **1−3**. Such an unusual magnetic behavior through an end-to-end azido pathway is explained on the basis of the axial-equatorial bridging mode as well as the bond parameters like the $Cu-N_3-Cu$ torsion angle.

Experimental Section

Caution! Perchlorate and azido complexes of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of the materials should be prepared, and it should be handled with care.

Synthesis

L1, L2, and L3 Ligands: The three Schiff bases were prepared by reflux of 2 mmol of pyridine-2-carbaldehyde and 2 mmol of *N*,*N*-dimethylethane-1,2-diamine, or *N*,*N*-diethylethane-1,2-diamine, or 4-(2-aminoethyl)morpholine, respectively, in 10 mL of methanol, according to the literature methods.[34−35]

$[Cu(L1)(N_3)]_n(ClO_4)_n$ (1): A methanolic solution (10 mL) of copper(II) perchlorate hexahydrate (2 mmol) was added to the hot methanolic solution (10 mL) of the L1 (2 mmol) ligand. To the resulting deep blue cold solution, an aqueous solution (5 mL) of sodium azide (2 mmol) was added dropwise with continuous stirring and filtered. Suitable single crystals for structure determination were obtained by slow evaporation of this solution in air. Yield ca. 60%. $C_{10}H_{15}ClCuN_6O_4$: calcd. C 31.4, H 4.0, N 22.0; found C 32.0, H 4.1, N 22.3%.

$[Cu(L2)(N_3)]_n(ClO_4)_n$ (2): A methanolic solution (10 mL) of copper(II) perchlorate hexahydrate (2 mmol) was added to the hot methanolic solution (10 mL) of the L2 ligand (2 mmol). To the resulting bluish-green cold solution, an aqueous solution (5 mL) of sodium azide (2 mmol) was added dropwise with continuous stirring. Suitable green single crystals for structure determination were obtained after a few days by slow evaporation of this dark green solution in air. Yield ca. 80%. $C_{12}H_{19}ClCuN_6O_4$: calcd. C 35.0, H 4.7, N 20.5; found C 35.2, H 4.6, N 20.2%.

$[Cu(L3)(N_3)]_n(ClO_4)_n$ (3): This complex was synthesized following the strategy adopted for complexes (**1**) and (**2**) using the ligand L3. Suitable single crystals for X-ray diffraction were obtained by slow evaporation of the final solution in a refrigerator. Yield ca. 75%. $C_{12}H_{17}ClCuN_6O_5$: calcd. C 33.9, H 4.0, N 19.8; found C 34.2, H 4.2, N 19.5%.

Crystallographic Data Collection and Refinement: The X-ray single-crystal data for compound **1** was collected on a modified STOE four-circle diffractometer. While the crystals of **2** and **3** were covered in nujol and mounted with vacuum grease on a glass fiber and transferred to a Bruker AXS P4 diffractometer[36] and data were measured at 293 K. The crystallographic data, the conditions for the intensity data collection and some features of the structure refinements are listed in Table 4. Graphite-monochromatized Mo-K_α radiation (λ = 0.71069 Å) and the ω-scan technique for **1** and ψ- scan technique for **2** and **3** were used to collect the data sets. The accurate unit-cell parameters were determined from automatic centering of 54 reflections ($9.4° < \theta < 13.7°$) for **1**, 37 reflections ($2.76° < \theta < 20.82°$) for **2** and 30 reflections ($4.75° < \theta < 12.49°$) for **3** and refined by least-squares method. A total of 2755 reflections (2709 independent reflections, $R_{int} = 0.0238$) for **1**; 3244 reflections (2740 independent reflections, $R_{int} = 0.0323$) for **2**; and 1960 reflections (1707 independent reflections, $R_{int} = 0.0221$) for **3**,were collected in the range $2.89° < \theta < 30.00°$, $2.02° < \theta < 25.00°$, and $2.75° < \theta < 25.00°$ for **1**, **2**, and **3** respectively. The structures were solved by direct methods using the SHELXS-86[37] computer program, and refined by full-matrix least-squares methods on F^2, using the SHELXL-93[38] program incorporated in the SHELXTL/PC V 5.03[39] program library and the graphics program PLATON.[40] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on calculated positions by use of the HFIX utility of the SHELXL-93 program. For complexes **1**, **2**, and **3,** respectively, the final *R* indices for all observed reflections are 0.0426, 0.0341, and 0.0469. Maximum and minimum peaks in the final difference Fourier syntheses were 0.29 and −0.44 $e\cdot Å^{-3}$ for **1**, 0.31 and −0.30 $e\cdot Å^{-3}$ for **2**, and 0.53 and −0.84 $e\cdot Å^{-3}$ for **3**. Significant bond parameters are given in Tables 1−3.

Physical Measurements: IR spectra (4000−400 cm^{-1}) were recorded from KBr pellets on a Nicolet 520 FT-IR spectrometer. Magnetic measurements were carried out with a DSM8 pendulum susceptometer equipped with a helium continuous-flow cryostat, working in the temperature range 300−4 K. The applied external magnetic field was 1.5 T. Diamagnetic corrections were estimated from Pascal constants. Electronic Spin Resonance spectra of the polycrystalline samples have been recorded at X-band frequency by using a Bruker ESP 300 E automatic spectrometer from room temperature to 4 K.

CCDC-168803, -168804, and -168805 for complexes **1**, **2**, and **3**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Funding for the work described here is provided by the Council of Scientific and Industrial Research (New Delhi) Grants Scheme (Granted to NRC) and is gratefully acknowledged. This research was also partially supported by CICYT (Spanish Government; Grant BQU2000-0791) and OENB (grant 6630). F. A. Mautner thanks Prof. C. Kratky and Dr. F. Belaj (University of Graz) for use of experimental equipment.

[1] J. S. Miller, A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385.
[2] A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, *Acc. Chem. Res.* **1989**, *22*, 392.
[3] D. Gatteschi, *Adv. Mater.* **1994**, *6*, 635.
[4] J.S. Miller, A. J. Epstein, W. M. Reiff, *Science* **1988**, *240*, 40.
[5] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* **1995**, *34*, 1793.
[6] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* **1994**, *33*, 484.
[7] A. Escuer, R. Vicente, M. A. S. Goher, F. A. Mautner, *Inorg. Chem.* **1996**, *35*, 6386.
[8] P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah, N. Ray Chaudhuri, *Inorg. Chem.* **2000**, *39*, 5147.
[9] J. Ribas, M. Monfort, C. Diaz, C. Bastos, X. Solans, *Inorg. Chem.* **1993**, *32*, 3557.
[10] J. Ribas, M. Monfort, R. Costa, X. Solans, *Inorg. Chem.* **1993**, *32*, 695.
[11] M. A. Halcrow, J. C. Huffman, G. Christou, *Angew. Chem. Int. Ed. Engl.* **1995**, *35*, 971.
[12] A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1994**, *33*, 1842.
[13] R. Vicente, A. Escuer, J. Ribas, M. S. El Fallah, X. Solans, M. Font Bardia, *Inorg. Chem.* **1995**, *34*, 1278.
[14] J. Ribas, M. Monfort, B. K. Ghosh, R. Cortes, X. Solans, M. Font Bardia, *Inorg. Chem.* **1996**, *35*, 864.
[15] M. Monfort, J. Ribas, X. Solans, *J. Chem. Soc., Chem. Commun.* **1993**, 350.
[16] M. Monfort, I. Resino, J. Ribas, H. Stoeckli-Evans, *Angew. Chem. Int. Ed.* **2000**, *39*, 191.
[17] F. A. Mautner, R. Cortes, L. Lezema, T. Rojo, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 96.
[18] J. Ribas, M. Monfort, I. Resino, X. Solans, P. Rabu, F. Maingot, M. Drillon, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2671.
[19] C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wanger, E. K. Barefield, *Inorg. Chem.* **1975**, *14*, 604.
[20] A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans, *Inorg. Chem.* **1993**, *32*, 1033.
[21] P. Chaudhuri, M. Guttmann, D. Ventur, K. Weighardt, B. Nuber, J. Weiss, *J. Chem. Soc., Chem. Commun.* **1985**, 1618.
[22] M. I. Arriortua, A. R. Cortes, L. Lezema, T. Rojo, X. Solans, *Inorg. Chim. Acta* **1990**, *174*, 263.
[23] A. Escuer, R. Vicente, J. Ribas, *J. Magn. Magn. Mater.* **1992**, *110*, 181.
[24] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* **1995**, *34*, 1793.
[25] J. Comarmond, P. Plumere, J. M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, I. Morgesten-badarau, *J. Am. Chem. Soc.* **1982**, *104*, 6330.
[26] O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin, Y. Jeannin, *Inorg. Chem.* **1983**, *22*, 2877.
[27] S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.* **1994**, *33*, 5555.
[28] P.J. Hay, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* **1975**, *97*, 4884.
[29] A. Escuer, R. Vicente, J. Ribas, M. S. El Fallah, X. Solans, M. Font-Bardia, *Inorg. Chem.* **1993**, *32*, 3727.
[30] C. S. Hong, Y. Do, *Angew. Chem. Int. Ed.* **1999**, *38*, 193.
[31] A. Escuer, C. J. Harding, Y. Dussart, J. Nelson, V. McKee, R. Vicente, *J. Chem. Soc., Dalton Trans.* **1999**, 223.

[32] T. K. Maji, P. S. Mukherjee, G. Mostafa, T. Mallah, J. Cano-Boquera, N. Ray Chaudhuri, *Chem. Commun.* **2001**, 1012.

[33] P. S. Mukherjee, S. Dalai, G. Mostafa, T. H. Lu, E. Rentschler, N. Ray Chaudhuri, *New J. Chem.* **2001**, *25*, 1203.

[34] G. Zakrzewski, L. Sacconi, *Inorg. Chem.* **1968**, *7*, 1034.

[35] P. Bamfield, R. Price, R. G. J. Miller, *J. Chem. Soc. (A)* **1969**, 1447.

[36] *XSCANS*, **1994**, Data Collection and Reduction Program, Version 2.2, Bruker AXS., Madison, Wisconsin, USA.

[37] G. M. Sheldrick, *SHELXS-86*, Program for the Solution of Crystal Structure. University of Gottingen, Germany, **1986**.

[38] G. M. Sheldrick, *SHELXL-93*, Program for the Refinement of Crystal Structure. University of Gottingen, Germany, **1993**.

[39] *SHELXTL 5.03* (PC-Version), Program library for the Solution and Molecular Graphics. Siemens Analytical Instruments Division, Madison, WI, **1995**.

[40] A. L. Spek, *PLUTON-92*, University of Utrecht, 3584, CH Utrecht, The Netherlands **1992**.

[41] O. Kahn, *Molecular Magnetism*, VCH, **1993**, Chap. 6.

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

[43] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193*, 1027.

[44] T. R. Felthouse, D. N. Hendrickson, *Inorg. Chem.* **1978**, *17*, 444.

Received August 15, 2001
[I01315]