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Article

Ferromagnetic Coupling in a 1D Coordination Polymer Containing a Symmetric $[Cu(\mu_{1,1}\text{-}N_3)_2Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ Core and Based on an Organic Ligand Obtained from the Solid State

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Addition of *rctt*-tetrakis(2-pyridyl)cyclobutane (2,2′-tpcb) in a Cu^{II}/N_3^- solution afforded the 1D coordination polymer $[Cu_3(N_3)_6(2,2'\text{-tpcb})(DMF)_2]_n$ (**1**). The ligand 2,2′-tpcb serves as a tetradentate bis-chelating ligand by linking linear $[(DMF)Cu(\mu_{1,1}\text{-}N_3)_2Cu(N_3)_2(\mu_{1,1}\text{-}N_3)_2Cu(DMF)]$ trinuclear units to produce a zigzag chain. Within each centrosymmetric trinuclear unit there exist two irregularly asymmetric end-on double azido-bridged $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ cores, while one of the largest $Cu–N_{azide}–Cu$ angles is observed. Magnetic susceptibility data, measured from 2 to 300 K, show bulk moderate ferromagnetic coupling within the magnetically isolated trinuclear units. These data were fitted to the appropriate equation derived from the Hamiltonian $H = -J_1(S_{A1}S_B + S_{A2}S_B) - J_2S_{A1}S_{A2}$, giving the parameters $J_1 = +70(3)\ cm^{-1}$, $J_2 = -3(2)\ cm^{-1}$, $g = 2.12(1)$, with an intertrimer interaction parameter $\theta = -0.74(2)$ K. The coupling constants were correlated with the structural parameters. Density functional calculations reproduce very well the experimental J values and show that ferromagnetism for this complex is mainly due to the topology of the magnetic orbitals and the different coordination spheres of two neighboring Cu^{II} atoms, resulting in a small overlap of the orbitals possessing the unpaired electrons.

Introduction

The azide anion, N_3^-, is one of the most commonly employed pseudohalide bridging ligands in the design of polynuclear 3d metal complexes and coordination polymers with characteristic and tunable physical properties. This ligand is very popular in the field of molecular magnetism[1] because of its ability to mediate ferromagnetic coupling under certain conditions.[1–4] When acting as a monatomic bridge (end-on coordination mode, EO), the azide ligand can link up to four metal ions;[5–7] using both terminal nitrogen atoms to coordinate (end-to-end, EE), it is capable of bridging up to six metal ions.[8] In general, EE azide bridges propagate antiferromagnetic interactions, whereas the EO coordination mode is associated with ferromagnetic coupling;[9] exceptions to this general statement have been reported.[10–17]

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Chart 1

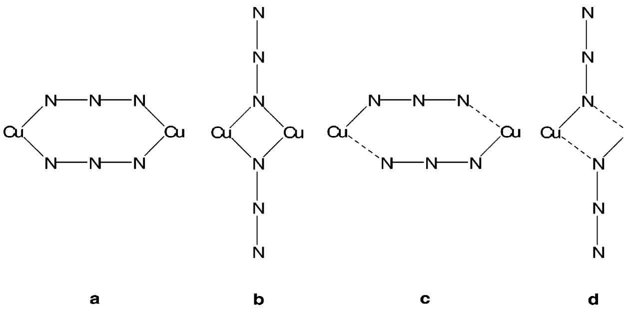
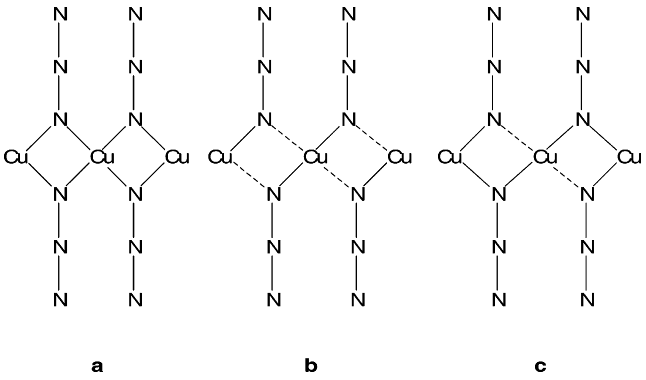


Chart 2



Among the transition-metal ions, Cu^{II} is the key player in metal-azide chemistry, because more than 40% of the crystal structures containing bridging EO or EE azides involve copper.[18] Doubly bridged Cu^{II} azide complexes have served as models for probing structure−property relations and testing theoretical treatments of the exchange coupling.[2,3] It is well-established that doubly bridged symmetric EE Cu^{II} azide complexes (part a of Chart 1) are strongly antiferromagnetic,[19,20] whereas Cu^{II} complexes with double symmetric EO azide bridges (part b of Chart 1) are strongly ferromagnetic,[21,22] given that the $Cu-N_{azide}-Cu$ angle is within the 95−104° range.[2,4,23] Asymmetric EE azido bridges (part c of Chart 1) usually lead to weak antiferromagnetic coupling,[20,24−28] whereas asymmetric EO azide bridges (part d of Chart 1) are rare and usually propagate weak to moderately strong ferromagnetic interactions.[28−33]

Apart from the coordination mode of the azide ligand, the superexchange mechanism in doubly bridged Cu^{II} EO-azide complexes is affected by several structural parameters such as the copper−copper separation, the $Cu-N_{azide}-Cu$ angle, the $Cu-N_{azide}$ bond lengths, the mean out-of-plane deviation of the azido group, the dihedral angles between the planes containing the Cu^{II} ions, and the stereochemistry around the metal centers.[2−4] The above parameters can be associated with the steric and electronic demands of the co-ligands present in the complexes of this kind.[14,34]

Herein, we report the synthesis, crystal structure, magnetic properties, and theoretical study of the 1D coordination polymer $[Cu_3(N_3)_6(2,2'\text{-tpcb})(DMF)_2]_n$ (**1**), where 2,2′-tpcb is the bis-chelating bridging ligand *rctt-tetrakis*(2-pyridyl)-cyclobutane (2,2′-tpcb).[35,36] **1** consists of magnetically isolated centrosymmetric trinuclear $[(DMF)Cu(\mu_{1,1}\text{-}N_3)_2Cu(N_3)_2(\mu_{1,1}\text{-}N_3)_2Cu(DMF)]$ units that are linked by the 2,2′-tpcb bridges. The double azide bridge within each $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core is irregularly asymmetric[37] (part c of Chart 2), with one of the four $Cu-N_{azido}$ distances being 2.599(7) Å and the $Cu-N_{azide}-Cu$ angle facing the long distance being 105.4(3)°. To our knowledge, there have been identified four other Cu^{II} complexes comprising a trinuclear unit related to that of **1**. Three, namely $[Cu_3(N_3)_6(Meinic)_2(DMF)_2]_n$,[38] $[Cu_3(N_3)_6(ampym)_2(DMF)_2]_n$,[39] and $[Cu_3(N_3)_4L_2]$,[40] where Meinic

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Table 1. Crystal Data and Structure Refinement for **1**

empirical formula	$C_{30}H_{34}Cu_3N_{24}O_2$
formula weight	953.43
cryst size	0.19 × 0.12 × 0.08
cryst syst	monoclinic
space group	$P2_1/c$
T, K	190(2)
θ range for data collection, (deg)	$1.12 \leq \theta \leq 22.5$
a, Å	10.266(1)
b, Å	18.116(2)
c, Å	10.347(1)
β, (deg)	90.53(1)
V, Å^3	1924.2(3)
Z	2
ρ_{calcd}, g cm^{-3}	1.65
μ, mm^{-1}	1.709
No. of measured reflns	9434
No. of unique reflns	2513
No. of observed reflns^a	2351
$R1^a$	0.0549
$wR2$	0.1233

^{a} $I > 2\sigma(I)$.

= methylisonicotinate, ampym = 2-aminopyrimidine and L$^-$ = hydridotris(3,5-dimethylpyrazolyl)borate, comprise a symmetric trinuclear unit (part a of Chart 2) and one, namely $[Cu_3(N_3)_6(det)_2]$,[41] where det = diethylenetriamine, comprises the asymmetric trinuclear unit shown in part b of Chart 2. The trinuclear unit found in **1** (part c of Chart 2) represents the only example of such an irregularly asymmetric trinuclear unit in Cu^{II} azide chemistry.

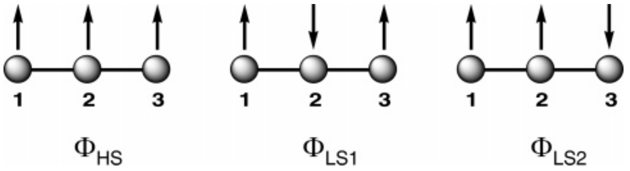
Experimental Section

Materials and Physical Measurements. All of the manipulations were performed under aerobic conditions using materials and solvents as received. 2,2′-tpcb was synthesized as reported.[35] IR spectra were recorded on a PerkinElmer PC16 FTIR spectrometer with samples prepared as KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were performed with a Carlo Erba EA 108 analyzer. Magnetic susceptibility measurements in the range of 2−300 K were carried out on a polycrystalline sample of **1** with a Quantum Design SQUID magnetometer, under magnetic fields of approximately 1.0 T between 300 and 30 K, and 0.03 T in the 30−2 K range, at the Magnetochemistry Service of the University of Barcelona. Diamagnetic corrections were estimated from Pascal tables.

Caution! Azide complexes and perchlorate salts are potentially explosive and should be handled in small quantities and with great caution.

Synthesis of Complex $[Cu_3(N_3)_6(2,2'\text{-tpcb})(DMF)_2]_n$ (1). To a stirred pale-blue solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.20 mmol) in DMF (7 mL) was added solid 2,2′-tpcb (0.036 g, 0.10 mmol). The resulting deep-blue solution was stirred for 10 min, during which time solid NaN_3 (0.026 g, 0.40 mmol) was added in small portions. The solution was turned to deep green, stirred for 1 h and allowed to stand undisturbed at room temperature for 2 days. Well-formed, X-ray quality green crystals of **1** appeared within this period. The crystals were collected by vacuum filtration, washed with DMF (2 × 2 mL) and Et_2O (2 × 5 mL), and dried in a vacuum over silica gel. The yield was ca. 60% (based on copper). Found: C, 37.76; H, 3.62; N, 35.58. Calcd for $C_{30}H_{34}Cu_3N_{24}O_2$: C, 37.79; H, 3.60; N, 35.26. Selected IR data (KBr, cm^{-1}): 2078(sh), 2040 (vs), 1650 (vs), 1602 (m), 1570 (w), 1476 (m), 1436 (m), 1378 (m), 1336 (w), 1304 (w), 1284 (m), 1256 (w), 1176 (w), 1110 (m), 1060 (w), 1028 (w), 794 (m), 766 (s), 676 (m), 642 (w), 570 (w), 528 (w), 510 (w).

Chart 3



X-ray Crystallography. A single crystal of **1** was mounted on the end of a glass fiber and optically centered in the X-ray beam of a Nonius Kappa CCD system for data collection. Cell constants were calculated from reflections obtained from the data collection. The structure was solved using direct methods. After anistropic refinement of all of the non-hydrogen atoms, methyl, methine, aromatic, and amide hydrogen atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. The crystal was a pseudo-merohedral twin via 2-fold rotation about the c axis. The twin fraction refined to 0.400(2). A θ cutoff of 22.5° was used, owing to a decrease in intensity data. The decrease in intensity can be ascribed to the twinning of the single crystal. A summary of data collection parameters is given in Table 1. Structure solution was accomplished with the aid of *SHELXS*[42] and refinement was conducted using *SHELXL-97*[42] locally implemented on a Pentium-based IBM compatible computer. All of the crystallographic manipulations were performed with the aid of *WingGX* v1.64.05.[43]

Computational Details. For the calculation of the exchange coupling constants for any polynuclear complexes with n different exchange constants, the energy of $n + 1$ spin configurations must be calculated.[44] In the case of the studied complex, to obtain the two J values, we have calculated the energy corresponding to three different spin distributions (Chart 3). A detailed description of the procedure employed to calculate the exchange coupling constants in dinuclear and polynuclear complexes can be found in refs 45−47. The following equations have been employed to calculate the exchange coupling constants:

$$E_{HS} - E_{LS1} = -2J_1 \qquad (1)$$

$$E_{HS} - E_{LS2} = -J_1 - J_2 \qquad (2)$$

The hybrid B3LYP functional[48−50] has been used in all of the calculations as implemented in *Gaussian-98*.[51] This functional provides excellent results for the calculation of the exchange coupling in a wide spectrum of transition-metal complexes.[2,52,53] We have employed a triple-ζ all-electron basis set for copper

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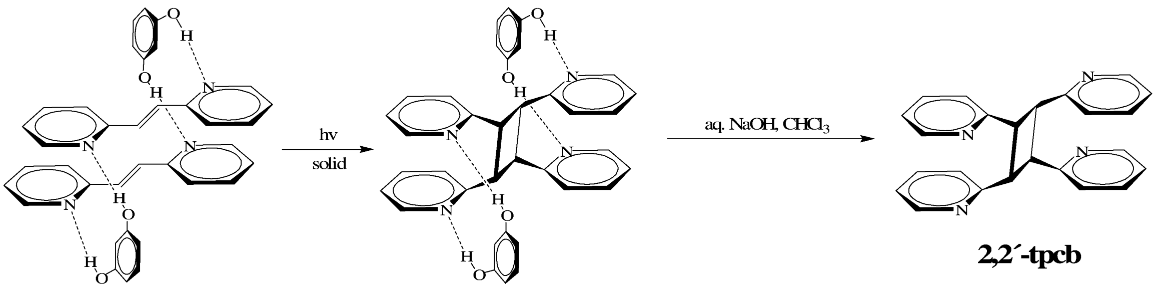
Chart 4



atoms[54] and a double-ζ all-electron for the other elements proposed by Ahlrichs et al.[55]

Results and Discussion

Synthesis and IR Spectrum. A supramolecular method that controls the formation of covalent bonds in the solid state was used to synthesize 2,2′-tpcb[35,56−59] (Chart 4). The reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with a half-molar equiv of 2,2′-tpcb and two molar equivs of NaN_3 afforded a green solution from which the green complex $[Cu_3(N_3)_6(2,2'\text{-tpcb})(DMF)_2]_n$ (**1**) can be crystallized in good yield (∼60%). The preparation is summarized by eq 3. The same product can be isolated from 3:1:6 (as expected), 2:1:2, and

$$3n\mathrm{Cu(ClO_4)_2{\cdot}6H_2O} + n(2,2'\text{-tpcb}) + 6n\mathrm{NaN_3} + 2n\mathrm{DMF} \xrightarrow{\mathrm{DMF}} [\mathrm{Cu_3(N_3)_6}(2,2'\text{-tpcb})(\mathrm{DMF})_2]_n\ (\mathbf{1}) + 6n\mathrm{NaClO_4} + 18n\mathrm{H_2O} \tag{3}$$

1:1:1 $Cu(ClO_4)_2{\cdot}H_2O$/2,2′-tpcb/NaN_3 reaction ratios. Attempts to increase the yield by layering the DMF solution with Et_2O led to the contamination of **1** with $NaClO_4$ (IR evidence). **1** seems to be the only isolable product from this reaction mixture in DMF. Despite our efforts, we could not obtain anionic or cationic complexes. It should be mentioned that direct reactions of Cu^{II} sources containing anions with a good coordination capacity, namely $Cu(NO_3)_2{\cdot}2.5H_2O$ and $CuSO_4{\cdot}5H_2O$ in MeOH led to complexes $[Cu_2(NO_3)_4(2,2'\text{-tpcb})]$ and $[Cu_2(SO_4)_2(2,2'\text{-tpcb})(H_2O)_2]_n{\cdot}9nH_2O$, respectively.[35]

In the IR spectrum, **1** exhibits an intense band centered at 2040 cm^{-1}, which is assigned to the asymmetric stretching mode of the azide. The appearance of a shoulder at 2078 cm^{-1} implies the existence of both bridging and terminal azide ligands[38] in **1**. The ν(C═O) and δ(OCN) vibrational modes of the coordinated DMF molecules appear at 1650 and 676 cm^{-1}, respectively.[60] Because of coordination, the ν(C═O) and δ(OCN) bands are shifted to lower and higher wavenumbers, respectively, when compared with the corresponding bands in the spectrum of DMF.[61] The ν(C═C) and ν(C═C) bands of 2,2′-tpcb are sensitive to coordination. The 1588, 1565, 1473, and 1431 cm^{-1} bands of the free ligand shift to slightly higher wavenumbers (1602, 1570, 1476, and 1436 cm^{-1}, respectively) upon coordination in the spectrum of **1**.

Description of Structure. **1** is a 1D coordination polymer built from centrosymmetric trinuclear $[(DMF)Cu(\mu_{1,1}\text{-}N_3)_2Cu(N_3)_2(\mu_{1,1}\text{-}N_3)_2Cu(DMF)]$ units that are linked by 2,2′-tpcb bridges. A perspective view of the trinuclear unit is shown in Figure 1. Interatomic distances and angles are given in Table 2. The coordination geometry around the central Cu(2) ion, which sits on an inversion center, conforms to an elongated octahedron. The equatorial plane of the octahedron is occupied by two terminal azide ligands in a trans orientation and two $\mu_{1,1}$-azide ligands. The elongated Jahn−Teller sites of the octahedron are occupied by another pair of $\mu_{1,1}$-azide ligands. Each of the two terminal Cu^{II} atoms adopt a square-pyramidal geometry with two $\mu_{1,1}$-azide ligands in a cis orientation and two pyridyl nitrogen atoms of the 2,2′-tpcb ligand in the basal plane, along with an oxygen atom from a DMF molecule at the apical site [Cu(1)−O(1) 2.172(6) Å]. As a result, the linkage between the central [Cu(2)] and each of the terminal metal ions [Cu(1) or Cu(1i)] is achieved through two $\mu_{1,1}$-azide ligands that form the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ subcore,[17,21,22,62−64] the metals being separated by 3.269(1) Å. The $Cu{-}N_{azide}$ distances and

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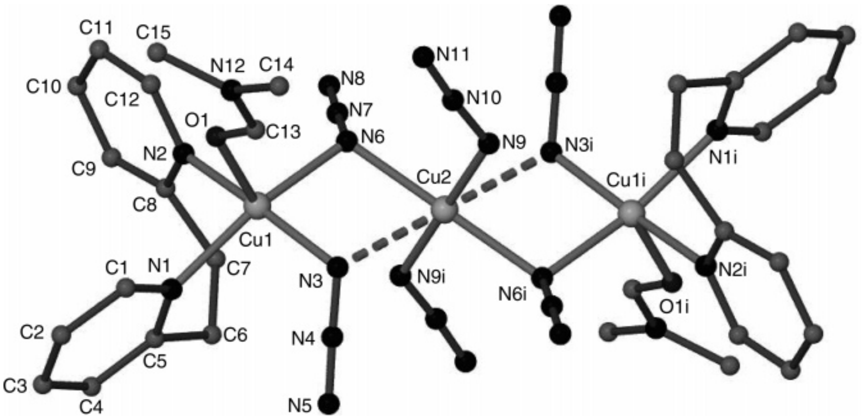

Figure 1. Perspective view of the trinuclear unit of $[Cu_3(N_3)_6(2,2'\text{-tpcb})(DMF)_2]_n$ (**1**). Hydrogen atoms have been omitted for clarity. Symmetry code: i $2 - x, -y, 1 - z$.

Table 2. Selected Interatomic Distances (Angstroms) and Angles (Degrees) Relevant to the Copper Coordination Spheres for **1**[a]

Cu(1)···Cu(2)	3.269(1)	Cu(2)−N(9)	1.964(9)
Cu(1)−N(3)	1.994(7)	Cu(2)−N(9i)	1.964(9)
Cu(1)−N(2)	2.021(7)	Cu(2)−N(6)	2.058(7)
Cu(1)−N(6)	2.052(8)	Cu(2)-N(6i)	2.058(7)
Cu(1)−N(1)	2.072(7)	Cu(2)−N(3)	2.599(7)
Cu(1)−O(1)	2.172(6)	Cu(2)−N(3i)	2.599(7)
N(3)−Cu(1)−N(2)	169.5(3)	N(3i)−Cu(2)−N(6)	107.4(3)
N(3)−Cu(1)−N(6)	87.3(3)	N(9i)−Cu(2)−N(6i)	93.2(3)
N(2)−Cu(1)−N(6)	89.4(3)	N(6)−Cu(2)−N(6i)	180.0(3)
N(3)−Cu(1)−N(1)	93.8(3)	N(6)−Cu(2)−N(9i)	86.8(3)
N(2)−Cu(1)−N(1)	86.3(3)	N(3i)−Cu(2)−N(9)	86.3(3)
N(6)−Cu(1)−N(1)	162.4(3)	N(6i)−Cu(2)−N(9)	86.8(3)
N(3)−Cu(1)−O(1)	97.9(3)	N(9)−Cu(2)−N(9i)	180.0(3)
N(2)−Cu(1)−O(1)	92.6(2)	N(3i)−Cu(2)−N(6i)	72.6(3)
N(6)−Cu(1)−O(1)	104.0(3)	N(3i)−Cu(2)−N(9i)	93.7(3)
N(1)−Cu(1)−O(1)	93.3(3)	N(6i)−Cu(2)−N(9i)	93.2(3)
N(3)−Cu(2)−N(6)	93.7(3)	Cu(1)−N(6)−Cu(2)	105.4(3)
N(3)−Cu(2)−N(3i)	180.0(3)	Cu(1)−N(3)−Cu(2)	89.8(3)
N(3)−Cu(2)−N(6i)	107.4(3)	N(5)−N(4)−N(3)	177.9(9)
N(3)−Cu(2)−N(9i)	86.3(3)	N(8)−N(7)−N(6)	178.8(9)
N(6)−Cu(2)−N(9)	93.2(3)	N(11)−N(10)−N(9)	175.5(10)

[a] Symmetry code: i $2-x, -y, 1-z$.

Cu−N_{azide}−Cu angles within the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ subcore are Cu(1)−N(6) 2.052(8), Cu(1)−N(3) 1.994(7), Cu(2)−N(6) 2.058(7), and Cu(2)−N(3) 2.599(7) Å, and Cu(1)−N(3)−Cu(2) 89.8(3)° and Cu(1)−N(6)−Cu(2) 105.4(3)°. Thus, one of the four Cu−N_{azide} distances within the dinuclear subcore is significantly longer than the other three. Therefore, the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ subcore in **1** can be described as irregularly asymmetric (part c of Chart 2); this is not depicted in Chart 1. The large Cu−N−Cu angle of 105.4(3)°, which is one of the largest Cu−N_{azide}−N angles observed[64] within a $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core, is associated with short Cu−N_{azide} distances [Cu(1)−N(6) 2.052(8) and Cu(2)−N(6) 2.058(7) Å]. The mean out-of-plane deviations of the azide groups (τ) are ca. 35 and 47° for the N(6)−N(7)−N(8) and N(3)−N(4)−N(5) ligands, respectively. The four atoms of the central square ring that define the mean plane are Cu(1), N(6), Cu(2), and N(3). The dihedral angle between the basal plane of the square-pyramidal Cu(1) ion and the equatorial plane of the elongated octahedral Cu(2) ion is close to orthogonal [71.05(1)°].

The trinuclear units of **1** are bridged via the terminal Cu^{II} atoms Cu(1) and Cu(1i) [$2 - x, -y, 1 - z$] by 2,2′-tpcb molecules to form well-isolated zigzag chains that run parallel to the *a* axis (Figure 2). Owing to the positioning of the nitrogen atoms in the 2-position of each pyridyl group, the 2,2′-tpcb ligand forms a boat-like, seven-membered chelate ring with each metal [Cu(1)−N(1) 2.072(7) and Cu(1)−N(2) 2.021(7) Å]. The pyridyl groups of each chelating moiety, as defined by the centroids of the aromatic rings, are separated by 4.51 Å across the cyclobutane ring and are splayed at an angle of ca. 82.7° with respect to the metal center. Thus, the 2,2′-tpcb molecule serves as a tetrafunctional bis-chelating ligand, wherein the two metal ions are, in effect, bridged by the cyclobutane unit (Cu···Cu separation 7.36 Å).

1 is the third example of a structurally characterized compound of any metal possessing the 2,2′-tpcb ligand. The two previously reported complexes are[35] the discrete dimer $[Cu_2(NO_3)_4(2,2'\text{-tpcb})]$ and the infinite 1D coordination array $[Cu_2(SO_4)_2(2,2'\text{-tpcb})(H_2O)_2]_n\cdot 9nH_2O$; in the latter, the sulfate ions serve to bridge two adjacent Cu^{II} centers, forming a chairlike, eight-membered ring.

Magnetic Properties. The variable-temperature magnetic susceptibility data for **1** were recorded between 300 and 2 K. The plot of $\chi_M T$ versus T is shown in Figure 3. The $\chi_M T$ value of 1.38 $cm^3\ mol^{-1}$ K at room temperature increases gradually as the temperature decreases to a maximum of 1.96 $cm^3\ mol^{-1}$ K at 14 K and then decreases quickly to 1.46 $cm^3\ mol^{-1}$ K at 2 K. The magnetic susceptibility behavior of **1** indicates bulk ferromagnetic coupling in good agreement with magnetization experiments, which show a quasi-saturated value of $M/N\beta$ equivalent to three electrons under an external field of 5 T at 2 K (Figure S1). Taking into account the linear structure of the trinuclear unit in **1** (Chart 5), the fit of the magnetic data was made using the appropriate equation[65] (including the intertrimer interaction parameter θ) derived from the Hamiltonian $H = -J_1(S_{A1}S_B + S_{A2}S_B) - J_2S_{A1}S_{A2}$. The best fit parameters were $J_1 = 70(3)\ cm^{-1}$, $J_2 = -3(2)\ cm^{-1}$, $g = 2.12(1)$, and $\theta = -0.74(2)$ K. The negative value of θ is responsible for the decay of $\chi_M T$ at low temperatures.

From the magnetic point of view, the Cu^{II} atoms within the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ subcore can be treated as singly

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(65) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

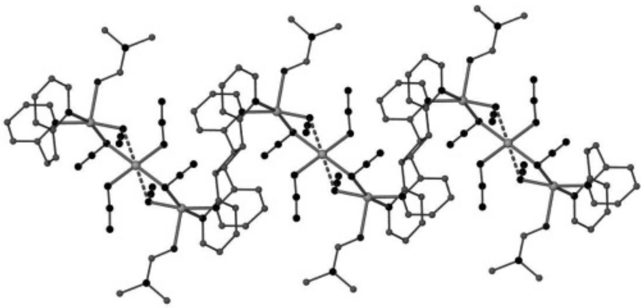


Figure 2. A view of the zigzag chain of **1**. Hydrogen atoms have been omitted for clarity.

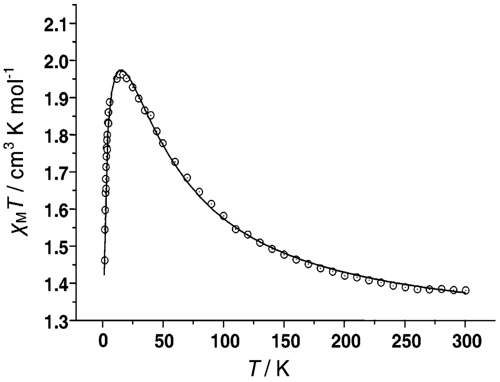


Figure 3. $\chi_M T$ versus T plot for **1**. The solid line represents the best fit of the experimental data (text for details).

bridged,[66] because one of the Cu−N$_{azide}$ distances is very long [Cu(2)−N(3) = 2.599(7) Å]. On the other hand, the Cu(1)−N(6)−Cu(2) angle, which is associated with short Cu−N distances, is 105.4(3)°. Density functional calculations on dinuclear complexes comprising the symmetrical [Cu($\mu_{1,1}$-N$_3$)$_2$Cu]$^{2+}$ core, reported by Ruiz et al.,[2] have shown that there is a clear correlation between the calculated J parameter and the θ angle:[67] the J value decreases from a maximum at about $\theta = 85°$ upon increasing θ, eventually reaching an antiferromagnetic regime for $\theta \geq 104°$. The τ angle corresponding to the out-of-plane shift of the azide ligands seems to have a negligible influence on the J value. The large ferromagnetic value of J_1, calculated for **1**, seems to be in contradiction with the above-mentioned theoretical study, which predicts an antiferromagnetic coupling between the metal centers. In addition, the linear trend ($J = -41.94\theta + 4440$ cm^{-1}) reported by Thompson and Tandon[4] for copper(II) complexes doubly bridged by $\mu_{1,1}$-diazine and $\mu_{1,1}$-azide ligands, predicts a J value of 20.36 cm^{-1} for **1**.

Chart 5

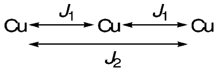
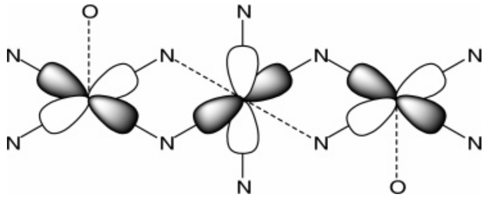


Chart 6



Theoretical Study. To understand the origin of the relatively strong ferromagnetic coupling found in **1**, we performed electronic structure calculations using density functional methods. The calculated J values using the B3LYP hybrid functional are +93 and −1.1 cm^{-1}, in good agreement with the experimental values of +70 and −3 cm^{-1} for the first (J_1) and second (J_2) neighbor interactions, respectively. The analysis of the molecular structure reveals that there are two possible exchange pathways between two neighboring Cu^{II} atoms: one that involves two short Cu−N bond distances corresponding to the large Cu−N$_{azide}$−Cu angle of 105.4(3)° and another that involves the very long Cu(2)−N(3) [Figure 1] distance of 2.599(7) Å. The exchange coupling through the latter pathway should be considered almost negligible as a result of the long Cu−N distance. As it was stated above, previous DFT studies on dinuclear doubly bridged EO-azido complexes, using the same methodology,[2] predict an antiferromagnetic behavior for complexes with Cu−N−Cu angles exceeding the value of 104°, which is in apparent contradiction with the results shown here. The explanation of this anomalous behavior of **1** can be found by analyzing the topology of the magnetic orbitals of two neighboring Cu^{II} atoms with respect to the coordination spheres (Chart 6). The magnetic orbital of the central Cu(2) ion lies on the equatorial plane of the octahedron because of the elongated octahedral geometry, whereas the magnetic orbital of the square-pyramidal Cu(1) ion lies on the square base of the pyramid. The equatorial/basal planes of Cu(2) and Cu(1) are almost perpendicular, as it was stated in the crystal-structure section, and in effect the magnetic orbitals of the two neighboring metal ions are almost perpendicular to each other.

To understand the origin of such ferromagnetic interactions, we performed calculations in two models with a coplanar arrangement of the magnetic orbitals. First, a trinuclear model was employed, with eight short Cu−N bond distances and the same Cu−N−Cu angle of 105.4° for all of the exchange pathways, increasing the Cu−N distances of the axial azide ligands coordinated to the central Cu^{II} atom up to 2.6 Å to keep its 4 + 2 coordination. Second, a symmetric dinuclear model was employed with the same bridging ligands but keeping DMF and 2,2′-tpcb as terminal ligands to have the same coordination sphere in the two neighboring Cu^{II} atoms. The calculated J values for the trinuclear model are +41.5 and −3.6 cm^{-1} for the first and second neighboring interactions, respectively, whereas a J value of −67 cm^{-1} is obtained for the dinuclear model. These results indicate that the ferromagnetism in **1** is basically due to two effects: the first one is the topology of the magnetic orbitals, as is shown by the weaker ferromagnetic coupling calculated for the coplanar trinuclear model in comparison with that found in **1** with an almost-perpendicular arrangement of the magnetic orbitals (Chart 6); the second one is the asymmetry induced in the exchange interaction due to

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[66] Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *Crystal Growth Des.* **2005**, *5*, 1119.

[67] The θ angle within a [Cu($\mu_{1,1}$-N$_3$)$_2$Cu]$^{2+}$ core is defined as the Cu−N$_{azide}$−Cu angle.

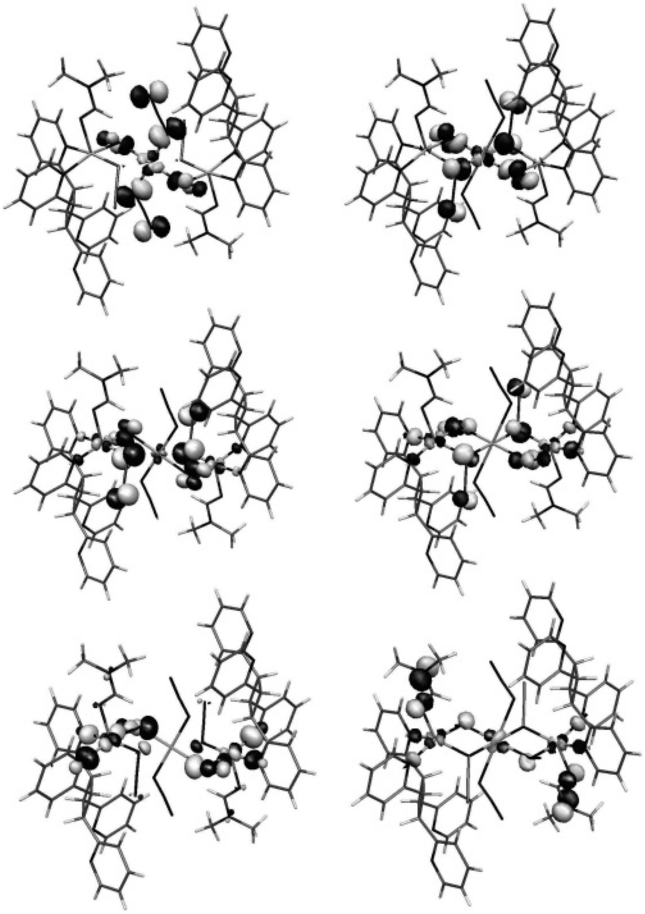

Figure 4. Three SOMOs for **1** (left) and for the coplanar trinuclear model (right).

the different coordination spheres of the neighboring Cu^{II} atoms. It is clear that only the symmetric dinuclear complex with a bridging Cu−N−Cu angle of 105.4° is antiferromagnetic. These two effects provide a weaker interaction between the magnetic orbitals of the neighboring Cu^{II} atoms, and despite the fact that the orbitals are not strictly orthogonal, the antiferromagnetic contribution is rather small; therefore, the exchange coupling is ferromagnetic according to the Kahn−Briat model.[65,68,69] The influence of the different coordination spheres of the Cu^{II} atoms can be clearly corroborated in Figure 4, where the SOMOs for the two studied trinuclear complexes are represented. The central Cu^{II} atom either in **1** or in the trinuclear model with a coplanar topology of the magnetic orbitals shows a very localized molecular orbital at higher energies, resulting in a small mixing with the orbitals of the other two Cu^{II} atoms and consequently in a weak antiferromagnetic contribution. This is reflected in a calculated ferromagnetic J value for both systems.

To test the accuracy of this methodology and the previously indicated conclusions, we calculated the J value of the dinuclear complex $[Cu_2(N_3)_6]^{2-}$ described recently by Saha et al.,[17] with a large Cu−N$_{azide}$−Cu bond angle of 104.3° and four short Cu−N bond distances. The experimental J value is -72 cm^{-1}, which is in agreement with the antiferromagnetic behavior that the theoretical study[2] predicts. We obtained a J value of -33 cm^{-1} for this complex using the B3LYP functional and a triple-ζ basis set with polarization. These results confirm the previous theoretical study, which predicts that a coplanar topology of the magnetic orbitals results in an antiferromagnetic coupling for large Cu−N$_{azide}$−Cu angles due to the loss of the accidental degeneracy, which is responsible for the ferromagnetic coupling in dinuclear EO azide-bridged Cu^{II} complexes.[2,70] However, the ferromagnetic behavior in **1** is due to the degeneracy of the magnetic orbitals, despite the large value of the Cu−N−Cu bond angle.

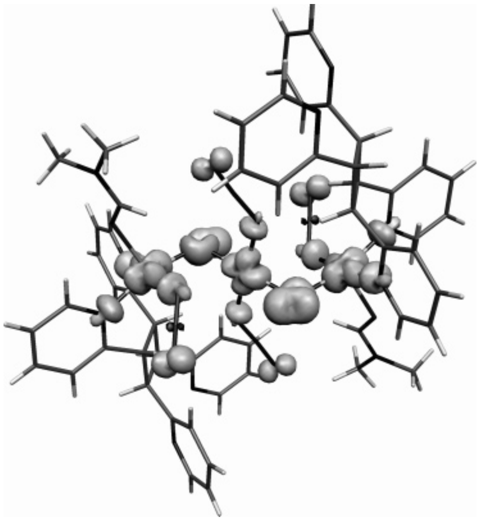

Figure 5. Representation of the spin-density map calculated at the B3LYP level for the quartet ground state of **1**. The isodensity surface represented corresponds to a value of 0.03 e$^-$/bohr^3 (clear and dark regions indicate positive and negative spin populations, respectively).

The representation of the spin distribution corresponding to the quartet ground state of **1** is plotted in Figure 4. The topology of the magnetic orbitals proposed in Chart 6 is confirmed in Figure 5, which shows the perpendicular orientation of the orbitals that possess the unpaired electrons between neighboring Cu^{II} atoms. The distribution of the spin density also reveals that spin delocalization is the main exchange mechanism.[71] As it is shown in Figure 4, all of the atoms with large spin density have the same sign, with the exception of the middle nitrogen atoms of the bridging azide ligands, which have a very small negative spin population, thus ruling out a spin polarization mechanism along the azido ligand. It is worth noting that the long Cu(2)−N(3) bond distance of 2.599(7) Å introduces a small break in the symmetry, making this exchange pathway practically pathless.

Conclusions

As we commented on a previous article,[38] the late O. Kahn had wondered[71] "...can the 1,1-azido group be considered

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(68) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 268.

(69) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1441.

(70) Cano, J.; Ruiz, E.; Alvarez, S.; Verdaguer, M. *Comments Inorg. Chem.* **1998**, *20*, 27.

(71) Aebersold, M. A.; Gillon, B.; Plantevin, O.; Pardi, L.; Kahn, O.; Bergerat, P.; von Seggern, I.; Tuczec, F.; Öhrström, L.; Grand, A.; Lelièvre-Berna, E. *J. Am. Chem. Soc.* **1998**, *120*, 5238.

as an almost universal ferromagnetic coupler, or is the stabilization of the parallel spin state only achieved in a limiting range of bridging angle values...?". The theoretical study by Ruiz et al.[2] supports the second possibility, where, for $\theta \geq 104°$, it is possible to have AF coupling. Magnetostructural studies by Thompson's group on several dinuclear copper(II) compounds involving a combination of a $\mu_{1,2}$-diazine and a $\mu_{1,1}$-N_3^- bridges suggest that the realm of the ferromagnetic coupling ceases for Cu−N−Cu angles greater than 108°.[4,23]

In this article, we have presented the synthesis, structural characterization, and magnetic study of a new complex comprising an irregularly asymmetric $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ subcore, where one of the highest reported θ angles is found along with a relatively strong ferromagnetic coupling. Theoretical analysis using density functional methods reveals that the ferromagnetic coupling in this compound is due to the topology of the magnetic orbitals that show a relatively perpendicular orientation and the asymmetric character of the neighboring Cu^{II} atoms due to different coordination spheres. The usual ferromagnetic coupling of the azide-bridged Cu^{II} complexes showing a coplanar arrangement of the magnetic orbitals is due to the accidental degeneracy of such orbitals; for large $Cu-N_{azide}-Cu$ angles, there is an increase in the energy gap, resulting in antiferromagnetic coupling, as found in the complex studied by Saha et al.[17] However, in our case, the almost-perpendicular orientation of the orbitals that possess the unpaired electrons results also in an accidental degeneracy, despite the large $Cu-N_{azide}-Cu$ angle in one exchange pathway.

Koner et al. have reported an anomalous magnetic behavior for an EO double-azido-bridged dinuclear Cu^{II} complex with weak antiferromagnetic coupling ($J = -8.5$ cm^{-1}) and a very small Cu−N−Cu angle of 89.1°.[72] However, in this case, there are two long $Cu-N_{azide}$ bond distances, resulting in a non-coplanar parallel topology of the magnetic orbitals, and thus that complex cannot be directly compared with the previously reported complexes with coplanar topology. A theoretical study to explain the magnetic behavior of the asymmetric azido-bridged dinuclear Cu^{II} complex has been recently reported.[44] The antiferromagnetic behavior found recently[17] in the $[Cu_2(N_3)_6]^{2-}$ dinuclear complex with a large $Cu-N_{azide}-Cu$ bond angle of 104.3° and four short $Cu-N_{azide}$ bond distances in the exchange pathway is in accordance with the dependence of the magnetic coupling on the $Cu-N_{azide}-Cu$ bond angle.

It is becoming apparent that co-ligands have a direct effect on the structural parameters in Cu^{II} complexes comprising the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core. To this end, a ligand derived from a template-directed solid-state photodimerization led to a polymeric complex where the magnetic orbitals of the metal ions bridged by EO-azide ligands are orthogonal, resulting in a ferromagnetic coupling. Work is in progress to synthesize more metal-azide complexes with bridging ligands derived from the solid state.

Acknowledgment. This research was partially supported by CICYT (Grant CTU2006/01759/BQU) and Comissió Interdepartamental de Ciència i Tecnologia (CIRIT) through Grants CTQ2005-08123-C02-02/BQU and 2005SGR-00036, respectively. The computing resources were generously made available in the CIRI and the Centre de Supercomputació de Catalunya (CESCA), with a grant provided by Fundació Catalana per a la Recerca (FCR) and the Universitat de Barcelona. T.C.S, G.S.P., and S.P.P. thank the Research Committee of the University of Patras (K. Caratheodory Program No. 03016) for support. We also thank the National Science Foundation (CAREER Award, L.R.M. DMR-0133138) for support of this work.

Supporting Information Available: *M* versus *H* plot for **1** at 2 K, and X-ray crystallographic file in CIF format, including atomic coordinates, thermal parameters, and complete listing of bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(72) Koner, S.; Saha, S.; Mallah, T.; Okamoto, K.-I. *Inorg. Chem.* **2004**, *43*, 840.