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Asymmetric Azido–Copper(II) Bridges: Ferro- or Antiferromagnetic? Experimental and Theoretical Magneto–Structural Studies

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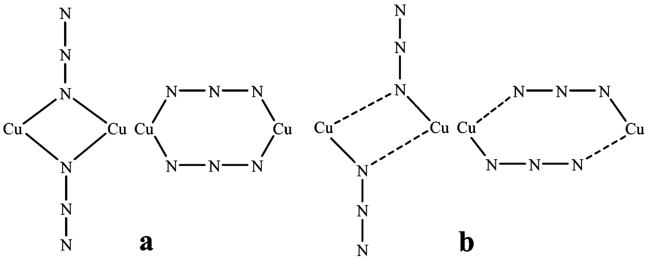
Reaction of NaN_3 with the $[Cu^{II}(tn)]^{2+}$ ion (tn = 1,3-diaminopropane) in basic aqueous solution yields the azido-bridged complex of formula $[Cu_2(tn)_2(N_3)_4]$ (**1**), which is characterized by X-ray crystallography. The structure of **1** is made up of dinuclear neutral complexes, of formula $[Cu_2(tn)_2(N_3)_4]$, resulting from the assembling of two mononuclear units through two equivalent end-on azide bridges connecting asymmetrically two $Cu(tn)(N_3)_2$ entities. These dinuclear units are connected through two asymmetric end-to-end N_3 bridges to form a chain of dimers. Magnetic measurements for compound **1** show weak antiferromagnetic exchange interactions between the Cu(II) ions. The magnetic data were modeled using the susceptibility expression derived for an alternating AF $S = 1/2$ chain. A very satisfactory fit over the whole temperature range was obtained with $g = 2.1438(4)$, $J_1 = –3.71(2)\ cm^{-1}$, and $J_2 = –3.10(2)\ cm^{-1}$ (J_1 and J_2 are the singlet–triplet separations). This magnetic behavior differs from those observed for similar examples which were reported as having alternating ferro- and antiferromagnetic exchange interactions; thus, DFT calculations were done to understand the nature of the magnetic coupling in such asymmetric end-on and end-to-end N_3 bridges. Theoretical results show that the double asymmetric end-on bridges produce antiferromagnetic coupling while the end-to-end ones can present ferro- or antiferromagnetic coupling depending on the copper coordination sphere.

Introduction

Studies of polynuclear transition metal complexes have received a great attention because of their rich structural and topological features and their interesting magnetic properties.[1] To build these molecular architectures, a large number of simple or sophisticated bridging ligands have been used; among them, the azide ion is particularly interesting because of its ability to act either in end-on ($\mu_{1,1}$) or in end-to-end ($\mu_{1,3}$) coordination mode (Chart 1), depending on the steric effects and the local environments of the metal ions. Thus, its transition metal systems display rich and fascinating structural architectures ranging from discrete polynuclear complexes to extended three-dimensional networks.[2−21] From the magnetic point of view, the coordination modes of the azide ligand associated with structural parameters (bond and dihedral angles, metal bridge bond lengths) greatly affect the nature and magnitude of the magnetic exchange interactions in these polynuclear azide complexes.[2−6]

Chart 1. Symmetric (a) and Asymmetric (b) End-On ($\mu_{1,1}$) and End-to-End ($\mu_{1,3}$) Coordination Modes in the Cu−Azide System



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(1) See, for example: (a) Decurtins, S.; Pellaux, R.; Antorrena, G.; Palacio, F. *Coord. Chem. Rev.* **1999**, *190*, 841. (b) Kahn, O.; Larionova, J.; Yakhmi, J. V. *Chem.*—Eur. J. **1999**, *5*, 3443. (c) Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleiman, M.; Desplanches, C.; Scuiller, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I.; Veillet, P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190*, 1023 and references therein. (d) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313 and references therein. (e) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103 and references therein.

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For the Cu−azide system, it is well established that complexes with double symmetric end-to-end ($\mu_{1,3}$) bridges are strongly antiferromagnetic. Those with double symmetric end-on bridges ($\mu_{1,1}$) (Chart 1a) are usually strongly ferromagnetic, but it has been proposed that, for Cu−N−Cu angle values larger than 104°, the coupling should be antiferromagnetic and there are not still known complexes fulfilling this geometrical condition.[4−6] For complexes with double asymmetric end-on ($\mu_{1,1}$) and end-to-end ($\mu_{1,3}$) bridges involving short and long Cu−N bonds (Chart 1b), the situation is less clear since these systems are very scarcely reported. Careful examination of the few examples reported to date reveals that the magnetic exchange is either ferromagnetic or antiferromagnetic.[7−21] For the doubly bridged asymmetric end-on complexes, the magnetic coupling is ranging from slightly ferromagnetic to slightly antiferromagnetic;[7−15] while, for the doubly bridged asymmetric end-to-end complexes, the magnetic coupling is ranging from slightly ferromagnetic to strongly antiferromagnetic.[8,16−19] Finally, for the coordinating polymers involving asymmetric bridges alternating both kinds of coordination modes (end-on and end-to-end bridges), only four examples have been structurally characterized to date;[13,14,20,21] all have been reported as presenting alternating weak ferromagnetic and weak antiferromagnetic exchange interactions assigned to the end-on and end-to-end Cu-azide bridges, respectively.

Herein, we report the study of a Cu−azide compound of formula $[Cu_2(tn)_2(N_3)_4]$ (**1**) with alternating asymmetric end-on ($\mu_{1,1}$) and end-to-end ($\mu_{1,3}$) bridges. During the course of this work, the crystal structure of **1** has been reported by others[22] but the magnetic investigations were not done. Since the magnetic properties reported for a few asymmetric end-on and end-to-end Cu(II)−azide compounds remain unclear, we report herein the magnetic properties of **1** and a general discussion, essentially based on density functional theory calculations (DFT) of the nature of the magnetic exchanges in such compounds.

Experimental Section

General Methods. Magnetic studies were carried out on a powder sample at 0.1 T after zero field cooling, in the temperature range 2−300 K, with a MPMS-XL SQUID magnetometer from Quantum Design. The susceptibility was corrected for the sample holder and the diamagnetic contributions of all atoms.

Results and Discussion

Synthesis and Single-Crystal X-ray Study. One-pot reaction between copper(II) chloride and sodium azide in basic aqueous solution in the presence of 1,3-diaminopropane (tn) gave, after further workup, the new compound $[Cu_2(tn)_2(N_3)_4]$ (**1**) as black prismatic crystals.[23] Since the crystal structure has been very recently reported in the literature,[22] we just briefly discuss some structural features relevant for the magnetic studies. The metal ion has an elongated square pyramidal environment (CuN_4N) with almost equivalent Cu−N bond lengths in the basal plane [2.010(3) and 2.009(3) Å from the azide ligands; 2.011(3) and 2.006(3) Å from the tn ligand]; the elongated apical position is occupied by the nitrogen atom N1 ($N1^{(i)}$ for Cu and N1 for $Cu^{(i)}$, Figure 1) of the other equivalent related azide bridge [$Cu−N1^{(i)}$ 2.473(3) Å]. A least-squares plane calculation shows that

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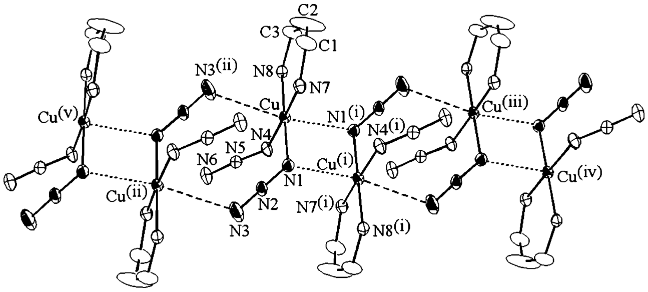

Figure 1. Ortep view showing the monodimensional chain of compound **1**. Codes of equivalent positions: (i) 2 − *x*, −*y*, −*z*; (ii) 1 − *x*, −*y*, −*z*; (iii) 1 + *x*, *y*, *z*; (iv) 3 − *x*, −*y*, −*z*; (v) −1 + *x*, *y*, *z*.

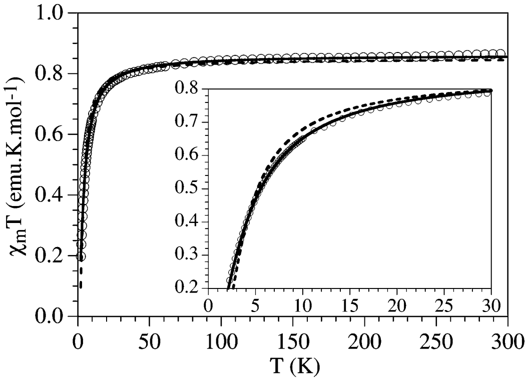

Figure 2. Thermal variation of the χ_mT product of the title compound showing the best fit to an $S = 1/2$ dimer model (dashed line) and to an alternating antiferromagnetic $S = 1/2$ chain model (solid line). The inset shows the low-temperature region.

the CuN4 base unit is essentially planar with a maximum deviation of 0.07 Å from the corresponding mean plane. The structure of **1** can be viewed as made up of discrete dinuclear neutral complexes, of formula $[Cu_2(tn)_2(N_3)_4]$, resulting from the assembling of two mononuclear $Cu(tn)(N_3)_2$ units through two equivalent asymmetric end-on azide bridges (Figure 1). The N4−N5−N6 azide is terminal while the N1−N2−N3 azide acts as an asymmetric end-on ligand with a long and a short Cu−N bond (2.473(3) and 2.010(3) Å). Careful examination of the interdinuclear distances reveals that the $[Cu_2(tn)_2(N_3)_4]$ units are connected each other through two equivalent long Cu−N3 distances (Cu−N3$^{(ii)}$ and Cu$^{(ii)}$−N3: 2.852(5) Å). Thus, we can describe the Cu coordination polyhedron as a strongly elongated octahedron and then the azide bridging unit as an essentially $\mu_{1,1,3}$-bridging ligand. Therefore, the structure of **1** can be described as a monodimensional chain as shown in Figure 1. The Cu⋯Cu intradinuclear distance across the N_3^- bridges, of 3.3178(6) Å, is in the range for those observed in other Cu(II)−N_3 derivatives (3.10−3.32 Å) but significantly shorter than the corresponding value observed between two adjacent dinuclear units (Cu⋯Cu$^{(ii)}$ 5.2562(6) Å). Note that the Cu⋯Cu distance of 6.835(2) Å reported for this structure in the ref 22 as the Cu⋯Cu distance between two dimers does not correspond to the shortest Cu⋯Cu distance between two adjacent dinuclear units value but to the Cu⋯Cu$^{(iii)}$ distance (Figure 1).

Magnetic Properties. The magnetic properties of the title compound are displayed in Figure 2 as the thermal variation of the product of the molar susceptibility times the temperature (χ_mT)/formula unit (2 copper ions). The room-temperature χ_mT value (0.85 emu·K·mol^{-1}) is close to the expected value for two magnetically isolated $S = 1/2$ Cu(II) ions. When being cooled, the χ_mT product remains constant down to ca. 50 K, and below this temperature it progressively decreases to reach a value of 0.20 emu·K·mol^{-1} at 2 K. This behavior indicates the presence of antiferromagnetic coupling between the copper centers through the N_3 bridges. From the structural data we can assume in a first approximation that the Cu(II) ions form dimers linked through the double asymmetric $\mu_{1,1}$-N_3 bridge. Consequently, we have fitted the magnetic data to the simple isotropic dimer model of Bleaney and Bowers;[26] this model gives a quite good fitting over the whole temperature range with $g = 2.13$ and $J = -4.84$ cm^{-1} (the Hamiltonian is written as $H = -JS_1S_2$).

The J value is in the range of those observed for the Cu−azide complexes involving similar bridges, but this range is very large as shown in Table 1 (from −16.8 cm^{-1} in $[Cu_2(L2)_2(N_3)_2](ClO_4)_2$ to +24.0 cm^{-1} in $[Cu_2(L1)_2(N_3)_2]$).[7−15] However, assignment of the J value to the $\mu_{1,1}$-N_3 double bridges remains uncertain since careful examination of Tables 1 and 2 reveals that, with the exception of the −105 cm^{-1} value in Table 2, the exchange J values through both types of bridges ($\mu_{1,1}$-N_3 double bridges and $\mu_{1,3}$-N_3 double bridges) are distributed in similarly wide ranges. In such conditions, theoretical calculations could be the best way to obtain the correct magnetic assignment (see below).

Examination of the magnetic fit shows a rounded decrease at low temperatures which is not very well reproduced with the dimer model (see inset in Figure 2); therefore, according to the crystal structure (Figure 1), we have to assume two magnetic exchange pathways: an exchange interaction through the asymmetric $\mu_{1,1}$-N_3 double bridges (J_{eo}) and a second one through the asymmetric $\mu_{1,3}$-N_3 double bridges (J_{ee}) (Scheme 1). The question now is whether these two asymmetric bridges give rise to alternating ferro/antiferromagnetic interactions or to alternating antiferromagnetic

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(23) Anal. Calcd for $C_3H_{10}CuN_8$: C, 16.25; H, 4.55; Cu, 28.66; N, 50.54. Found: C, 16.41; H, 4.52; Cu, 28.61; N, 50.44. Infrared spectra (ν/cm^{-1}): 3265 s, 3227 br, 3138 w, 2923 w, 2877 w, 2085 s, 2036 br, 2016 m, 1581 m, 1468 w, 1436 w, 1398 w, 1338 w, 1273 w, 1172 m, 1144 w, 1105 w, 1074 m, 1026 m, 928 m, 882 w, 664 m, 607 w, 501 w, 419 w, 354 m. Crystal structure determination: $T = 288$ K, Xcalibur 2 diffractometer (Oxford Diffraction), Mo Kα radiation ($\lambda = 0.710\,73$ Å). Structure determination: direct methods and successive Fourier difference syntheses; refinement on F^2. CH_2 hydrogen atoms: calculated [d(C−H) = 0.95 Å] and $U_{iso} = 1.3U_{equ}$(C). NH_2 hydrogen atoms: located by difference Fourier maps. Scattering factors and corrections for anomalous dispersion: *International Tables for X-ray Crystallography*. Thermal ellipsoid drawing: ORTEP program.[24,25] Crystal data: $C_6H_{20}N_{16}Cu_2$, $M = 443.42$, $P2_1/n$, a (Å) = 6.8525(2), b (Å) = 6.7667(2), c (Å) = 18.4164(6), β (deg) = 99.6(1), V (Å^3) = 842.1(4), $Z = 2$, D_{calcd} (g·cm^{-3}) = 1.75. Reflections unique: 1805, $R_{int} = 0.016$. Reflections with $I > 4\sigma(I)$: 1346. $N_v = 109$, $R(F_o) = 0.038$, $R_w(F_o) = 0.055$, and GOF = 1.292.

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Table 1. Structural and Magnetic Parameters for Asymmetric Cu(II)$-\mu_{1,1}$-N$_3$ Complexes Involving Only Azide Bridges (J = Singlet$-$Triplet Separation: $H = -JS_1S_2$ or $H = -J\Sigma S_iS_{i+1}$)

compds[a]	short Cu−N/Å	long Cu−N/Å	J/cm^{-1}	ref
$[Cu_2(L1)_2(N_3)_2]$	2.019(4)	2.551(4)	+24.0	7
$[Cu_2(L2)_2(N_3)_2](ClO_4)_2$	2.098(3)	2.513(4)	−16.8	8
$[Cu_2(L3)_2(N_3)_2(H_2O)_2](PF_6)_2$	1.927(6)	2.851(5)	−5.80	9
$[Cu_2(L4)_2(N_3)_2]$	1.998(3)	2.505(3)	−8.5	10
$[Cu_2(L5)_2(N_3)_2]$	2.039(7)	2.440(7)	−1.84	11
$[Cu_2(L6)_2(N_3)_2]$	1.988(10)	2.443(9)	−2.63	12
$[Cu_2(L7)_2(N_3)_2]$	1.985(6)	2.447(6)	−1.79	12
$[Cu_2(L8)_2(N_3)_4]$	2.016(4)	2.381(4)	−3.06	13b
$[Cu(L9)(N_3)_2]_n$	1.969(2)	2.683(3)	−2.70	14
$[Cu_2(L10)_2(N_3)_2](ClO_4)_2$	1.972(7)	2.563(8)	−3.20	15

[a] L1 = 7-amino-4-methyl-5-aza-3-hepten-2-onato(1−); L2 = Medien = methyldiethylenetriamine; L3 = terpy = 2,2′:6′,2″-terpyridine; L4 = 1-(*N*-salicylideneamino)-2-aminoethane(1−); L5 = *N*-(3-aminopropyl)salicylaldimine(1−); L6 = *N*-[2-(ethylamino)ethyl]salicylaldimine(1−); L7 = 7-(ethylamino)-4-methyl-5-azahept-3-en-2-one(1−); L8 = aepi = 1-(2-aminoethyl)piperidine; L9 = bpy = 2,2′-bipyridine; L10 = *N*,*N*-bis(2-methylpyridyl)(3,5-dimethyl-2-hydroxybenzyl)amine.

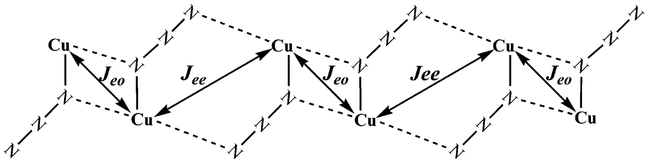
Table 2. Structural and Magnetic Parameters for Asymmetric Cu(II)$-\mu_{1,3}$-N$_3$ Complexes Involving Only Azide Bridges (J = Singlet$-$Triplet Separation: $H = -JS_1S_2$, $H = -J\Sigma S_iS_{i+1}$, or $H = -J\Sigma(S_{2i}S_{2i-1} - \alpha S_{2i}S_{2i+1})$ with $\alpha = J_F/|J_{AF}|$)

compds[a]	short Cu−N/Å	long Cu−N/Å	J/cm^{-1}	ref
$[Cu_2(L11)_2(N_3)_2](ClO_4)_2$	1.996(3)	2.327(3)	−7.5	16
$[Cu_2(L12)_2(N_3)_2](ClO_4)_2$	1.976(4)	2.482(5)	−28.0	16
	1.971(4)	2.439(5)		
	1.986(5)	2.385(6)		
	1.983(5)	2.569(7)		
$[Cu_2(L13)_2(N_3)_2](ClO_4)_2$	1.996(3)	2.276(3)	−3.6	16
$[Cu_2(L14)_2(N_3)_2](ClO_4)_2$	2.099(5)	2.379(7)	+9	8
$[Cu_2(L15)_2(N_3)_2](ClO_4)_2$	2.093(3)	2.309(3)	−105	8
$[Cu_2(L11)_2(N_3)_2](BPh_4)_2$	1.985(4)	2.252(5)	−13	17
$[Cu(L16)_2(N_3)_2]_n$	2.029(5)	2.611(6)	+1.6	18
$[Cu_2(L17)_2(N_3)_4]_n$	2.044(4)	2.373(4)	+16.8	19

[a] L11 = Me$_5$dien = 1,1,4,7,7-pentamethyldiethylenetriamine; L12 = Et$_5$dien = 1,1,4,7,7-pentaethyldiethylenetriamine; L13 = EtMe$_4$dien = 4-ethyl-1,1,7,7-tetramethyldiethylenetriamine; L14 = Et$_3$dien = triethyldiethylenetriamine; L15 = Medpt = methyldipropylenetriamine; L16 = 4-(dimethylamino)pyridine; L17 = bben = 1,2-bis(benzylamino)ethane.

interactions. Careful analysis of the magnetic behaviors of the few discrete and polymeric examples involving only azide bridges (asymmetric $\mu_{1,1}$-N$_3$ double bridges in Table 1 and asymmetric $\mu_{1,3}$-N$_3$ double bridges in Table 2) reveals different magnetic behaviors for both kinds of asymmetric double bridges; they display strong antiferromagnetic to significant ferromagnetic couplings with two large ranges of the J values (from −16.8 to +24.0 cm^{-1} for asymmetric $\mu_{1,1}$-N$_3$ double bridges and from −105 to +16.8 cm^{-1} for asymmetric $\mu_{1,3}$-N$_3$ double bridges). Thus, to fit the magnetic data, we have assumed in a first fit alternating ferro- and an antiferromagnetic interactions through the two kinds of bridges. Accordingly, we have tried to fit the magnetic data using the model of Borrás et al.[27] for an alternating ferro/antiferromagnetic $S = 1/2$ chain with the exchange model of Scheme 1 (the Hamiltonian is written as $H = -J\Sigma(S_{2i}S_{2i-1} - \alpha S_{2i}S_{2i+1})$ with $\alpha = J_F/|J_{AF}|$). All the attempts made with this model failed since they led to very good agreements in

Scheme 1. Representation of the Magnetic Coupling Model for Compound **1**



the whole temperature range but only with negative α values ($\alpha = J_F/|J_{AF}| = J_2/|J_1|$), indicating that the nature of the exchange interactions must be antiferromagnetic in both cases.

Thus to correctly fit the magnetic data, we have used the alternating antiferromagnetic $S = 1/2$ chain model of Hatfield.[28] This model reproduces very satisfactorily the magnetic properties over the whole temperature range, including the rounded decrease at low temperatures (solid line in Figure 2), with the set of parameters $g = 2.1438(4)$, $J_1 = -3.71(2)$ cm^{-1}, and $J_2 = -3.10(2)$ cm^{-1}; i.e., $\alpha = J_2/J_1 = +0.83$ (solid line in Figure 2) and J_1 and J_2 are the singlet−triplet separations. Therefore, from the fit of the magnetic data, we can conclude that in the title compound the two kinds of bridges (double asymmetric $\mu_{1,1}$-N$_3$ and double asymmetric $\mu_{1,3}$-N$_3$ bridges) present weak, although noticeable, antiferromagnetic couplings. In addition, at this step of study, it is impossible to assign J_1 and J_2 values to the two kinds of bridges (J_{eo} and J_{ee}) since the magnetic model gives a very satisfactorily fit with good quantitative J values (J_1 and J_2) but does not allow their assignment to the J_{eo} and J_{ee} exchange interactions. As discussed above, the J_1 and J_2 values cannot be assigned correctly from the experimental values of Tables 1 and 2. However, since the exchange coupling values summarized in Tables 1 and 2 are calculated distinctly for discrete double $\mu_{1,1}$-N$_3$ and $\mu_{1,3}$-N$_3$ bridges while, in **1**, these double bridges are alternatively connected (Scheme 1), it looks important to compare also the J_1 and J_2 values to those calculated for the scarcely reported examples involving similar alternating double asymmetric $\mu_{1,1}$-N$_3$ and $\mu_{1,3}$-N$_3$ bridges. Consequently, we have compared the magnetic data of **1** to those depicted in Table 3 for four similar examples structurally characterized.[13a,14,20,21] Examination of the magnetic results reveals that the antiferromagnetic behavior found in compound **1** ($J_1 = -3.71$ cm^{-1} and $J_2 = -3.10$ cm^{-1}) does not agree with the alternating ferromagnetic and antiferromagnetic behaviors found for the four examples (Table 3). This unusual behavior of **1** makes the situation of this system more unclear and preclude any simple magneto−structural correlation. Note that, for the four reported examples, the ferromagnetic exchange coupling (J_2) was assigned to the double asymmetric $\mu_{1,1}$-N$_3$ bridges, while the antiferromagnetic one (J_1) was assigned to the double asymmetric $\mu_{1,3}$-N$_3$ bridges; such magnetic assignment has been justified, by the four groups,[13a,14,20,21] from a magneto−structural correlation that has been established for double symmetric Cu−azide bridged complexes involving only short Cu−N$_3$ bridges

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Table 3. Structural and Magnetic Parameters for Asymmetric Cu(II)−$\mu_{1,1,3}$-N$_3$ Bridges (J_1, J_2 = Singlet−Triplet Separations: $H = -J\Sigma(S_{2i}S_{2i-1} - \alpha S_{2i}S_{2i+1})$ with $\alpha = J_F/|J_{AF}|$)[a]

	Cu−N/Å and *J* values				
	$\mu_{1,1}$ (eo)		$\mu_{1,3}$ (ee)		
compds[b]	short	long	short	long	ref
[Cu(L9)(N$_3$)$_2$]$_n$	1.973(3)	2.604(3)	1.973(3)	2.849(4)	14
	J_2 = +4.60 cm^{-1}		J_1 = −2.90 cm^{-1}		
[Cu(L18)(N$_3$)$_2$]$_n$	1.994(3)	2.449(3)	1.994(3)	2.710(3)	20
	J_2 = +12.76 cm^{-1}		J_1 = −6.56 cm^{-1}		
	2.007(3)	2.648(4)	2.007(3)	2.741(4)	13a
[Cu(L19)(N$_3$)$_2$]$_n$	2.014(3)	2.520(3)	2.014(3)	2.655(5)	
	J_2 = +0.15 cm^{-1}		J_1 = −2.80 cm^{-1}		
	2.020(6)	2.847(8)	2.020(6)	2.653(8)	21
[Cu(L20)(N$_3$)$_2$]$_n$	2.018(6)	2.614(8)	2.018(6)	2.426(8)	
	J_2 = +24.70 cm^{-1}		J_1 = −7.00 cm^{-1}		
[Cu(tn)(N$_3$)$_2$]$_n$	2.010(3)	2.473(3)	2.010(3)	2.852(5)	this work
	J_2 = −3.10 cm^{-1}		J_1 = −3.71 cm^{-1}		

[a] The magnetic assignment of J_1 and J_2 values corresponds to that reported by each group. [b] L18 = phen = 1,10-phenanthroline; L19 = aepy = 1-(2-aminoethyl)pyrrolidine; L20 = Me$_2$Eten = *N*,*N*-dimethyl-*N*′-ethylenediamine.

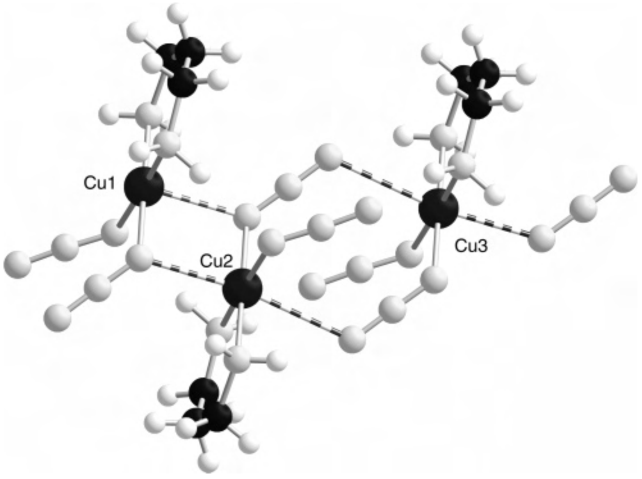

Figure 3. Representation of the molecular structure of the trinuclear model employed for the calculations. The carbon, nitrogen, and hydrogen atoms are represented by spheres of different shades of gray, from dark to bright, respectively. The long Cu−N bonds have been indicated with a multiband cylinder.

(Chart 1a)[4−6] but not for asymmetric bridges for which the situation remains unclear. It looks likely that the situation should be different for the asymmetric N$_3$-bridged compounds since the long Cu−N bonds observed strongly affect the orientation of the magnetic orbitals. This is in agreement with the magnetic data depicted in Tables 1−3 and with the magnetic fit of compound **1** which reveals antiferromagnetic exchange for both bridges, clearly different from that reported for the four examples involving similar bridges. At last, as a supplementary proof of the difficulty to correctly estimate the magnetic exchange values, we can point out that the compound [Cu(L19)(N$_3$)$_2$]$_n$ (Table 3) has been described by two different groups. Recently, the magnetic fit of this compound led to the *J* values of −3.22 and +17.0 cm^{-1}, assigned respectively by the authors to the $\mu_{1,1}$ and $\mu_{1,3}$ double bridges ($J_{eo} = J_2 = -3.22$ cm^{-1} and $J_{ee} = J_1 = +17.0$ cm^{-1}).[13b] This magnetic assignment, which is very different from that given in the first report on the basis of the same structural data ($J_{eo} = J_2 = +0.15$ cm^{-1} and $J_{ee} = J_1 = -2.80$ cm^{-1}; Table 3),[13a] was ascertained by MO calculations on spin dimers using the extended Hückel tight binding method.[13b] Finally, to understand these unclear magnetic behaviors and the magnetic assignment of the *J* values for the two types of bridges, we have undertaken DFT calculations.

Theoretical Study Using DFT Methods. To understand the reason of the unclear magnetic behavior of the asymmetrical end-on and end-to-end azido complexes (see Tables 1−3), we have undertaken a theoretical study using methods based on density functional theory (see Appendix for computational details). Hence, we have selected for the study the compound described in this work and three recent asymmetrical dinuclear complexes, two of them with a double end-to-end coordination and the third one with a double end-on azido bridging ligand, obtained by Escuer et al.[8] These dinuclear complexes will allow us to simplify the study of the magneto−structural correlations because they have only one exchange pathway. We have calculated the exchange coupling constants for the chain compound **1** using a trinuclear model (Figure 3). In this system, we have three different *J* values (J_{12}, J_{23}, and J_{13}; the notation correspond to the labels of Figure 3): the first interaction corresponds to a double end-on asymmetrical bridge with a long Cu−N bond distance of 2.473 Å on each pathway, the second *J* value is related with the exchange interaction through a double end-to-end asymmetrical bridging ligand with a Cu−N bond distance of 2.852 Å on each pathway, and the third *J* value, which is not considered usually in the experimental fits, corresponds to the interaction through a single end-to-end bridging ligand with two long Cu−N bond distances (2.473 and 2.852 Å).

The calculated *J* values using a model considering the three exchange coupling constants (see Appendix for computational details) are $J_{12} = -1.0$ cm^{-1}, $J_{23} = -4.8$ cm^{-1}, and $J_{13} = +3.2$ cm^{-1}. As we did in the experimental fit, we have also considered the case with only two *J* values, obtaining in such case $J_{12} = -3.1$ cm^{-1} and $J_{23} = -3.7$ cm^{-1}. It is worth to keep in mind that the values obtained are relatively small and close to the accuracy of the theoretical method employed. As conclusion, it seems that the double end-on and double end-to-end couplings are both antiferromagnetically coupled and the exchange coupling through the $\mu_{1,3}$-N$_3$ asymmetric bridges seems slightly greater than that of the $\mu_{1,1}$-N$_3$ asymmetric bridges.

Traditionally, the double end-on azido bridging ligands were considered as one of the prototype ligands to induce a ferromagnetic coupling in Cu(II) complexes as well as the double end-to-end azido bridging ligands for the antiferromagnetic interactions. However, these rules are not as general as it was considered because, for asymmetric complexes, there are end-on and end-to-end complexes with the opposite behavior showing antiferromagnetic and ferromagnetic coupling, respectively (see Tables 1 and 2).

Hence, according to the analysis of the *J* values indicated in the literature for the asymmetrical cases, the usual magnetic behavior seems to be the opposite of that in the symmetrical complexes. In some asymmetrical compounds

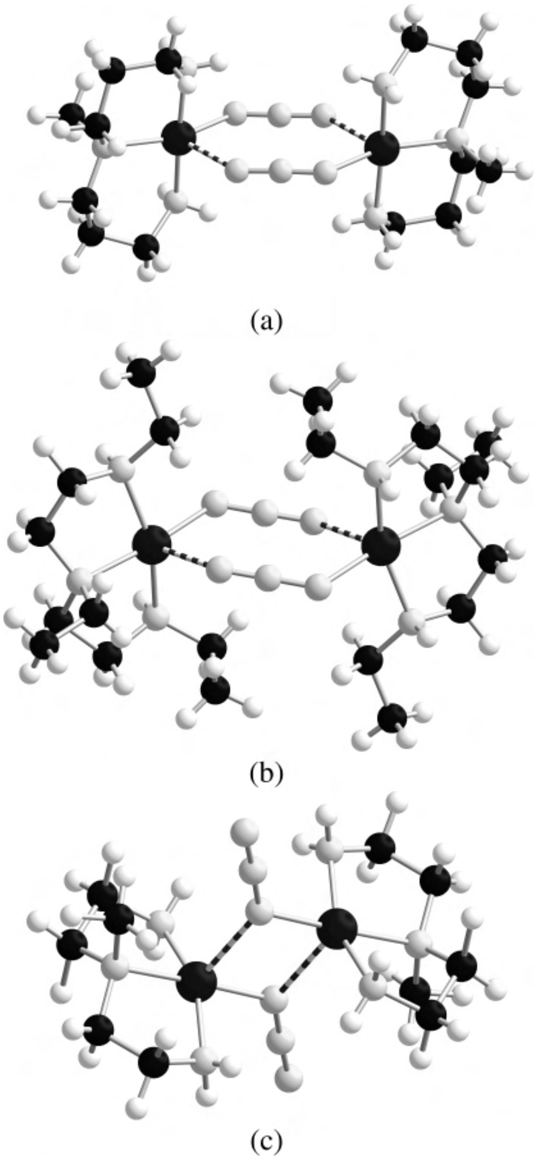

Figure 4. Representation of the molecular structure of the three dinuclear complexes employed for the calculations: (a) $[Cu_2(L15)_2(N_3)_2](ClO_4)_2$; (b) $[Cu_2(L14)_2(N_3)_2](ClO_4)_2$; (c) $[Cu_2(L2)_2(N_3)_2](ClO_4)_2$. The carbon, nitrogen, and hydrogen atoms are represented by spheres of different shades of gray, from dark to bright, respectively. The longest Cu−N bonds have been indicated with a multiband cylinder.

with the two types of bridging modes, the *J* values obtained from the fit of the experimental magnetic susceptibility could be assigned wrong,[13a,14,20,21] because the authors assumed a ferromagnetic coupling for the end-on bridge and the antiferromagnetic behavior for the end-to-end one, as it is well-known for the symmetrical complexes. However, there are also some examples that do not follow such rule as, for instance, our compound with two antiferromagnetic couplings.

To simplify the complexity of the system with different kinds of interactions, we have calculated the *J* values for some asymmetrical dinuclear complexes recently synthesized by Escuer et al. (Figure 4).[8] The experimental *J* value obtained for the end-to-end $[Cu_2(L15)_2(N_3)_2](ClO_4)_2$ complex is astonishingly large -105 cm^{-1}, despite a long Cu−N bond distance of 2.309 Å, while for the second $[Cu_2(L14)_2(N_3)_2](ClO_4)_2$ complex, despite a similar relative long Cu−N bond distance (2.379 Å), the exchange coupling is ferromagnetic with a *J* values of $+9$ cm^{-1} (Table 2).[8] Our calculated *J* value reproduces correctly the sign of these interactions obtaining for these two end-to-end complexes values of -22.9 and $+10.4$ cm^{-1}, respectively. The difference between these two complexes was attributed previously by Escuer et al. to the different Cu−(N····N)−Cu torsion angles (between the copper atoms and the two external nitrogen atoms), being for these complexes 11.3 and 35.8°, respectively.[8,16,19] We have performed the calculation of the exchange constant for a modified $[Cu_2(L15)_2(N_3)_2](ClO_4)_2$ (Table 2) with a torsion angle of 36.0° obtaining a *J* value of -14.6 cm^{-1}. This value indicates that the torsion angle is not the unique structural parameter that controls the sign and strength of the exchange coupling in the asymmetrical end-to-end azido complexes for a fixed Cu−N bond distance. Hence, we have tried a second model of $[Cu_2(L15)_2(N_3)_2](ClO_4)_2$ where we have modified the coordination sphere of the Cu(II) cations until reaching a τ parameter of 0.20 corresponding to the ferromagnetic $[Cu_2(L14)_2(N_3)_2](ClO_4)_2$ complex instead of the original 0.23 value for the antiferromagnetic complex ($\tau = 0$ square pyramid and $\tau = 1$ trigonal bipyramid)[29] obtaining a value of $+4.9$ cm^{-1} for such model. This result is relatively close to that obtained for the $[Cu_2(L14)_2(N_3)_2](ClO_4)_2$ complex ($+10.4$ cm^{-1}) showing that the symmetry of the coordination sphere plays a fundamental role in the coupling of such complexes even more important than the Cu−(N····N)−Cu torsion angle.

In the case of the end-on coordination of the bridging ligands, we have studied the complex $[Cu_2(L2)_2(N_3)_2](ClO_4)_2$ (Figure 4c) that presents an experimental *J* value of -16.8 cm^{-1} with a longest Cu−N bond distance of 2.513 Å. The calculated value of -4.0 cm^{-1} also corroborates the antiferromagnetic nature of the interaction, being slightly smaller than the experimental value. The analysis of the experimental data for similar compounds (Table 1) shows that most of the complexes have a weak antiferromagnetic coupling in agreement with our theoretical result.

The main parameter to control the strength of the interaction for both types of coordination is indeed the value of the longest Cu−N bond distance. The variation of the *J* values with such distance for the $[Cu_2(L15)_2(N_3)_2](ClO_4)_2$ and $[Cu_2(L2)_2(N_3)_2](ClO_4)_2$ complexes is represented in Figure 5. In the case of an end-to-end coordination there is a strong reduction of the antiferromagnetic coupling when increasing the Cu−N bond distance, resulting even in a weak ferromagnetic coupling for distances larger than 2.6 Å. However, for the end-on coordination the dependence of the exchange coupling with the Cu−N distance shows a progressive decay being the coupling in all cases antiferromagnetic.

If we turn back to our model of the chain compound, the hexacoordinated copper atoms have a torsion angle for the end-to-end coordination of 55.1° and a longest Cu−N($\mu_{1,3}$-N_3) distance of 2.852 Å; theses values are larger than those

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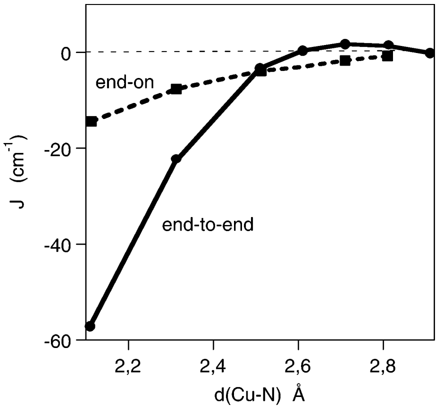

Figure 5. Representation of the dependence of the calculated exchange coupling constants with the longest Cu−N bond distances for the complexes with the coordination end-to-end and end-on, $[Cu_2(L15)_2(N_3)_2](ClO_4)_2$ (black circles) and $[Cu_2(L2)_2(N_3)_2](ClO_4)_2$ (black squares) complexes, respectively.

corresponding to the asymmetric dinuclear complexes. We have calculated the *J* value isolating a dinuclear end-to-end azido complex of our model complex obtaining a weak ferromagnetic interaction with $J = +1.0$ cm^{-1} in agreement with the results of Figure 5. This value is different from that obtained with the trinuclear model and indicates that the coordination of one of the azido groups to three copper atoms must be preserved to describe correctly the magnetic behavior of this compound. For the end-on coordination, we have also generated a dinuclear model obtaining a *J* value of -3.2 cm^{-1} in agreement with the weak antiferromagnetic couplings obtained with the trinuclear model and with the expected value for a longest Cu−N bond distance of 2.474 Å in Figure 5.

Conclusions

This work concerns a detailed study of the magnetic properties of the asymmetric azido-bridged complex of formula $[Cu_2(tn)_2(N_3)_4]$ (**1**) with an experimental and theoretical magneto−structural study of the asymmetric azido−copper(II) complexes reported by different groups. Compound **1** displays a monodimensional Cu(II) chain generated by alternating $\mu_{1,1}$-N_3 and $\mu_{1,3}$-N_3 asymmetric bridges. Magnetic measurements show alternating antiferromagnetic exchange couplings $J_1 = -3.71$ cm^{-1} and $J_2 = -3.10$ cm^{-1}; on the basis of the analysis of the *J* values indicated in the literature for the Cu(II) complexes involving asymmetric azide bridges (Tables 1 and 2), it was difficult to assign correctly the J_1 and J_2 values. The magnetic behavior of compound **1** is unusual since the four similar examples investigated in the literature have been reported as having alternating ferro- and antiferromagnetic exchange couplings. Thus, to understand this difference and to ascertain the magnetic assignment suggested for this compound and those reported for the four similar compounds (Table 3), we have undertaken a theoretical study on the basis of DFT calculation and careful analysis of the exchange coupling parameters reported for asymmetrically bridged dinuclear compounds (Tables 1 and 2). For compound **1**, the DFT calculations are in agreement with the nature of the antiferromagnetic exchange coupling for both kinds of bridges and show that the magnetic interaction through the $\mu_{1,3}$-N_3 asymmetric bridges should be slightly larger than that of the $\mu_{1,1}$-N_3 asymmetric bridges. For the four examples structurally similar to **1**, the magnetic assignment (ferromagnetic for $\mu_{1,1}$-N_3 bridges and antiferromagnetic for $\mu_{1,3}$-N_3 bridges) has been ascertained by the four different groups from a magneto−structural correlation that has been established for symmetric analogue complexes. The theoretical calculations show that the magnetic exchange couplings in such alternating asymmetric bridges should be the opposite of that established for the symmetric analogues; thus, the *J* values obtained from the experimental fit could be wrongly assigned in the four compounds. Note that one of these compounds has been reported recently by another group with a correct magnetic assignment.[13b]

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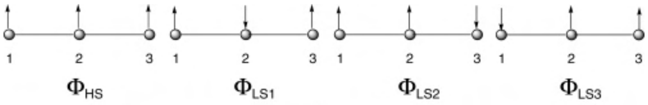
Appendix

For the calculation of the exchange coupling constants for any polynuclear complex with *n* different exchange constants, the energy of $n + 1$ spin configurations must be calculated. In the case of the studied asymmetrical trinuclear complex to obtain the two *J* values, we have calculated the energy corresponding to three different spin distributions (see **1**).



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A detailed description of the procedure employed to calculate the exchange coupling constants in dinuclear and polynuclear complexes can be found in refs 30 and 31. The following equations have been employed to calculate the exchange coupling constants for the asymmetrical trinuclear complex:

$$E_{HS} - E_{LS1} = -J_{12} - J_{23} \tag{1}$$

$$E_{HS} - E_{LS2} = -J_{23} - J_{13} \tag{2}$$

$$E_{HS} - E_{LS3} = -J_{12} - J_{13} \tag{3}$$

The hybrid B3LYP functional[32−34] has been used in all calculations as implemented in Gaussian03.[35] This functional

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(30) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.

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provides excellent results for the calculation of the exchange coupling in wide spectra of transition metal complexes.[36−38] The use of the nonprojected energy of the broken symmetry solution as the energy of the low spin state within the DFT framework provides good results because it avoids the cancellation of the nondynamic correlation effects as stated recently by works of Kraka and Cremer group.[39] We have employed a triple-ζ all electron basis set for copper atoms[40] and a double-ζ all electron for the other elements proposed by Ahlrichs et al.[41] The convergence in the energy during the SCF process was reduced until 10^{-9} due to the small energy differences involved in the studied complexes.

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