

# An Azide-Bridged Copper(II) Ferromagnetic Chain Compound Exhibiting Metamagnetic Behavior

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The one-dimensional chain complex  $[\text{Cu}_2(\mu_2\text{-}1,1\text{-N}_3)_2(\mu_2\text{-}1,3\text{-NO}_3)_2(\mu_2\text{-}1,3\text{-Me}_3\text{NCH}_2\text{CO}_2)_2]_n$  (**1**) contains three different bridge groups,  $\mu_2\text{-}1,1\text{-azide}$  (end-on),  $\mu_2\text{-nitrate}$ , and  $\mu_2\text{-syn,syn-carboxylate}$ , arranged so that the azide and carboxylate groups bridge equatorially and dictate the intrachain magnetic behavior between the copper magnetic orbitals. Variable-temperature magnetic susceptibility studies at low field, and magnetization studies at variable field, reveal dominant intrachain ferromagnetism ( $J = 26 \text{ cm}^{-1}$ ) but also much weaker interchain ferromagnetism ( $\Theta = 2.3 \text{ K}$ ) and antiferromagnetism ( $J_{\text{eff}} = -0.18 \text{ cm}^{-1}$ ). The structure has been rationalized in terms of a layered magnetic model with antiferromagnetic coupling between ferromagnetically coupled layers, leading to metamagnetic behavior. The intrachain ferromagnetism is explained satisfactorily using extended Hückel molecular orbital calculations, which show clearly that orbital countercomplementarity exists on the part of the two magnetic bridge groups (azide and carboxylate), despite the very large azide bridge angle ( $119.5^\circ$ ).

## Introduction

One-dimensional alternating chain compounds frequently result from the reaction of metal salts with a combination of different ligands with multiple bridge capacity, e.g. bpm (2,2'-bipyrimidine) and OH,<sup>1–3</sup> or bpm and oxalate.<sup>4,5</sup> Alternating ferromagnetic and antiferromagnetic exchange terms have been assigned to the complexes  $\{[\text{Cu}(\text{bpm})(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_n\}$ <sup>1</sup> and  $\{[\text{Cu}(\text{bpm})(\text{OH})(\text{NO}_3)]\cdot\text{H}_2\text{O}\}_n$ ,<sup>2</sup> with the alternating bis( $\mu_2$ -hydroxy) fragments responsible for the ferromagnetic components. The small Cu–OH–Cu angles ( $95.5$  and  $95.7^\circ$ , respectively) fall in the ferromagnetic realm for dinuclear systems with the same spin-coupled core, which were shown by Hatfield *et al.* to change from antiferromagnetic to ferromagnetic behavior in the bridge angle range  $(\alpha) > 97.5^\circ > (\alpha)$ .<sup>6</sup>

The azide ligand has shown a remarkable variety of bonding motifs in its different bridging modes, and a number of chain structures involving both  $\mu_2\text{-}1,1\text{-N}_3$  (end-on) and  $\mu_2\text{-}1,3\text{-N}_3$  (end-to-end) bridges have been investigated. Uniform chain structures have been observed with 1,3-azides<sup>7–10</sup> and 1,1-azides<sup>11</sup>

linking pseudo-octahedral Ni(II) centers, with net antiferromagnetic coupling in the 1,3-cases. For a 1,1-azide case, with Ni–N<sub>3</sub>–Ni angles of  $101.4$  and  $105.0^\circ$ , chain ferromagnetism was observed, consistent with the expected properties of the 1,1-azide bridge in this angle range.<sup>12,13</sup> Alternating nickel(II) azide chain structures have been studied with a combination of 1,1- and 1,3-azide bridges, but despite very small 1,1-azide bridge angles ( $98.1$ ,<sup>14</sup>  $85.16$ ,  $84.3$ ,  $83.2^\circ$ <sup>15</sup>) net antiferromagnetic coupling is observed. An alternating manganese(II) azide chain structure with a mixture of 1,1- and 1,3-azide bridges, and a Mn–N<sub>3</sub>–Mn bridge angle of  $101.0^\circ$ , exhibits net antiferromagnetic exchange.<sup>16</sup> Alternating chain compounds with combinations of 1,1-azide and oxamate (Cu)<sup>17</sup> and 1,3-azide and oxalate (Ni)<sup>18</sup> lead to systems dominated by antiferromagnetic coupling but with a ferromagnetic azide component in the former case.

A number of azide-bridged copper(II) chain compounds involving just 1,1-azides,<sup>19,20</sup> and combinations of 1,1- and 1,3-azides<sup>21–23</sup> have been structurally determined, but to our knowledge none have been examined magnetically. The structure of an interesting mixed-ligand chain compound,  $[\text{Cu}_2(\mu_2\text{-}1,1\text{-N}_3)_2(\mu_2\text{-}1,3\text{-NO}_3)_2(\mu_2\text{-}1,3\text{-Me}_3\text{NCH}_2\text{CO}_2)_2]_n$  (**1**) containing  $\mu_2\text{-}1,1\text{-azide}$ ,  $\mu_2\text{-}1,3\text{-carboxylate}$ , and  $\mu_2\text{-}1,3\text{-nitrate}$  bridges, with a very large azide bridge angle ( $119.5^\circ$ ), was published

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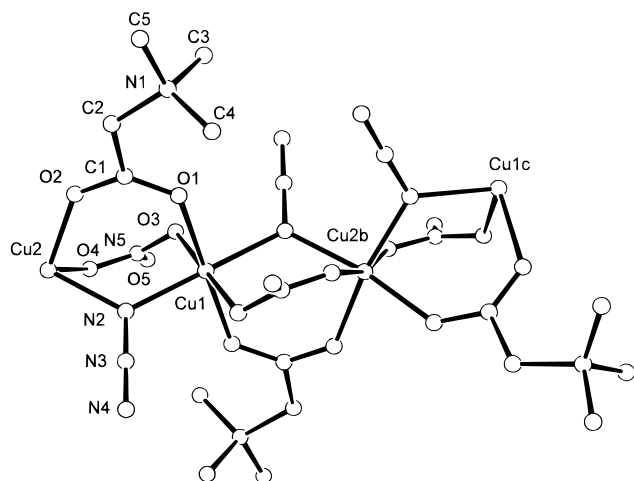
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**Figure 1.** Segment of the chain structure of  $[\text{Cu}_2(\mu_2\text{-}1,1\text{-N}_3)_2(\mu_2\text{-}1,3\text{-NO}_3)_2(\mu_2\text{-}1,3\text{-Me}_3\text{NCH}_2\text{CO}_2)_2]_n$  (**1**).

recently.<sup>24</sup> Our recent studies<sup>12,13</sup> on  $\mu_2\text{-}1,1$ -azide-bridged dicopper(II) complexes suggested that this complex might exhibit antiferromagnetic intrachain behavior, and so the complex was synthesized, its crystal structure reinvestigated, to confirm the identity of the compound, and its variable-temperature magnetic properties examined.

### Experimental Section

**Physical Measurements.** An infrared spectrum was recorded as a Nujol mull using a Mattson Polaris FT-IR instrument. Microanalyses were carried out by Canadian Microanalytical Service, Delta, Canada. Variable-temperature (1.8–305 K) magnetic data were obtained on polycrystalline samples of **1** using a fully automated Oxford Instruments superconducting Faraday susceptometer equipped with a Sartorius 4432 microbalance (main solenoid field 1.5 T, gradient field  $10 \text{ T m}^{-1}$ ), a Metronique Ingenierie MS03 SQUID magnetometer, and an ac susceptometer at various frequencies. The instruments were calibrated with  $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (SQUID) and  $\text{Hg}[\text{Co}(\text{NCS})_4]$  (Faraday susceptometer). The usual corrections for diamagnetism were estimated from Pascal's constants. The TIP correction was  $-60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  (per copper atom).

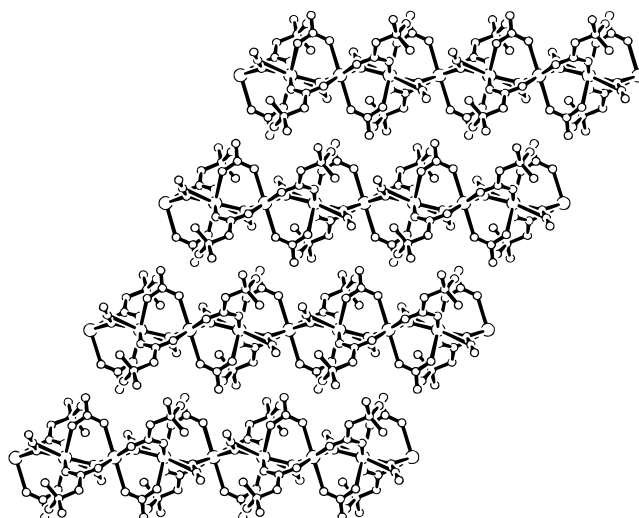
**Safety Note!** Azide complexes are potentially explosive, and caution should be exercised when dealing with such derivatives. However, the small quantities used in this study were not found to present a hazard. In our laboratory small quantities of azide complexes are routinely tested for their explosive potential by controlled mechanical impact.

**Synthesis of the Complex.**  $[\text{Cu}_2(\mu_2\text{-}1,1\text{-N}_3)_2(\mu_2\text{-}1,3\text{-NO}_3)_2(\mu_2\text{-}1,3\text{-Me}_3\text{NCH}_2\text{CO}_2)_2]_n$  (**1**). **1** was synthesized according to the published procedure<sup>24</sup> and obtained as dark green crystals. Anal. Calcd for  $[\text{Cu}(\text{C}_5\text{H}_{11}\text{NO}_2)(\text{N}_3)(\text{NO}_3)]$ : C, 21.10; H, 3.90; N, 24.61. Found: C, 21.37; H, 3.91; N, 24.89. Infrared absorptions agree with those reported previously.<sup>24</sup>

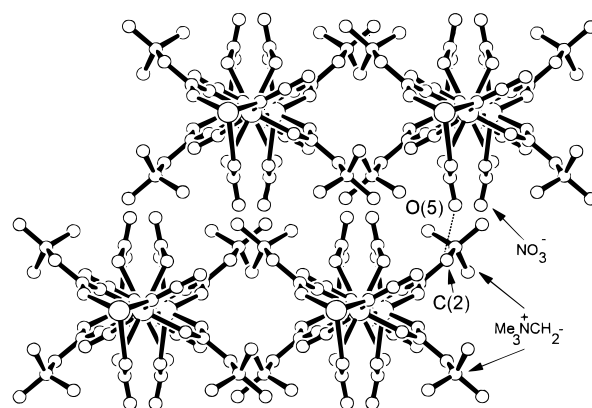
The structural identity of **1** was confirmed by comparison of X-ray data with those already published.<sup>24</sup> The space group and cell dimensions (Rigaku AFC6S) were found to agree exactly with those quoted. Molecular dimensions quoted in this paper have been determined from the previously published atomic coordinates.<sup>24</sup>

### Results

**Crystal Structure of 1.** From a structural viewpoint **1** is most unusual. A segment of the alternating, zigzag polymeric chain running parallel to the *c* axis is shown in Figure 1. Each pair of copper(II) centers is linked by  $\mu_2\text{-}1,1$ -azide and  $\mu_2\text{-}1,3$ -carboxylate groups in the equatorial plane. In plane Cu–N and Cu–O distances ( $<2 \text{ \AA}$ ) are substantially shorter than axial



**Figure 2.** View of **1** down the "b" axis, showing the arrangement of adjacent chains.

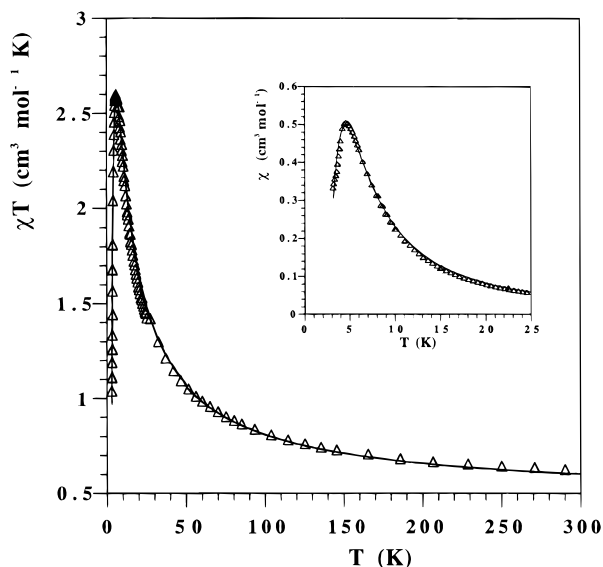


**Figure 3.** View of **1** down the "c" axis, showing the close approach of nitrate and  $(\text{Me}_3\text{NCH}_2)^+$  groups.

contacts to a third  $\mu_2\text{-}1,3$ -nitrate bridge (Cu–O 2.419(4), 2.446(3) Å). The structural repetition along the chain occurs at every fifth copper center, with a *cis*-arrangement of azide and carboxylate bridges linking the first three metals, which then becomes reversed at the third copper center, such that both the azide and the carboxylate are *trans*. The nitrate bridges adopt an alternating *trans* structure throughout the chain.

From a magnetic point of view the copper centers would be defined by a ground state ( $d_x^2-y^2$ ) that is based on the equatorial plane that includes just the azide and carboxylate bridges, and exchange interactions along the chains would be expected to depend predominantly on these bridges. The apical nitrate bridges are considered orthogonal in a magnetic sense and so would be considered to contribute little to the overall exchange process. The  $\mu_2\text{-}1,1$ -azide bridge subtends an angle of  $119.5(2)^\circ$  at the two copper centers, with a copper–copper separation of  $3.436(1) \text{ \AA}$ . Figure 2 illustrates an extended view across a layer of parallel chains, down the "b" axis. Figure 3 illustrates a view down the "c" axis, effectively along the chains, and shows the proximity of the bulky quaternary ammonium sites and the exterior oxygen atoms of the bridging nitrate groups. The shortest interchain contacts exceed  $3 \text{ \AA}$  (e.g. O(2)–C(3')  $3.323(6) \text{ \AA}$ , O(3)–C(5')  $3.370(6) \text{ \AA}$ , O(4)–C(5')  $3.363(8) \text{ \AA}$ , O(5)–C(2')  $3.170(5) \text{ \AA}$ , N(4)–C(2')  $3.457(7) \text{ \AA}$ ) and in most cases are greater than the sum of the van der Waals radii. The closest distance between copper centers in adjacent chains is  $8.762(3) \text{ \AA}$ . Figure 3 illustrates the O5–C2' nitrate contact. Another longer contact between the azide nitrogen N(4) and

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**Figure 4.** Variable-temperature magnetic data for **1**. The solid line represents the best fit to eq 3 ( $T$  included as  $T - \Theta$ ), with  $g = 2.26$ ,  $J = 26.0 \text{ cm}^{-1}$ ,  $g_{\text{eff}} = 2.0$ ,  $J_{\text{eff}} = -0.18 \text{ cm}^{-1}$ , and  $\Theta = 2.3 \text{ K}$  ( $R = 9 \times 10^{-5}$ ). The inset shows the maximum in the susceptibility curve at 4.5 K.

C(2), along the “b” axis, is considered of possible significance to the interchain coupling (vide supra). Since there are no solvent molecules in the structure, and only aliphatic hydrogen atoms lie in close proximity to the nitrate groups, normal hydrogen bonding interactions are not considered to be significant. Therefore any interchain interactions must be regarded as largely electrostatic in nature and are reasonably associated with the charge of the quaternary ammonium sites and the formally negative charge of the core of the chain associated with the nitrate and azide groups.

While magneto–structural correlations in chain compounds are difficult to assess, the effect of bridge geometry on magnetic properties has been interpreted for simple dinuclear copper(II) complexes bridged by  $\mu_2$ -1,1-azide,<sup>12,13</sup> and despite predictions based on spin polarization theory, which assume that at all azide bridge angles ferromagnetic coupling will prevail,<sup>25</sup> systematic studies on  $\mu_2$ -1,1-azide-bridged dicopper(II) complexes, with azide bridge angles in the range  $98.3$ – $124.1^\circ$ ,<sup>12,13</sup> which contain in addition a  $\mu_2$ -(N–N) aromatic diazine bridge, have shown that when the angle exceeds  $108^\circ$  the azide is responsible for antiferromagnetic coupling. The role of the two equatorial bridges in **1** should therefore be viewed in the context of this observation.

**Magnetic Properties of 1.** The temperature dependence of the product  $\chi_m T$  for **1** ( $\chi_m$  being the magnetic susceptibility per copper atom) under an applied field  $H = 50 \text{ G}$ , in the temperature range  $2.1$ – $305 \text{ K}$ , is shown in Figure 4. The value of  $\chi_m T$  at room temperature is  $0.62 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , a value which is somewhat larger than that expected for a magnetically isolated copper(II) ion ( $0.41 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for  $g = 2.1$ ). Upon cooling down of the sample,  $\chi_m T$  continuously increases and reaches a value of  $2.63 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at  $6 \text{ K}$ . This behavior is indicative of strong ferromagnetic coupling between the copper(II) ions in the chain. Below  $6 \text{ K}$ ,  $\chi_m T$  decreases rapidly and, in addition, a susceptibility maximum is observed at  $4.5 \text{ K}$  (for applied fields lower than  $3500 \text{ G}$ ), as shown in the inset of Figure 4. The presence of this susceptibility maximum is a clear indication that an antiferromagnetic interchain coupling occurs. Ac

susceptibility measurements performed in the temperature range  $4$ – $20 \text{ K}$ , and at different frequencies, show neither an out-of-phase signal nor frequency-dependent behavior. The choice of a magnetic model that accounts for this magnetic behavior requires a careful examination of the structure of **1**. The magnetically important repeating unit in **1** (Figure 1) is really the trinuclear unit comprising Cu(1)–Cu(2b)–Cu(1c), with the cis-disposition of the end-on azido and syn–syn carboxylato groups. However, within this unit, it is unlikely that the two exchange couplings will be significantly different, and so despite the overall trans arrangement of the repeating trinuclear units, a simple effective model would involve a uniform chain, with a single overall  $J$  value between adjacent copper(II) centers. To our knowledge no analytical expression has yet been established for a ferromagnetic copper(II) uniform chain. However Baker *et al.*<sup>26</sup> proposed the expression given in eq 1

$$\chi = \frac{N\beta^2 g^2 (A)^{2/3}}{4kT (B)} \quad (1)$$

$$A = 1.0 + 5.7980x + 16.9027x^2 + 29.3769x^3 + 29.8329x^4 + 14.0369x^5$$

$$B = 1.0 + 2.7980x + 7.0087x^2 + 8.6538x^3 + 4.5743x^4$$

$$x = J/2kT$$

for ferromagnetic  $S = 1/2$  chains. This expression was derived from a high-temperature series expansion. The fitting of the experimental data (Figure 4; expressed as  $\chi_m T$  versus  $T$ ) for  $T > 10 \text{ K}$  to this expression gives  $g = 2.26$ ,  $J = 26.0 \text{ cm}^{-1}$ ,  $\text{TIP} = 60 \times 10^{-6} \text{ emu}$ ,  $R = 1.8 \times 10^{-5}$  ( $R$  is the agreement factor defined as  $\sum_i [(\chi_m T)_{\text{obs}}(i) - (\chi_m T)_{\text{calc}}(i)]^2 / \sum_i [(\chi_m T)_{\text{obs}}(i)]^2$ ). Because of the occurrence of an interchain antiferromagnetic coupling (see above), a two-dimensional approach involving a “chain of chains”<sup>27</sup> was attempted to fit the data from room temperature to  $4 \text{ K}$ . In this model, at a given temperature, an effective total spin,  $S_{\text{eff}}$ , can be associated with the ferromagnetic chain, and  $S_{\text{eff}}$  can be calculated from eq 2, where  $\chi_{\text{FC}}$  is the

$$S_{\text{eff}}(S_{\text{eff}} + 1) = 2\chi_{\text{FC}} T \quad (2)$$

susceptibility calculated for the ferromagnetic chain (FC) through expression (1). For  $T < 10 \text{ K}$ , the  $\chi_{\text{FC}} T$  values are so large ( $\chi T > 2.3$ ) that  $S_{\text{eff}}$  takes values large enough ( $S_{\text{eff}} > 1.7$ ) to be treated as a classical spin. In this sense it is possible to use the classical spin model (eq 3) derived by Fisher<sup>28</sup> to describe the magnetic susceptibility

$$\chi_m = \frac{Ng^2\beta^2}{3kT} S_{\text{eff}}(S_{\text{eff}} + 1) \frac{(1 + u)}{(1 - u)} \quad (3)$$

$$u = \coth[J_{\text{eff}} S_{\text{eff}}(S_{\text{eff}} + 1)/kT] - kT/S_{\text{eff}}(S_{\text{eff}} + 1)$$

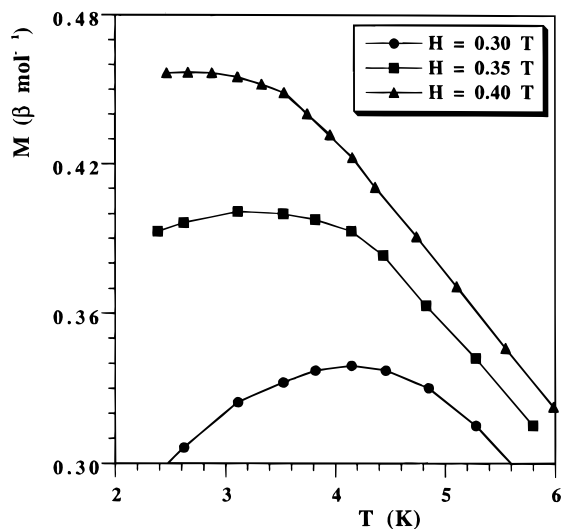
( $\chi_{2D}$ ) of this “chain of chains” model.<sup>27</sup> Although the use of this model reproduces well both the position and height of the maximum of the susceptibility curve, the experimental susceptibility data below  $4 \text{ K}$  decrease more slowly than calculated through eq 3. This feature suggests that weak ferromagnetic interactions between the magnetic planes may also occur. Therefore, the inclusion of an additional Weiss-like parameter  $\Theta$ , which accounts for the magnetic interaction between the layers of chains ( $T$  replaced by  $T - \Theta$  in eq 3) was considered necessary. A full analysis using the modified eq 3 gives  $g =$

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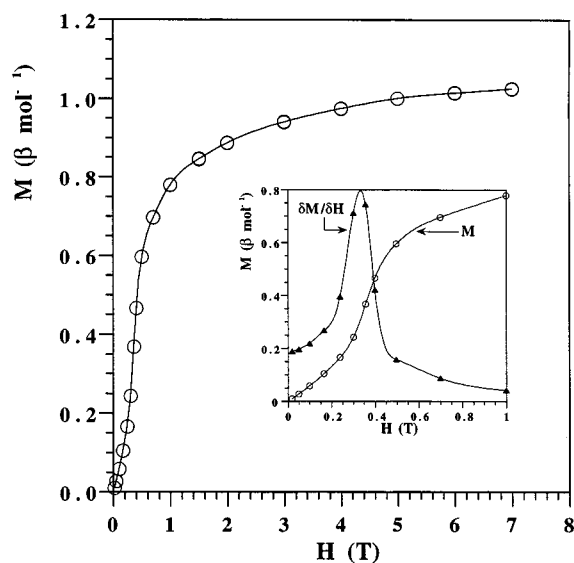
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**Figure 5.** Magnetization ( $M$ ) data for **1** at low temperature as a function of external field ( $H$ ).



**Figure 6.** Field dependence of  $M$  for **1** at 2 K. The inset shows plots of  $M$  and  $\delta M/\delta H$  versus  $H$  in the low-field region.

2.26,  $J = 26.0 \text{ cm}^{-1}$ ,  $g_{\text{eff}} = 2.0$  (fixed),  $J_{\text{eff}} = -0.18 \text{ cm}^{-1}$ , and  $\Theta = 2.3 \text{ K}$  ( $R = 9 \times 10^{-5}$ ). The experimental  $\chi_{\text{m}}T$  data and the best fit line (solid line) using these derived parameters are illustrated in Figure 4.

The peculiar magnetic properties of **1** at low temperatures are consistent with a metamagnetic behavior. The temperature dependence of the magnetization  $M$  at various fields is shown in Figure 5. For values of the applied field less than 3500 G the  $M$  versus  $T$  curves display a maximum at  $\approx 4.2 \text{ K}$ , revealing the occurrence of an interchain antiferromagnetic coupling. This maximum in  $M$  disappears when the applied magnetic field reaches 3500 G. The field thus overcomes the interchain antiferromagnetic interaction, and the compound behaves in a ferromagnetic fashion. This metamagnetic behavior is confirmed by the field dependence of the magnetization at 2 K which is shown in Figure 6. The experimental data reveal a maximum of the first derivative  $\delta M/\delta H$  (inset of Figure 6) (or a change of sign of the second derivative  $\delta^2 M/\delta H^2$ ) around 3500 G corresponding to the field-induced transition from an antiferromagnetic to a ferromagnetic state. The value of the saturation magnetization at 2 K (Figure 6) is very close to  $1 N\beta \text{ mol}^{-1}$ , which confirms that all the  $S_{\text{Cu}} = 1/2$  centers are aligned along the same direction.

Metamagnetic behavior in one-dimensional compounds has already been reported for ferromagnetic copper(II) chains,<sup>29</sup> ferrocenium charge transfer salts forming ferromagnetic chains,<sup>30</sup> oximate-bridged  $\text{Mn}^{\text{III}}\text{Cu}^{\text{II}}$  ferromagnetic chain compounds,<sup>27</sup> and recently oximate-bridged  $\text{Mn}^{\text{II}}\text{Cu}^{\text{II}}$  ferrimagnetic chain compounds.<sup>31</sup>

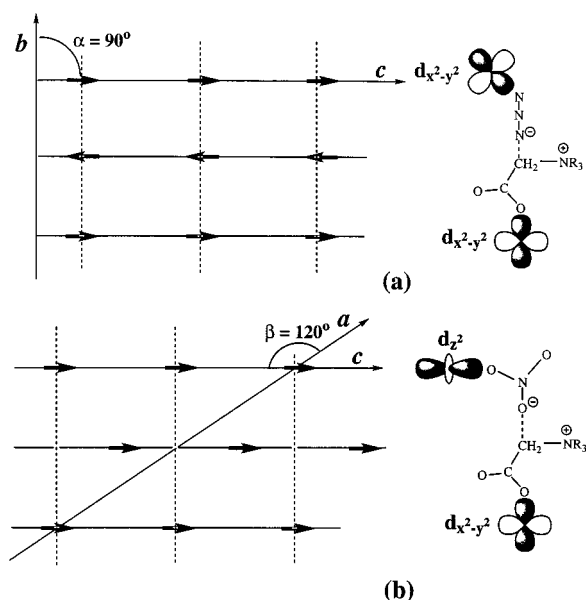
## Discussion

The two main points concerning the magnetic properties of **1** which deserve attention are (i) the possible magnetic lattice structure that causes the metamagnetic behavior and (ii) the origin of the observed intrachain ferromagnetic coupling.

**(i) Metamagnetic Behavior of 1.** It is clear from the magnetic study that the intrachain magnetic coupling is ferromagnetic ( $J = 26 \text{ cm}^{-1}$ ). Given that EPR experiments on single crystals of ferromagnetic chains have established that the spin vectors are aligned parallel to the chain axis, in contrast to a ferrimagnetic chain where they are perpendicular to the chain axis,<sup>32</sup> it is reasonable to assume that the direction of the local spins in **1** will run parallel to the  $c$  axis. The  $J_{\text{eff}}$  and  $\Theta$  parameters can reasonably be associated with interchain magnetic interactions in different directions in the crystal (one ferromagnetic,  $\Theta > 0$ , and the other antiferromagnetic,  $J_{\text{eff}} < 0$ ), but a deeper magnetostructural analysis is required in order to establish the overall spin topology.

In fact, interchain dipolar as well as exchange effects may be operative, and it is difficult to predict which one would be dominant. Looking at the lattice of **1** it can be seen that the closest interchain contacts in the  $bc$  plane occur along the  $b$  axis (shortest copper–copper separation  $8.76 \text{ \AA}$ ) (Figure 7a) and involve the negative azido bridge and the positive quaternary ammonium group (the  $\text{N}(4)\cdots\text{C}(2)'\text{-NMe}_3$  distance is  $3.46 \text{ \AA}$ ). Two magnetically active bridges are thus weakly linked, and an antiferromagnetic interaction could be anticipated through this pathway, if the exchange effects were operative. On the other hand, given that the copper(II) chains are related by a unit cell translation along the  $b$  axis ( $b$  and  $c$  axes are perpendicular,  $\alpha = 90^\circ$ ), any dipolar interactions would lead also to antiferromagnetic interactions in the  $bc$  plane. Therefore exchange and dipolar effects would lead to antiferromagnetic coupling between adjacent chains in the  $bc$  plane. In the  $ac$  plane, the closest metal–metal distance is  $10.5 \text{ \AA}$ , and the closest contact of possible magnetic significance involves the negative nitrate anion and the positive quaternary ammonium group (the  $\text{O}(5)(\text{nitrate})\cdots\text{C}(2)'(-\text{NMe}_3)$  distance is  $3.17 \text{ \AA}$ ) (Figure 3). Due to the fact that the nitrate group is not in the magnetic plane, any magnetic exchange via this group would lead most likely to ferromagnetic interactions. On the other hand, the dipolar interactions in this  $ac$  plane are predicted to be ferromagnetic also (the value of the  $\beta$  angle ( $120^\circ$ ) causes the

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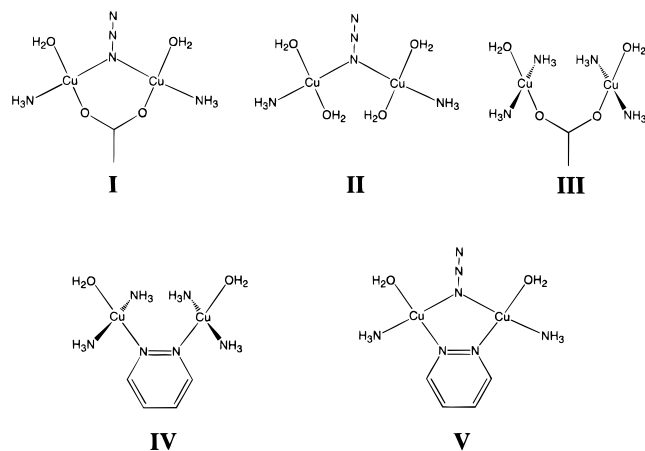
**Figure 7.** Arrangement of the spin vectors in **1** showing the intrachain ferromagnetic coupling (*c* axis) and the interlayer (a) antiferro- (*bc* plane) and (b) ferromagnetic (*ac* plane) interactions (see text).

copper atoms of neighboring chains to be displaced by a half period; Figure 7b). In summary, the three-dimensional spin interactions can be illustrated by just considering the *bc* and *ac* planes: the ferromagnetic chains running along the *c*-axis ( $J = 26 \text{ cm}^{-1}$ ) are ferromagnetically coupled along the *a* axis ( $\Theta = 2.3 \text{ K}$ ) to build ferromagnetic layers (*ac* plane), which are antiferromagnetically coupled along the *b* axis ( $J_{\text{eff}} = -0.18 \text{ cm}^{-1}$ ). When an external magnetic field  $H$  larger than 3500 G is applied, the Zeeman energy (about  $0.3 \text{ cm}^{-1}$ ) is large enough to overcome the interlayer antiferromagnetic interaction (ca.  $0.18 \text{ cm}^{-1}$ ) and, consequently, the solid orders ferromagnetically.

**(ii) Ferromagnetic Intrachain Interaction.** In the case of dinuclear copper(II) complexes, it is well-known that syn–syn carboxylate bridges and end-on azido bridges, with an angle at the azido bridge larger than  $108^\circ$ ,<sup>12,13</sup> cause antiferromagnetic coupling. Consequently, the expected intrachain magnetic coupling in **1** should be antiferromagnetic. However, when the bridging ligands are different, the two bridges may either add or counterbalance their effects. This problem was treated by Nishida et al.<sup>33</sup> and McKee et al.,<sup>34</sup> these phenomena being known as orbital complementarity and countercomplementarity, respectively. In the present case, the antiferromagnetic contributions of each bridge almost cancel each other out (i.e. these bridges exhibit an orbital countercomplementarity) and the ferromagnetic term dominates ( $J_{\text{T}} = J_{\text{AF}} + J_{\text{F}}$  with  $|J_{\text{AF}}|$  being smaller than  $J_{\text{F}}$ ).

In order to show the occurrence of this phenomenon in **1** we have used Hoffmann's approach,<sup>35</sup> in which the magnitude of the antiferromagnetic term ( $J_{\text{AF}}$ ) is considered to be proportional to the square of the energy gap ( $\Delta$ ) between the two-singly occupied molecular orbitals (SOMO's). The value of  $\Delta$  has been computed through MO calculations of the extended Hückel

**Chart 1**



type.<sup>36</sup> In **1** an end-on azido bridge and a carboxylato bridge connect the two copper(II) centered magnetic orbitals. This bridging arrangement is shown in the model dinuclear copper(II) system **I** (Chart 1), in which the azido bridging angle was fixed at  $119.5^\circ$  and the other structural parameters (bond angles and distances) were averaged from the experimental ones. With the aim of analyzing independently the role of each bridging unit, we have also performed extended Hückel calculations on the models shown in **II** and **III**. In model **II**, the carboxylato bridge has been replaced by two water molecules, whereas in **III** the azido bridge is substituted by two ammonia molecules. In this latter case, a rotation of  $90^\circ$  along the O(carboxylato)–Cu–O(water) axis has been carried out in order to avoid the ammonia contacts (we have checked that the energies of the appropriate orbitals are not affected significantly by this rotation).

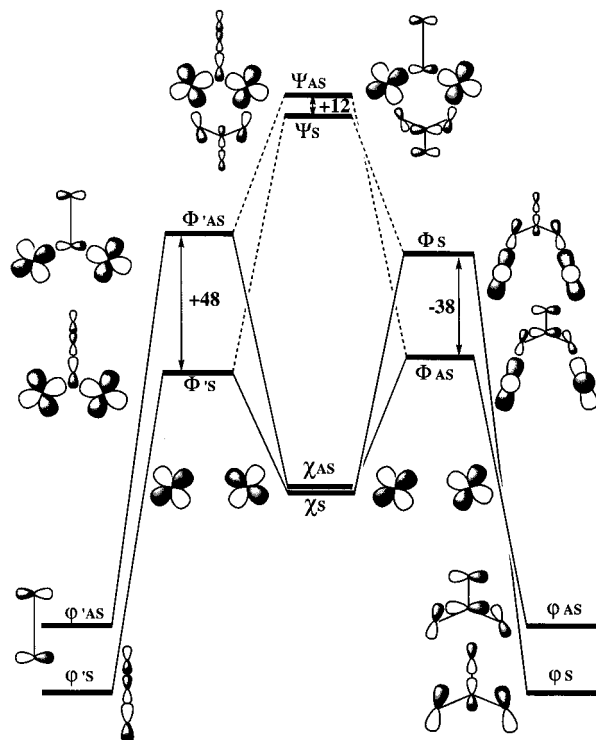
The results of the calculations are illustrated in Figure 8. The bottom of the center of Figure 8 shows the in-phase and out-of-phase combinations of the metal orbitals ( $d_{x^2-y^2} \pm d_{x^2-y^2}$ ; denoted as  $\chi_{\text{S}}$  and  $\chi_{\text{AS}}$ ) which interact with the symmetry-adapted HOMO's of the bridging ligand carboxylate (denoted as  $\varphi_{\text{S}}$  and  $\varphi_{\text{AS}}$ ) or azide (denoted as  $\varphi'_{\text{S}}$  and  $\varphi'_{\text{AS}}$ ) to give the corresponding SOMO's  $\Phi_{\text{S}}$  and  $\Phi_{\text{AS}}$  (single carboxylato bridge, model **III**) and  $\Phi'_{\text{S}}$  and  $\Phi'_{\text{AS}}$  (single 1,1-azido bridge, model **II**). The subscripts AS and S refer to antisymmetric and symmetric character with respect to a mirror plane perpendicular to the molecular plane of the models. The energy gap,  $\Delta = E_{\text{AS}} - E_{\text{S}}$ , in both cases is important and in agreement with the antiferromagnetic coupling observed in complexes where only one of these bridges is present. In model **III** (absence of the azido bridge) the higher SOMO is the symmetric  $\Phi_{\text{S}}$ , whereas in model **II** (absence of the carboxylato bridge) the higher SOMO is the antisymmetric  $\Phi'_{\text{AS}}$ . This is the reason for the difference in the sign of  $\Delta$  ( $+48$  and  $-38 \text{ meV}$ ) in these two cases and is the origin of the countercomplementarity of the two bridges. Considering the two azido HOMO's, the antisymmetric one ( $\varphi'_{\text{AS}}$ ) interacts more strongly with the metal orbitals, and consequently the energy of the SOMO  $\Phi'_{\text{AS}}$  is raised above that of the symmetric one  $\Phi'_{\text{S}}$ . The reverse situation is found in the case of the carboxylato bridge (the energy of the SOMO  $\Phi_{\text{S}}$  is raised above that of  $\Phi_{\text{AS}}$  due to the stronger interaction of its symmetric HOMO,  $\varphi_{\text{S}}$ ). Therefore, when we consider the simultaneous presence of both bridges the difference in energy ( $\Delta$ ) of the SOMO's  $\Psi_{\text{AS}}$  and  $\Psi_{\text{S}}$  ( $12 \text{ meV}$ ) is very small, and so the resulting antiferromagnetic term would be very small, leading to a situation where the ferro-

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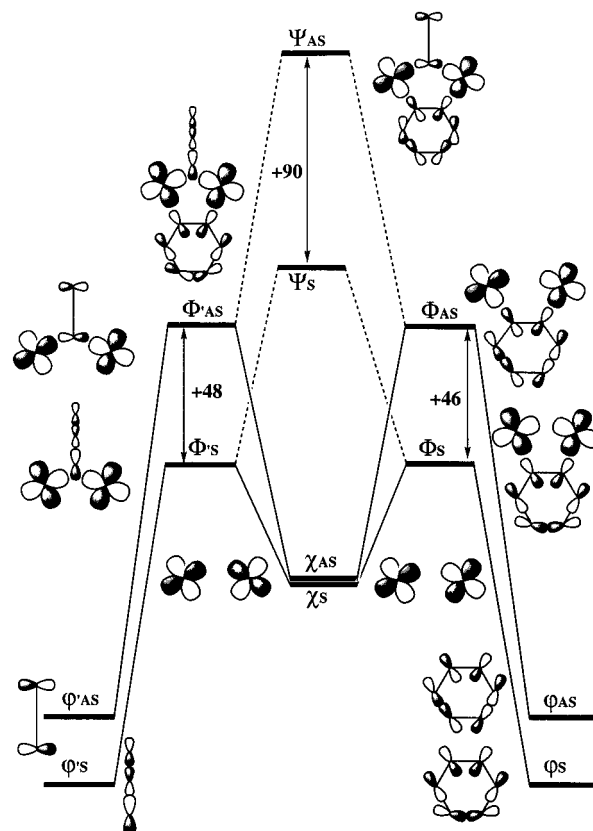


**Figure 8.** MO diagram for a model dinuclear copper(II) unit with a 1,1-azido bridge (left), a *syn,syn*-carboxylato bridge (right), and both bridging ligands (center) relating to models **II**, **III**, and **I**, respectively. The values of the energies correspond to the energy gap ( $\Delta = E_{AS} - E_S$ ) in meV between the two SOMO's in each case (left, center, and right).

magnetic term would become dominant, which is exactly the situation observed for **1**.

In most previously reported cases of countercomplementarity in dicopper(II) complexes involving hydroxo (or alkoxo) and carboxylato bridges,<sup>33,37</sup> although the antiferromagnetic term was significantly reduced, it still was the dominant term. However, in a few cases,<sup>34,37–39</sup> the effect of the carboxylato was large enough to produce net ferromagnetism. As far as we are aware **1** is the first compound where the countercomplementarity effects yield a net ferromagnetic interaction with a combination of end-on azide and carboxylate.

It is interesting to note that, in dinuclear copper(II) complexes where the end-on azido and diazine (e.g. pyridazine, phthalazine) ( $N_2$ ) ligands act as bridges simultaneously,<sup>12,13</sup> for angles at the azido bridges close to that of **1** (ca.  $120^\circ$ ), a very strong antiferromagnetic coupling ( $2J \approx -800 \text{ cm}^{-1}$ ) was observed. This can be easily understood in the light of the complementarity of these bridging ligands. To illustrate this situation an analogous study to that done with **1** has been carried out on the model compounds **II**, **IV**, and **V** (Chart 1). Models **IV** and **V** are related to **III** and **I**, the carboxylato being replaced by pyridazine. The results of the corresponding MO calculations are summarized in Figure 9. When we consider the case when only the azide or the pyridazine acts as a bridge (models **II** and **IV**, respectively), the corresponding antisymmetric HOMO of the bridging ligand interacts more strongly with the metal orbitals, yielding in both cases large and very similar energy



**Figure 9.** MO diagram for a model dinuclear copper(II) unit with a 1,1-azido bridge (left), a pyridazine bridge (right), and both bridging ligands (center) relating to models **II**, **IV**, and **V**, respectively. The values of the energies correspond to the energy gap ( $\Delta = E_{AS} - E_S$ ) in meV between the two SOMO's in each case (left, center, and right).

gaps between the corresponding SOMO's (48 and 46 meV, respectively). Due to the fact that both bridges combine more efficiently with the same SOMO (orbital complementarity) when they bridge simultaneously (model **V**), they add their effects, thus increasing the energy gap of the SOMO's  $\Psi_{AS}$  and  $\Psi_S$  (90 meV; see the center of Figure 9, top). This is the origin of the large antiferromagnetic interaction observed in these systems.

## Conclusion

The polymeric azide/carboxylate chain compound  $[\text{Cu}_2(\mu_2-1,1-\text{N}_3)_2(\mu_2-1,3-\text{NO}_3)_2(\mu_2-1,3-\text{Me}_3\text{NCH}_2\text{CO}_2)_2]_n$  (**1**) exhibits a remarkable arrangement of bridges between the copper(II) centers and illustrates dramatically the countercomplementary effect imposed by the carboxylate bridge, which attenuates the effect of the antiferromagnetic azide bridge to the point where net ferromagnetic behavior is observed. This is supported by molecular orbital calculations. The low-temperature magnetism reveals interlayer antiferromagnetic coupling, which leads to metamagnetic behavior. The choice of bridges exhibiting orbital countercomplementarity can perhaps be used to advantage in the synthesis of chain and layer materials, which may exhibit enhanced spontaneous magnetic behavior.

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