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# Strong Antiferromagnetic Coupling in Cis-$\mu$-1,3-Azide-Bridged Copper(II) Dimers: Trigonal-Bipyramidal vs Quadratic Planar Coordination with a Nearly Identical Binucleating Ligand System

**Felix Tuczek***[†] **and Wolfgang Bensch**[‡]

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität Mainz,
Staudingerweg 9, D-55099 Mainz, Germany, and Anorganische Chemie, Johann Wolfgang von Goethe
Universität, Marie-Curie-Strasse 11, D-60439 Frankfurt a.M., Germany

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The structure of the complex $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$ (L-Et is the anion of *N,N,N′,N′*-tetrakis[2-(1-ethylbenzimidazolyl)]-2-hydroxy-1,3-diaminopropane) has been redetermined and has been found to deviate significantly from that published earlier (McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765). The space group of our product is $P2_1/n$ with the lattice parameters $a = 14.104(2)$ Å, $b = 22.406(4)$ Å, $c = 15.989(2)$ Å, and $\beta = 98.05(2)°$ ($Z = 4$), which cannot be transformed into those given by McKee et al. ($C2/m$, $a = 19.082$ Å, $b = 23.896$ Å, $c = 13.230$, and $\beta = 116.21°$). In addition, the copper coordination in the complex cation is found to be close to trigonal-bipyramidal whereas the geometry in the structure of McKee et al. is more square-pyramidal. However, strong antiferromagnetic coupling ($-2J > 1200$ cm$^{-1}$) is also found for our product which is close to the value obtained earlier ($-2J > 1100$ cm$^{-1}$). Hence, a cis $\mu$-1,3 bridging azide group is able to mediate strong superexchange without contribution of a second bridging ligand (alkoxide), and a tetragonal ground state is not a necessary condition for strong antiferromagnetism as stated by McKee et al. To our knowledge, the $-2J$ value of > 1200 cm$^{-1}$ represents a new lower limit for single bridging azide in copper dimers.

## Introduction

Binuclear copper azide systems have been of considerable interest due to the broad range of their structural and magnetic properties.[1] In particular, azide can act as a bridging ligand in an end-on ($\mu$-1,1) and end-to-end (cis $\mu$-1,3) fashion. It is now well established that $\mu$-1,1 bridging gives ferro- and $\mu$-1,3 bridging antiferromagnetic coupling between the copper centers. Extensive experimental and theoretical work has been directed toward a detailed understanding of these magneto−structural correlations.[1−6] Moreover, binuclear copper azide systems have been studied as structural models for copper-containing enzymes involved in the reversible binding and activation of dioxygen like hemocyanin (Hc).[7−9] One of the systems investigated in this respect is the binuclear copper complex $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$.[8] The X-ray structure investigation of this system revealed that the binucleating ligand coordinates to each of the coppers with one benzimidazolyl N and one amino N and that the two copper centers are bridged by the central alkoxide group of the L-Et ligand and azide. The resulting 5-fold copper coordination was shown to be predominantly square-planar with one benzimidazolyl N being directed out of this plane with a considerably longer bond length. The complex was further shown to be diamagnetic at room temperature, i.e. strongly antiferromagnetically coupled with a $-2J$ value estimated to be >1100 cm$^{-1}$. In contrast, the analogous acetate-bridged $Cu_2$(L-Et) complex was found to behave weakly ferromagnetically. The striking difference between the two systems was ascribed mainly to the different coordination geometry of the copper ions: whereas the azide-bridged complex is approximately tetragonal, i.e. has a $d_{x^2-y^2}$ ground state, the acetate-bridged complex has a trigonal-bipyramidal coordination with a $d_{z^2}$ ground state. In the tetragonal coordination, the alkoxo group can contribute to the superexchange involving the $d_{x^2-y^2}$ orbitals, in contrast to the trigonal-bipyramidal coordination where it cannot bridge the $d_{z^2}$ orbitals and hence cannot give a contribution to $-2J$. The authors concluded that tetragonality of the copper(II) systems is important for attaining diamagnetism in bridged Cu dimers as well as the biological system hemocyanin.

The $[Cu_2(L\text{-}Et)(N_3)]^{2+}$ dimer has also been studied spectroscopically[10] and theoretically,[11] and it has been shown that the CT spectrum can be used to probe individual superexchange pathways contributing to the ground state $-2J$ value.[11−13] In this respect, it appeared of interest to experimentally separate

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[†] Johannes Gutenberg Universität Mainz.

[‡] Johann Wolfgang von Goethe Universität.

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(1) (a) Kahn, O. *Molecular Magnetism*; VCh Publishers: Weinheim, New York, 1993. (b) Kahn, O. In *Magnetostructural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985.

(2) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.

(3) Chaudhuri, P.; Oder, K.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2818.

(4) Comarmond, J.; Plumeré, Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330.

(5) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877.

(6) Charlot, M. F.; Kahn, O.; Chaillet, M.; Larrieu, C. *J. Am. Chem. Soc.* **1986**, *108*, 2574.

(7) Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; pp 116−150.

(8) The ligand L-Et is the anion of *N,N,N′,N′*-tetrakis[2-(1ethylbenzimidazolyl)]-2-hydroxy-1,3-diaminopropane: McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765.

(9) Sorrell, T. N.; O'Connor, C. J.; Anderson, O. P.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 4199.

(10) Pate, J. E.; Ross, P. K.; Thamann, T. J.; Reed, C. A.; Karlin, K. D.; Sorrell, T. N.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 5198.

(11) Tuczek, F.; Solomon, E. I. *Inorg. Chem.* **1993**, *32*, 2850.

(12) Solomon, E. I.; Tuczek, F.; Root, D. E.; Brown, C. A. *Chem. Rev.* **1994**, *94*, 827.

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**Table 1.** Structure Determination Summary

| | |
|---|---|
| empirical formula | $C_{43}H_{44}B_2Cu_2F_8N_{13}O$ |
| color; habit | green; irregular |
| cryst size | 0.1 × 0.1 × 0.1 mm |
| cryst system | monoclinic |
| space group | $P2_1/n$ |
| unit cell dimens | $a = 14.104(3)$ Å<br>$b = 22.406(4)$ Å<br>$c = 15.989(3)$ Å<br>$\beta = 98.05(3)°$ |
| $V$ | 5003(3) Å$^3$ |
| $Z$ | 4 |
| fw | 1059.6 |
| $D$(calc) | 1.407 Mg/m$^3$ |
| abs coeff | 0.927 mm$^{-1}$ |
| $F$(000) | 2164 |
| temp | 300 K |
| wavelength | 0.7107 Å |
| index ranges | $-16 \le h \le 16, 0 \le k \le 25, 0 \le l \le 18$ |
| no. of reflcns collcd | 8140 |
| no. of independent reflcns | 7901 ($R_{\text{int}} = 0.00\%$) |
| no. of obsd reflcns | 4325 ($F > 6.0\sigma(F)$) |
| refinement method | full-matrix least squares |
| quantity minimized | $\sum w(F_o - F_c)^2$ |
| H atoms | riding model, fixed isotropic $U$ |
| weighting scheme | $w^{-1} = \sigma^2(F) + 0.0030F^2$ |
| no. of params refined | 584 |
| final $R$ indices (obsd data) | $R = 7.20\%$ |
| goodness-of-fit | 1.65 |
| largest and mean $\Delta/\sigma$ | 0.005, 0.001 |
| data-to-param ratio | 7.4:1 |
| largest diff peak | 0.87 e Å$^{-3}$ |
| largest diff hole | 0.56 e Å$^{-3}$ |

the contributions of the azide and alkoxide bridges to the ground state antiferromagnetic coupling in order to check whether both contributions are in fact important for ground state superexchange. However, synthesis of the complex $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$ lead to a product whose diffraction pattern could not be indexed on the basis of the structure reported by these authors. Hence, we decided to structurally characterize the reaction product by X-ray crystallography. The result of this analysis is presented below. In addition, magnetic measurements were carried out on our product which are analyzed and compared to the results of McKee et al.

## Experimental Section

**Preparation and Spectroscopic Analysis.** The complex was prepared according to the literature.[8] Elemental analysis of the product gave 48.0% C, 4.9% H, and 17.2% N (calculated: 48.5% C, 4.6% H, 17.1% N). Single crystals of the complex were grown by slowly diffusing ether into acetonitrile or nitromethane solutions of the reaction product. Independent of the treatment of the product (raw, from acetonitrile or nitromethane), X-ray powder spectra always gave the same pattern which could not be indexed on the basis of crystal structure given by McKee et al. but is found to be consistent with the X-ray structure determination given below. The UV/vis spectrum of an acetonitrile solution and the Raman spectrum of the crystalline substance were found to be identical to those reported.[10] In particular, the asymmetric stretch of the azide group was found at 2025 cm$^{-1}$. The IR spectrum showed a single peak for $\nu_{\text{asym}}$ ($N_3$) at 2021 cm$^{-1}$ with a much smaller (ca. 5%) peak at 2050 cm$^{-1}$ (Nujol), in contrast to a doublet at 2020 and 2050 cm$^{-1}$ reported by McKee et al. The 2050 cm$^{-1}$ peak has been ascribed to an impurity by these authors.

**X-ray Crystallographic Analysis.** Relevant crystallographic data and structure determination parameters are given in Table 1. Cell parameters were refined by the least-squares method with 25 data (21-24.6° in $2\theta$). Intensity data were collected at room temperature on a STOE AED II diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.7107$ Å) with the $\omega - 2\theta$ scan technique. Four standard reflections were measured every 4 h. No significant decay during the data collection was observed. To control the orientation, 17 reflections were checked every 4 h. Lorentz and polarization corrections were applied to the data, but there was no absorption correction. The structure was solved and refined with the program package SHELX TL plus. The two $BF_4^-$ ions are disordered. The disorder was treated in the following way. The temperature factors of the F atoms in each $BF_4^-$ group were fixed and the site occupation factors (sof) were refined. During this procedure the B−F and the F−F distances were restraint at 1.370(1) and 2.237(1) Å. This leads to sof's of 0.77/0.23 and 0.52/0.48 for the F atoms in the two preferential orientations of the two $BF_4^-$ ions. In the next stages of refinement the B atoms were refined with anisotropic displacement parameters (ADP) whereas the F atoms were refined isotropically. One of the C atoms of an ethyl group is also disordered. The refinement with a split site leads to a 50/50 occupation. These atoms as well as all other non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated at idealized positions and were treated as rigid groups. The highest residual electron density (0.87 e Å$^{-3}$) in the last difference Fourier synthesis are located near the F atoms. Important interatomic distances and bond angles are listed in Tables 2 and 3.

**Table 2.** Bond lengths (Å)

| | | | |
|---|---|---|---|
| Cu(1)−O | 1.978(6) | Cu(1)−N(1) | 2.072(6) |
| Cu(1)−N(2) | 2.052(7) | Cu(1)−N(3) | 2.048(6) |
| Cu(1)−N(13) | 1.997(10) | Cu(2)−O | 1.934(5) |
| Cu(2)−N(6) | 2.088(6) | Cu(2)−N(7) | 2.023(6) |
| Cu(2)−N(8) | 2.061(8) | Cu(2)−N(11) | 2.027(12) |
| O−C(22) | 1.428(10) | N(11)−N(12) | 1.151(22) |
| N(12)−N(13) | 1.174(21) | C(1)−C(22) | 1.503(12) |
| C(22)−C(23) | 1.454(14) | | |

**Table 3.** Bond Angles (deg)

| | | | |
|---|---|---|---|
| O−Cu(1)−N(1) | 84.9(3) | O−Cu(1)−N(2) | 119.7(2) |
| N(1)−Cu(1)−N(2) | 81.1(3) | O−Cu(1)−N(3) | 120.9(2) |
| N(1)−Cu(1)−N(3) | 83.2(3) | N(2)−Cu(1)−N(3) | 115.1(3) |
| O−Cu(1)−N(13) | 93.0(4) | N(1)−Cu(1)−N(13) | 177.6(4) |
| N(2)−Cu(1)−N(13) | 99.2(4) | N(3)−Cu(1)−N(13) | 98.8(4) |
| O−Cu(2)−N(6) | 85.4(2) | O−Cu(2)−N(7) | 127.4(2) |
| N(6)−Cu(2)−N(7) | 81.0(2) | O−Cu(2)−N(8) | 123.5(3) |
| N(6)−Cu(2)−N(8) | 82.3(3) | N(7)−Cu(2)−N(8) | 104.7(3) |
| O−Cu(2)−N(11) | 93.3(4) | N(6)−Cu(2)−N(11) | 177.4(4) |
| N(7)−Cu(2)−N(11) | 101.5(4) | N(8)−Cu(2)−N(11) | 96.6(4) |
| Cu(1)−O−Cu(2) | 135.7(3) | Cu(1)−O−C(22) | 111.5(5) |
| Cu(2)−O−C(22) | 111.7(5) | N(11)−N(12)−N(13) | 176.9(11) |
| O−C(22)−C(1) | 109.1(6) | O−C(22)−C(23) | 110.4(7) |
| C(1)−C(22)−C(23) | 112.6(8) | N(6)−C(23)−C(22) | 111.0(7) |

**Magnetic Measurements.** Variable-temperature susceptibility data were recorded at 18 kG on a Princeton Applied Research vibrating sample magnetometer controlled by an Atari Mega ST2 computer. In order to minimize systematic errors, the binuclear copper complex and an equivalent amount of the $HL\text{-}Et{\cdot}0.5H_2O$ ligand were measured separately and the resulting magnetic moment data subtracted from each other.

## Results and Discussion

The complex $[Cu_2(L\text{-}Et)(N_3)][BF_4]_2$ was reported to crystallize in the monoclinic space group $C2/m$ with the lattice parameters $a = 19.082(3)$ Å, $b = 23.896(3)$ Å, $c = 13.230(2)$ Å, $\beta = 116.21°$, and $V = 5412$ Å$^3$. The essential features of this structure which is here denoted as ***2*** were presented in ref 8. Therefore, only significant differences between ***2*** and our structure **1** will be discussed in this section. Atom designations for ***2*** are given in italic and for **1** in roman notation. Compound **1** crystallizes in the monoclinic space group $P2_1/n$, and the lattice parameters given by McKee et al. for ***2*** cannot be transformed into the lattice parameters of **1**. The essential parts of both structures are shown in Figures 1 and 2. The Cu−O−Cu plane is always perpendicular to the paper plane; Figure 1 is a "front" view of **1** (a) and ***2*** (b) with the azide group in the foreground, and Figure 2 is a "rear" view of **1** (a) and ***2*** (b) with the alkoxo

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(13) Tuczek, F.; Solomon, E. I. *J. Am. Chem. Soc.* **1994**, *116*, 6916.

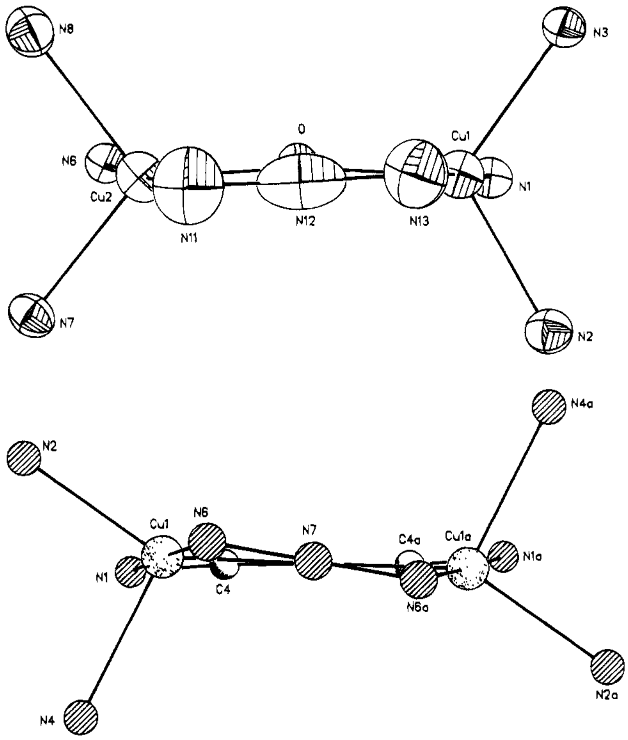

**Figure 1.** (a) Top: "Front view" of the central part of structure **1** (azide coming out of the paper plane) with thermal ellipsoids. The $Cu_2-N_3$ plane is perpendicular to the paper plane. (b) Bottom: Same perspective of structure *2* without thermal ellipsoids.

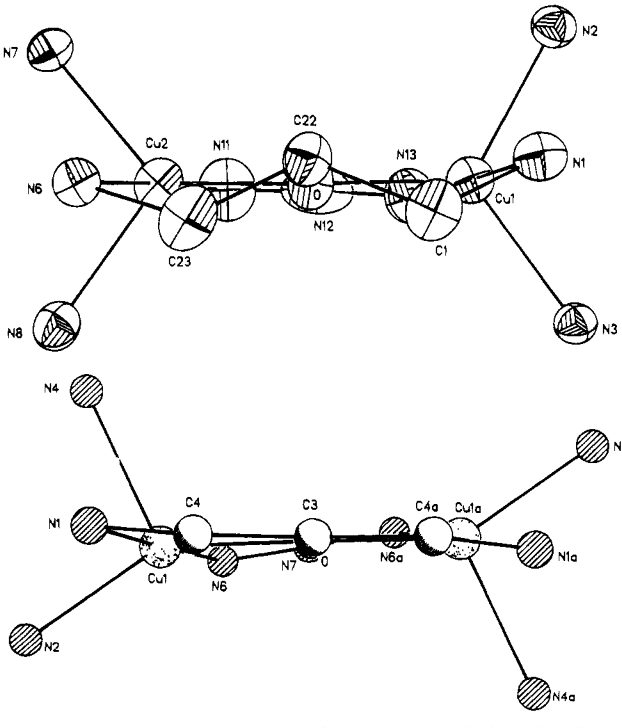

**Figure 2.** (a) Top: "Rear view" of structure **1** (including the alkoxide group and the central part of the ligand coming out of the paper plane) with thermal ellipsoids. The $Cu_2-N_3$ plane is perpendicular to the paper plane. (b) Bottom: Same perspective of structure *2* without thermal ellipsoids.

group in the foreground. In **1**, the coordination about the two independent Cu atoms Cu1 and Cu2 is close to trigonal-bipyramidal (cf. Tables 2 and 3). Thus, the apical atoms N1 and N13 (or N6 and N11) lie approximately on an axis (bond angle 177.6°) going through Cu1 (or Cu2; bond angle 177.4°), and the three equatorial nitrogen atoms have angles of 119.7, 120.9, and 115.1° around Cu1 (or 104.7, 127.4, and 123.5° around Cu2). The angles between the axial and equatorial ligands range from 81.0 to 101.5°. In general, the coordination about Cu1 is closer to ideal than about Cu2. In contrast, the coordination about the Cu atom in *2* (Figures 1b and 2b) is much more distorted from trigonal-bipyramidal and has been described as a distorted tetragonal pyramid. Closer examination of the bond angles of **1** (Table 3) reveals that the distortion from trigonal-bipyramidal symmetry of *2* is mainly due to a rotation of the two benzimidazolyl nitrogens N2 and N3 (or N7 and N8) around the axis N1−Cu1−N13 (or N6−Cu2−N11) in **1** such that one nitrogen gets closer to the Cu−O−Cu plane and the other one more perpendicular to it.

Correspondingly, the "equatorial" bond angles which are close to 120° in **1** (*vide supra*) are changed to 143.8, 98.6, and 114.2° in *2*, and *N1*, *N2*, *N6*, and *O* form the base of a square-planar pyramid with *N4* at the apical position. In addition, the Cu−benzimidazolyl-N bond lengths become different in *2*, i.e. 1.99 Å for the basal and 2.11 Å for the apical distance, whereas they are fairly equal in **1** (2.052, 2.048 and 2.023, 2.061 Å, respectively). The spatial arrangement of the L-Et ligands in **1** is also different compared with the arrangement in *2*. Figure 2 shows the origin of these structural differences: whereas the *C4−C3(O)−C4a* group in *2* is planar and a 2-fold (crystallographic) axis is going through *C3−O−N7* (Figure 2b), the analogous C23−C22(O)−C1 group in **1** is puckered (*vide infra*) (Figure 2a). The Cu1−Cu2 separation of 3.624(2) Å and the Cu1−O−Cu2 angle of 135.7° are comparable with the values found for *2*.

In view of the structural differences evidenced between our product **1** and that of McKee et al. (*2*) we decided to study the magnetic properties of **1** as well. In order to eliminate systematic errors (quartz sample tube, diamagnetic correction) as far as possible, the complex **1** and an identical molar amount of the ligand ($HL\text{-}Et{\cdot}0.5H_2O$) were measured separately and the raw data (emu's) subtracted from each other (Figure 3). This leaves a difference of the molar susceptibility $\Delta\chi_M$ which only involves a contribution $P$ (%) due to the two coppers, the diamagnetic correction $\Delta\chi_M{}^{dia}$ for the two $BF_4$ groups and one azide (minus that of $0.5H_2O$), a temperature independent paramagnetism (TIP) due to Cu(II), and the contribution $(1 - P)$ of a paramagnetic impurity which is assumed to be due to the precursor (two $S = {}^1/_2$ Cu(II)'s). Consequently, $\Delta\chi_M$ is fitted with the expression

$$\Delta\chi_M = P(2N\mu_B{}^2g^2/3kT)[1 + \exp(-2J/kT)/3]^{-1} + (1 - P)(2N\mu_B{}^2g^2/4kT) + \Delta\chi_M{}^{dia} + \mathrm{TIP}$$

With $-2J > 1200$ cm$^{-1}$, the fit gave values for of ($\Delta\chi_M{}^{dia}$ + TIP) of $-20 \times 10^{-6}$ cm$^3$/mol and $P$=98% ($g$=2). Theoretical curves with $-2J < 1200$ cm$^{-1}$ indicated an upward curvature of $\chi_M(T)$ which could have been detected in our measurement but it absent in the data (Figure 3). Hence, 1200 cm$^{-1}$ represents a lower limit for the $-2J$ value of **1**. Note that this value is close to $-2J > 1100$ cm$^{-1}$ given for **2** by McKee et al. The structural and magnetic data obtained on **1** therefore indicate that our system has a trigonal-bipyramidal copper coordination yet is as diamagnetic as the system **2** whose copper environment is closer to a square-pyramidal. Since the trigonal-bipyramidal copper coordination in **1** involves a $d_{z^2}$ ground state, the alkoxy group cannot contribute to the ground state antiferromagnetic coupling (Figure 4a) and the $-2J$ value of >1200 cm$^{-1}$ must be entirely due to the azide group. In addition, the copper coordination of complex **1** is very similar to that of the analogous acetato-bridged complex $[Cu_2(L\text{-}Et)(OAc)]^{2+}$ which

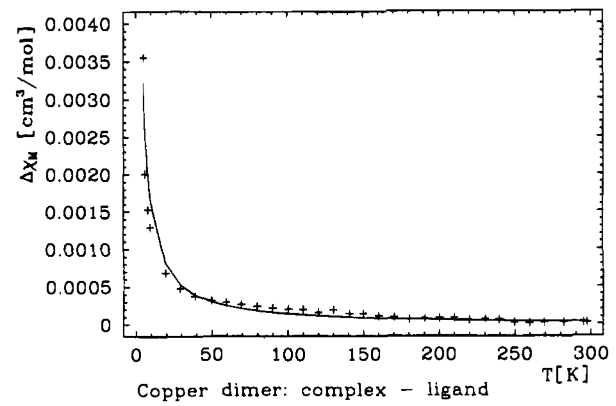

**Figure 3.** Magnetic susceptibility (data and fit) of complex **1** *vs* temperature. The susceptibility of the ligand and the sample tube are subtracted (see text).

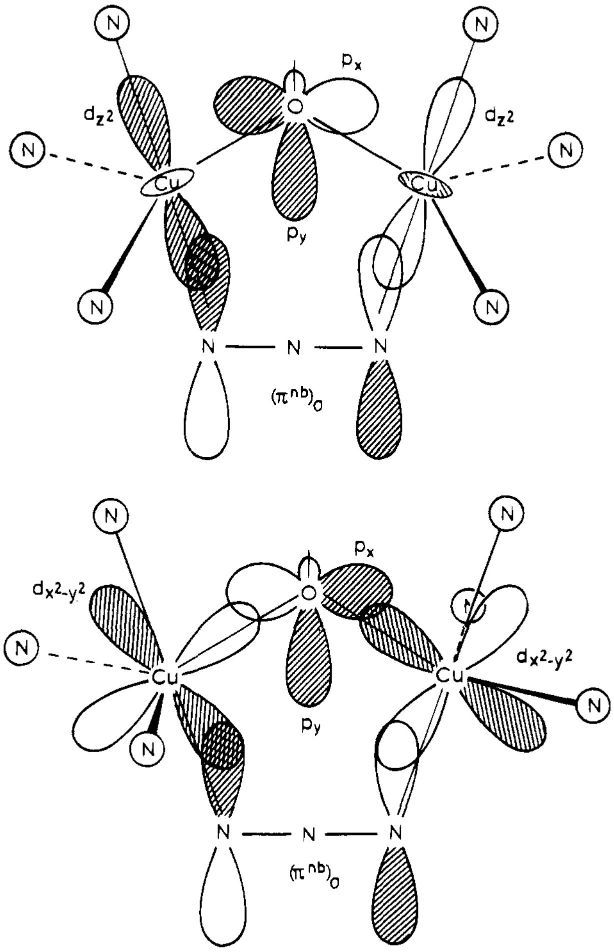

**Figure 4.** Structures **1** (a, top) and **2** (b, bottom) (schematically) with copper and ligand (azide, alkoxide) valence orbitals. Atomic orbital designations refer to individual coordinate systems.

also has a $d_{z^2}$ ground state.[8] The structural similarity between **1** and the acetato complex is also borne out by the fact that the lattice parameters of **1** and the $[Cu_2(L\text{-}Et)(OAc)](ClO_4)_2$ system agree to within 1%. However, the acetato complex exhibits a weakly ferromagnetic coupling between the copper centers ($2J = 24$ cm$^{-1}$). Thus, the comparison between **1** and the $\mu$-acetato complex demonstrates that the drastic change in the magnetic properties is entirely due to the change of the bridging ligand while the complex binding geometry is unaffected.

The results obtained for the structural and magnetic properties of **1** are clearly in contrast to the hypothesis of McKee et al. that a $d_{x^2-y^2}$ ground state is a necessary condition for strong antiferromagnetic coupling in copper azide and peroxide dimers. According to this assumption, the second bridge (alkoxide) is needed to promote strong superexchange between the two $d_{x^2-y^2}$ orbitals (Figure 4b) leading to a $-2J$ value of over 1000 cm$^{-1}$. It is well-known that the acetate bridge is a very weak and cis $\mu$-1,3 bridging azide a fairly strong mediator of superexchange. However, our data allow us to directly compare these two ligands in a similar binding geometry where other bridging ligands do not contribute to $-2J$. To our knowledge, the lower limit of $-1200$ cm$^{-1}$ obtained for single bridging azide is the highest ever determined. Kahn et al. have found a $-2J$ value of 309 cm$^{-1}$ for a binuclear copper complex bridged by a single end-on azide group.[14] The $-2J$ value is much lower than in our case as this complex contains two additional (nonbridging) azide groups coordinated to the copper centers which delocalize electron density of the Cu(II) centers and thus reduce the value of the singlet–triplet splitting appreciably. An indication that $-2J$ per end-on bridging azide may be larger than $-300$ cm$^{-1}$ is also provided by copper complexes with two end-on azide bridges which are diamagnetic at room temperature.[2] Finally, a binuclear Cu(II) complex with an azide–phenolate double bridge similar to the azide–alkoxide bridge of **1** and **2** has been prepared for which a $-2J$ value of $-1800$ cm$^{-1}$ has been given.[9] The copper coordination in this complex has also been described as tetragonal, and a strong superexchange pathway via the phenolate group has been invoked in order to explain the magnitude of $-2J$. In view of our result, the majority of this antiferromagnetic coupling is due to the bridging azide and the phenolate group may only give a minor contribution to $-2J$.

The reason for the extraordinarily strong antiferromagnetic interaction in binuclear end-on azide-bridged copper dimers is due to a combined interaction of the doubly occupied $(\pi^{nb})_\sigma$ HOMO and the unoccupied $(\pi^*)_\sigma$ LUMO of the azide with the highest energy, singly occupied d orbitals of the Cu(II) centers: [11] The azide $(\pi^{nb})_\sigma$ orbital interacts with the antisymmetric combination of copper d orbitals (*cf.* Figure 4a,b) and makes this molecular orbital the LUMO of the whole complex. On the other hand, the unoccupied azide $(\pi^*)_\sigma$ orbital at about +4 eV above the HOMO[11] interacts with the symmetric combination of d orbitals (not displayed in Figure 4) which becomes the HOMO of the complex (symmetric and antisymmetric refer to a mirror plane between the two coppers). Hence, both interactions act to increase the HOMO–LUMO gap, and the resulting HOMO–LUMO splitting is large (calculated value for $[Cu_2(L\text{-}Et)(N_3)]^{2+}$: 6700 cm$^{-1}$ [11]). This corresponds to strong antiferromagnetic coupling. The admixture of the $(\pi^*)_\sigma$ azide orbital in the HOMO of the complex corresponds to back-bonding which goes well beyond the usual description of azide as pseudohalogen.[15]

The fact that two different structures, **1** and **2**, result from the same preparation is somewhat puzzling. Note, however, that in structure **2** the coordination around the central (alkoxide) C atom of the L-Et ligand connecting the two ligand arms is exactly planar (Figure 2b); hence, this C atom cannot be sp$^3$ hybridized as required by the secondary alcoholate function at this place.[8] This planarity is also a consequence of the crystal symmetry of **2** which contains a crystallographic $C_2$ axis going through this C–O bond and the central N of the azide group (*vide supra*). In contrast, the same C atom in structure **1** (Figure 2a) as well as in the acetato-bridged dimer[8] has bond angles which are consistent with a sp$^3$ hybridization, i.e. a secondary

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(14) Bkouche-Waksman, I.; Boillot, M.-L.; Kahn, O.; Sikorav, S. *Inorg. Chem.* **1984**, *23*, 4454.

(15) Jones, K. In *Comprehensive Inorganic Chemistry*; Pergamon Press: Oxford, U.K., 1973; Vol. 2, Chapter 19 (Nitrogen), pp 147–388.

alcohol function. Hence, our azide structure **1** also preserves the crystal structure of the acetate-bridged complex whereas McKee et al. observe a change from $P2_1/n$ (acetate bridged) to $C2/m$ (azide-bridged complex *2*) which is obviously triggered by the change of hybridization of the central L-Et C atom from $sp^3$ to $sp^2$. We tentatively assume that the L-Et ligand has been oxidized in *2*;[16] from the overall stoichometry, the L-Et ligand should be present as enolate and not as ketone. In order to exhibit overall $C_2$ symmetry, the C−C double bond could either oscillate between the "left" and the "right" arm of the ligand or be localized but disordered in the crystal. Thus, it is understandable that our azide complex crystallizes in the same space group as the acetate complex whereas *2* crystallizes in a different space group. Nevertheless, it is surprising that the lattice parameters of **1** are within 1% of those of the acetate-bridged complex as the acetate group is more bulky than azide and the methyl group exceeds somewhat the cage of the L-Et ligand (see ref 8). Obviously, the dimensions of the unit cell are primarily determined by the L-Et ligand and the "additional" methyl group in $(CH_3)COO^-$ (as compared to the triatomic $N{-}N{-}N^-$) can be accommodated in the structure without change of the lattice parameters.[17]

## Summary and Conclusion

The structure of the azide-bridged, binuclear complex $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$ (**1**) has been determined with X-ray crystallography and has been shown to differ from the structure published earlier (*2*). The main difference between **1** and *2* is the coordination of the copper ions which is approximately square-planar in *2* and trigonal-bipyramidal in **1**, which can be traced back to a different coordination of the central C atom of the L-Et ligand. The structure of **1** is isomorphous to that of the acetate-bridged system $[Cu_2(L\text{-}Et)(OAc)](ClO_4)_2$. Magnetic measurements on **1** lead to a new lower limit for single bridging azide of $-2J \geq 1200$ cm$^{-1}$ and indicate that a tetragonal ground state is not a necessary condition for strong antiferromagnetic coupling.

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**Supplementary Material Available:** Tables of atomic coordinates and isotropic displacement coefficients, bond lengths and bond angles, anisotropic displacement coefficients, and H-atom coordinates with isotropic displacement coefficients (8 pages). Ordering information is given on any current masthead page.

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[16] Following this hypothesis, we have tried to actually make *2* by bubbling air for 6 h through the solution of Cu(II) and the L-Et ligand and then adding azide. In fact, we obtained a powder diffraction pattern from the raw product which was different from that of **1** but neither consistent with that of *2*. Subsequent recrystallization from acetonitrile/ether again gave the diffraction pattern of **1**.

[17] In addition, the counterions $BF_4^-$ and $ClO_4^-$ have the same size.