Three New Polynuclear Copper(II) Complexes with the Symmetric $[Cu(\mu_{1,1}-N_3)_2Cu]^{2+}$ Core and Pyridine Derivatives: Syntheses, Structure, and Magnetic Behavior

Albert Escuer,[†] Mohamed A. S. Goher,[‡] Franz A. Mautner,[§] and Ramon Vicente*,[†]

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647, 08028-Barcelona, Spain,
Department of Chemistry, Faculty of Science, Alexandria University, Alexandria 21321, Egypt, and
Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria

Received September 22, 1999

Three new polynuclear copper(II) complexes, derived from the end-on azido bridging ligand and pyridine derivatives, have been synthesized, and their crystal structures have been determined by X-ray diffraction methods; they are the dinuclear compounds $[Cu_2(\mu_{1,1}-N_3)_2(4\text{-Etpy})_4(\mu-NO_3)_2]$ (**1**), and $[Cu_2(\mu_{1,1}-N_3)_2(3\text{-ampy})_4(\mu-NO_3)_2]\cdot C_2H_5OH$ (**2**), and the trinuclear $[Cu_3(\mu_{1,1}-N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (**3**). 4-Etpy is 4-ethylpyridine, 3-ampy is 3-aminopyridine, and Meinic is methylisonicotinate. Compound **1,** $C_{28}H_{36}Cu_2N_{12}O_6$, crystallized in the monoclinic system, space group $P2_1/n$, with $a = 12.355(9)$ Å, $b = 12.474(4)$ Å, $c = 12.854(6)$ Å, $\beta = 117.68(4)°$, and $Z = 2$. Compound **2,** $C_{22}H_{30}Cu_2N_{16}O_7$, crystallized in the triclinic system, space group $P\bar{1}$, with $a = 9.695(2)$ Å, $b = 10.895(2)$ Å, $c = 7.909(2)$ Å, $\alpha = 96.81(3)°$, $\beta = 96.40(3)°$, $\gamma = 96.56(3)°$ and $Z = 1$. Compound **3**, $C_{20}H_{28}Cu_3N_{22}O_6$, crystallized in the monoclinic system, space group $P2_1/n$, with $a = 7.755(2)$ Å, $b = 14.680(5)$ Å, $c = 15.810(5)$ Å, $\beta = 102.81(2)°$, and $Z = 2$. **1**−**3** have the symmetric $[Cu(\mu_{1,1}-N_3)_2Cu]^{2+}$ core and structural parameters outside the previously reported range. Magnetic susceptibility data, measured from 2 to 300 K, show strong ferromagnetic coupling for the dinuclear end-on compounds **1** and **2** and bulk moderate ferromagnetic coupling for the trinuclear compound **3**. These data were fitted to the appropriate equations derived from the Hamiltonian $\mathbf{H} = -\mathbf{J}S_1S_2$ for **1** and **2** and from the Hamiltonian $\mathbf{H} = -\mathbf{J_1}(S_{A1}S_B + S_{A2}S_B) - \mathbf{J_2}S_{A1}\cdot S_{A2}$ for **3**, giving the parameters $J = 230.1(1)$ cm^{-1}, $g = 2.17(0.01)$ for **1**, $J = 223.2(2)$ cm^{-1}, $g = 2.16(0.01)$ for **2**, and $J_1 = 47.3(2)$ cm^{-1}, $J_2 = -22.5(1)$ cm^{-1}, $g_A = 2.26(0.02)$, $g_B = 2.07(0.03)$ for **3.** The magnetic susceptibility data can be correlated with the structural parameters.

Introduction

Recently, there has been great interest in the magnetic coupling in end-on (EO) azido-bridged copper(II) complexes with the $[Cu(\mu_{1,1}-N_3)_2Cu]^{2+}$ core stimulated by the determination of the spin distribution in the spin triplet ground state[1] in the previously published[2] compound $[Cu_2(\mu_{1,1}-N_3)_2(\text{t-Buty})_4](ClO_4)_2$ (t-Buty = *p-tert*-butylpyridine) and by the publication of two theoretical papers[3,4] studying the effect of the structural parameters (Cu−N(azido) distance, mean Cu−N−Cu angle (θ), and mean out-of plane deviation of the azido group (τ)) on the exchange coupling constants of complexes of this kind. Previously, the study of dinuclear copper(II) compounds involving a combination of a $\mu_{1,2}$-diazine and a $\mu_{1,1}$-N_3 azide bridge had provided support for antiferromagnetic exchange of the $\mu_{1,1}$-N_3 azide bridge at Cu−N−Cu angles exceeding 108°.[5,6]

In the case of the dinuclear copper(II) compounds with only $\mu_{1,1}$-N_3 azido bridges, the number of structurally and magnetically studied compounds with the symmetric $[Cu(\mu_{1,1}-N_3)_2Cu]^{2+}$ core is very low[2,7−9] and the predicted magneto−structural correlation can be tested only in a short range of structural parameters, i.e., mean Cu−N−Cu angle (θ) between 100.5 and 104.6° and mean out-of plane deviation of the azido group (τ) between 6.9 and 20.1° (Chart 1).

Here, with the aim of increasing the structural and magnetic data for the end-on azido-bridged copper(II) complexes, we present the syntheses and the structural and magnetic study of two new dinuclear compounds with the above-mentioned structure: $[Cu_2(\mu_{1,1}-N_3)_2(4\text{-Etpy})_4(\mu-NO_3)_2]$ (**1**) and $[Cu_2(\mu_{1,1}-N_3)_2(3\text{-ampy})_4(\mu-NO_3)_2]\cdot C_2H_5OH$ (**2**). 4-Etpy is 4-ethylpyridine and 3-ampy is 3-aminopyridine. **1** and **2** present θ angles outside of the previously reported values (98.2(2) and 97.5(1)° for **1** and **2**, respectively). Also, **1** and **2** present τ angles outside of the previously reported values (31.3(2) and 35.6(2)° for **1** and **2**, respectively). The variable temperature magnetic susceptibility measurements of **1** and **2** indicate strong ferromagnetic coupling.

We also present the synthesis and the structural and magnetic study of the trinuclear end-on azido-bridged copper(II) complex

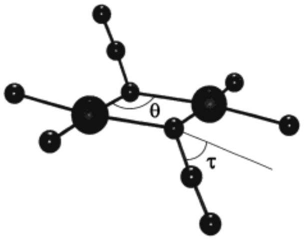
---

[†] Universitat de Barcelona.
[‡] Alexandria University.
[§] Technische Universität Graz.

(1) Aebersold, M. A.; Gillon, B.; Plantevin, O.; Pardi, L.; Kahn, O.; Bergerat, P.; von Seggern, I.; Tuczek, F.; Öhrström, L.; Grand, A.; Lelièvre-Berna, E. *J. Am. Chem. Soc.* **1998**, *120*, 5238.
(2) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1984**, *23*, 490.
(3) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122.
(4) Adamo, C.; Barone, V.; Bencini, A.; Totti, F.; Ciofini, I. *Inorg. Chem.* **1999**, *38*, 1996.
(5) Thompson, L. K.; Tandon, S. S.; Manuel, M. E. *Inorg. Chem.* **1995**, *34*, 2356.
(6) Thompson, L. K.; Tandon, S.S. *Comments Inorg. Chem.* **1996**, *18*, 125.
(7) Tandon, S. S.; Thompson, L. K.; Manuel, M. E.; Bridson, J. N. *Inorg. Chem.* **1994**, *33*, 5555.
(8) Van Albada, G. A.; Lakin, M. T.; Veldman, N.; Spek, A. L.; Reedjik, J. *Inorg. Chem.* **1995**, *34*, 4910.
(9) Comarmond, J.; Plumeré, P.; Lehn, J.-M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgensten-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330.

10.1021/ic991135c CCC: \$19.00

Chart 1



with the same symmetric $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(Meinic)_2(DMF)_2]$ (**3**). Meinic is methylisonicotinate. The variable temperature magnetic susceptibility measurements of **3** indicate bulk ferromagnetic coupling. Previously to **3**, as far as we know, only the structurally similar complex $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(L)_2]$ was reported,[10] where L = hydridotris(3,5-dimethylpyrazolyl)borate.

Experimental Section

Physical Measurements. IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. Magnetic susceptibility measurements were carried out on polycrystalline samples with a superconducting quantum interference device (SQUID) apparatus working in the range 2−300 K under magnetic fields of approximately 0.1 T. Diamagnetic corrections were estimated from Pascal tables.

Synthesis. *Warning!* The reported azido complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

(a) $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-}Etpy)_4(\mu\text{-}NO_3)_2]$ (1). Copper(II) nitrate trihydrate (0.72 g, 3 mmol) and 4-ethylpyridine (0,75 g, 7 mmol) were mixed in 40 cm^3 of acetone. An aqueous solution (5 cm^3) of NaN_3 (0.39 g, 6 mmol) was added to this mixture with continuous stirring. DMF was then added to dissolve any precipitate, and the final clear solution mixture was allowed to stand in a desiccator containing a beaker filled with diethyl ether until good quality crystals formed. Yield ca. 45% (with respect to copper). Anal. Calcd for $C_{28}H_{36}Cu_2N_{12}O_6$: C, 44.0; H, 4.8; N, 22.0; Cu, 16.6. Found: C, 44.0; H, 4.6; N, 21.7; Cu, 16.3.

(b) $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-}ampy)_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (2). An ethanol solution of 3-aminopyridine (0.58 g, 8 mmol) was added to $Cu(NO_3)_2\cdot 3H_2O$ (0.72 g, 3 mmol) dissolved in ethanol (20 cm^3). Upon dropwise addition of NaN_3 (0.32 g, 5 mmol) dissolved in 5 cm^3 of water, a precipitate was obtained. DMF was then added to the heterogeneous mixture until there was complete dissolution of the precipitate. The final solution mixture was filtered and allowed to stand in a refrigerator for ca. two months until small black crystals of the complex formed. Yield ca. 50% (with respect to copper). Anal. Calcd for $C_{22}H_{30}Cu_2N_{16}O_7$: C, 34.9; H, 4.0; N, 29.6; Cu, 16.8. Found: C, 34.7; H, 3.9; N, 29.9; Cu, 16.7.

(c) $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(Meinic)_2(DMF)_2]$ (3). Copper(II) nitrate trihydrate (0.72 g, 3 mmol) and methyl isonicotinate (1.10 g, 8 mmol) were mixed together in acetone (30 cm^3) followed by dropwise addition of an aqueous solution (5 cm^3) of NaN_3 (0.39 g, 6 mmol) until an olive-green precipitate was formed. DMF was then added until the precipitate disssolved. The clear solution mixture was then boiled for about 15 min and allowed to stand in an open beaker for several weeks to deposit black, well-formed crystals of the complex. Yield: 20% (with respect to copper). Anal. Calcd for $C_{20}H_{28}Cu_3N_{22}O_6$: C, 27.8; H, 3.3; N, 35.7; Cu, 22.1. Found, C 27.6, H, 3.2; N, 35.5; Cu, 22.0.

Crystal Structure Analyses of 1, 2, and 3. The X-ray single-crystal data for the three compounds were collected on a modified STOE four-circle diffractometer. Crystal size of **1 2**, and **3**, respectively]: 0.75 mm × 0.30 mm × 0.20 mm; 0.40 mm × 0.25 mm × 0.10 mm; 0.40 mm × 0.25 mm × 0.20 mm. The crystallographic data, the conditions retained for the intensity data collection, and some features of the structure refinements are listed in Table 1. Graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å) with the ω-scan technique was used to collect the data sets. The accurate unit-cell parameters were determined from automatic centering of 40 reflections (6.0° < θ < 13.0°) for **1**, 24 reflections (7.7° < θ < 12.6°) for **2**, and 24 reflections (7.0° < θ < 14.0°) for **3** and refined by least-squares methods. A total of 4116 reflections (3371 independent reflections, R_{int} = 0.0336) for **1**, 2982 reflections (2771 independent reflections, R_{int} = 0.0259) for **2**, and 4361 reflections (3625 independent reflections, R_{int} = 0.0427) for **3** were collected in the range 3.12° < θ < 27.99°, 3.02° < θ < 25.00°, and 2.77° < θ < 26.98° for **1**, **2**, and **3**, respectively. Intensity decays of 6%, 3%, and 3% for control reflections (−1 4 −1; −1 2 1; 0 4 2), (1 −2 1; 2 −1 1; 4 0 0), and (1 1 4; −1 −2 −1; 2 2 −2) for **1**, **2**, and **3**, respectively, measured after every set of 100 reflections, were observed during data collection. Corrections were applied for Lorentz polarization effects, for intensity decay, and for absorption using the DIFABS[11] computer program. The structures were solved by direct methods using the SHELXS-86[12] computer program and refined by full-matrix least-squares methods on F^2, using the SHELXL-93[13] program incorporated in the SHELXTL/PC, version 5.03,[14] program library and the graphics program PLUTON.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were obtained from ΔF maps and subsequently fixed geometrically with the HFIX utility.[14] In the case of **2**, two split orientations with 50% occupancy, related by an inversion center, were introduced for the atoms of disordered lattice solvent molecule (EtOH). For **1**, **2**, and **3**, respectively, the final R indices for all observed reflections are 0.0561, 0.0499, and 0.0481 and the number of refined parameters are 224, 244, and 243. The maximum and minimum peaks in the final difference Fourier synthesis are respectively 0.53 and −0.43 e Å^{-3} for **1**, 0.64 and −0.62 e Å^{-3} for **2**, and 0.37 and −0.66 e Å^{-3} for **3**. Significant bond parameters are reported in Tables 2−4.

Table 1. Crystal Data and Structure Refinement for Compounds $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-}Etpy)_4(\mu\text{-}NO_3)_2]$ (**1**), $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-}ampy)_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (**2**), and $Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(Meinic)_2(DMF)_2]$ (**3**)

	1	2	3
chemical formula	$C_{28}H_{36}Cu_2N_{12}O_6$	$C_{22}H_{30}Cu_2N_{16}O_7$	$C_{20}H_{28}Cu_3N_{22}O_6$
fw	763.76	757.70	863.26
space group	$P2_1/n$	P-1	$P2_1/n$
a, Å	12.355(9)	9.695(2)	7.755(2)
b, Å	12.474(4)	10.895(2)	14.680(5)
c, Å	12.854(6)	7.909(2)	15.810(5)
α, deg	90.0	96.81(3)	90.0
β, deg	117.68(4)	96.40(3)	102.81(2)
γ, deg	90.0	96.56(3)	90.0
V, Å^3	1754(2)	817.4(3)	1755.1(9)
Z	2	1	2
temp, °C	20(2)	20(2)	20(2)
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69
d_{calc}, g·cm^{-3}	1.446	1.539	1.634
μ(Mo Kα), mm^{-1}	1.269	1.367	1.870
R^a	0.0561	0.0499	0.0481
R^2w ^{b}	0.1235	0.1220	0.1073

^{a} $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $Rw(F_o)^2 = \{\Sigma[w((F_o)^2 - (F_c)^2)^2]/\Sigma[w(F_o)^4]\}^{1/2}$.

---

(10) Lam, M. H. W.; Tang, Y.-T.; You, X.-Z.; Wong , W.-T. *Chem. Commun.* **1997,** 957.

(11) Walker, N.; Stuart, D. *Acta Crystallogr*. **1983**, *A39*, 158.

(12) Sheldrick, G. M. *SHELXS-86, Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1986.

(13) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1993.

(14) *SHELXTL, Program Library for the Solution and Molecular Graphics*, version 5.03 (PC version); Siemens Analytical Instruments Division: Madison, WI, 1995.

(15) Spek, A. L. *PLUTON-92*; University of Utrecht: Utrecht, The Netherlands, 1992.

Results and Discussion

Spectra. (a) $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-Etpy})_4(\mu\text{-}NO_3)_2]$ (1). The electronic spectrum of the solid sample shows a very strong broad band centered around 370 nm and a distinct absorption band of moderate intensity due to $N_3 \rightarrow$ Cu(II) CT transitions. The d−d transition appeared as a broad band with a maximum around 630 nm. The IR spectrum shows the azide asymmetric stretch as a very strong sharp band at 2060 cm^{-1}. The absorption bands of the nitrate and 4-Etpy mask the azide symmetric stretch in the region 1350−1270 cm^{-1}. The strong bands at 1447, 1420, 1381, and 1322 cm^{-1} are due to bridging bidentate nitrato ligands.[16]

(b) $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-ampy})_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (2). The IR absorption bands observed in the spectrum of the complex at 3429 (vs), 3326 (s), and 3218 (s) cm^{-1} are tentatively assigned to the vibrational modes of free EtOH and are superimposed on those of the amino group. The asymmetric stretch mode of the azide appears as a very strong band at 2080 cm^{-1}. The band at 1277 cm^{-1} may be assigned to the nitrate group mixed with the symmetric stretching mode of the azide ligand, suggesting asymmetric μ-1,1 azide bridging. The bands at 1493 (s), 1454 (s), and 1317 (vs) cm^{-1} suggest the bidentate chelating nitrato ligand.[16] The electronic spectrum of the solid complex exhibits a very strong band centered around 415 nm and a distinct absorption band of moderate intensity around 540 nm, as found for other copper(II) azide complexes containing μ-1,1 N_3 groups, assigned to the N_3 Cu^{II} CT transitions. The d−d band appears as a broad band centered around 630 nm.

(c) $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (3). The IR spectrum exhibits the asymmetric azide stretch as two very strong peaks at 2080, 2050 cm^{-1} and the symmetric stretch as a medium-to-strong band at 1278 cm^{-1}, suggesting asymmetric azido ligands. The carbonyl stretch band of Meinic, 1735 cm^{-1}, appears almost at the same position as in the spectrum of free Meinic, suggesting no participation of the C═O group in bonding formation. DMF shows a very strong and broad band centered around 1661 cm^{-1} due to the C═O mode. This band is shifted to lower frequency and appears as a sharp band at 1642 cm^{-1}, suggesting the coordination of DMF through its carbonyl oxygen. In DMF, this complex exhibits a strong band at 410 nm associated with the $N_3 \rightarrow Cu^{II}$ CT absorption transition, in addition to the d−d band around 730 nm.

Crystal Structures. (a) $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-Etpy})_4(\mu\text{-}NO_3)_2]$ (1). The structure of **1** consists of the well-isolated dinuclear formula units $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-Etpy})_4(NO_3)_2]$ in which the copper(II) atoms are bridged by two azido ions in EO fashion. An ORTEP drawing with the atom-labeling scheme is shown in Figure 1. The main bond lengths and angles are given in Table 2. The copper(II) atoms represent 4 + 1 + 1 coordination. The Cu(1)−N(11), Cu(1)−N(11A), Cu(1)−N(1), and Cu(1)−N(2) in-plane short distances are 1.996(3), 2.004(3), 2.005(4), and 1.992(3) Å, respectively. Two nitrate ions are up and down relative to the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core, acting also as bridging ligands and completing the 4 + 1 + 1 coordination of the copper(II) atoms; the Cu(1)−O(1) and Cu(1)−O(2A) long distances are 2.426(3) and 2.708(4) Å, respectively. The four atoms of the central square ring Cu(1)−N(11)−Cu(1A)−N(11A) are in a plane. The Cu(1)−N(11)−Cu(1A) angle (θ) is 98.3(2)°, and the mean out-of plane deviation of the azido group (τ) is 31.3(2)°. The intradimer Cu−Cu distance is 3.024(1) Å. The minimum interdinuclear Cu−Cu distance is 7.353(5) Å.

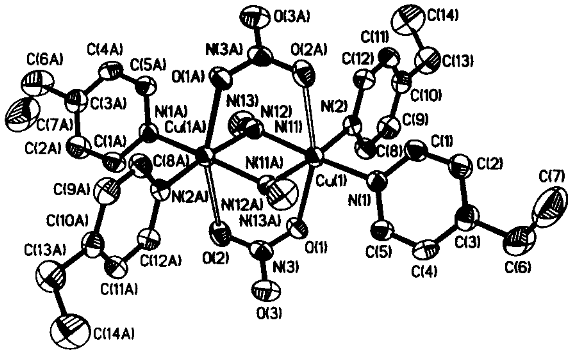


Figure 1. ORTEP drawing (40% probability) with atom labeling scheme of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-Etpy})_4(\mu\text{-}NO_3)_2]$ (**1**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-Etpy})_4(\mu\text{-}NO_3)_2]$ (**1**)[a]

Copper Environment			
Cu(1)···Cu(1A)	3.024(1)	Cu(1)−N(2)	1.992(3)
Cu(1)−N(11)	1.996(3)	Cu(1)−N(1)	2.005(4)
Cu(1)−N(11A)	2.004(3)	Cu(1)−O(1)	2.426(3)
Cu(1)−O(2A)	2.708(4)	N(11)−Cu(1A)	2.004(3)
N(2)−Cu(1)−N(11)	91.6(1)	N(2)−Cu(1)−N(1)	93.0(1)
N(11)−Cu(1)−N(1)	172.0(1)	N(2)−Cu(1)−N(11A)	173.3(1)
N(11)−Cu(1)−N(11A)	81.8(2)	N(1)−Cu(1)−N(11A)	93.5(1)
N(2)−Cu(1)−O(1)	96.0(1)	N(11)−Cu(1)−O(1)	88.0(1)
N(1)−Cu(1)−O(1)	97.9(1)	N(11A)−Cu(1)−O(1)	84.8(1)
N(2)−Cu(1)−O(2A)	97.6(1)	N(11)−Cu(1)−O(2A)	78.8(1)
N(11A)−Cu(1)−O(2A)	80.3(1)	N(1)−Cu(1)−O(2A)	94.1(1)
O(1)−Cu(1)−O(2A)	161.3(1)		
Azido and Nitrato Ligands			
N(11)−N(12)	1.212(5)	N(12)−N(13)	1.123(5)
O(1)−N(3)	1.258(5)	O(2)−N(3)	1.250(5)
N(3)−O(3)	1.234(5)		
Cu(1)−N(11)−Cu(1A)	98.2(1)	N(12)−N(11)−Cu(1)	122.4(3)
N(12)−N(11)−Cu(1A)	125.0(3)	N(13)−N(12)−N(11)	178.4(5)
O(3)−N(3)−O(2)	119.7(4)	O(3)−N(3)−O(1)	119.1(5)
O(2)−N(3)−O(1)	121.2(4)		

[a] Symmetry code: (A) $-x, -y, -z + 1$.

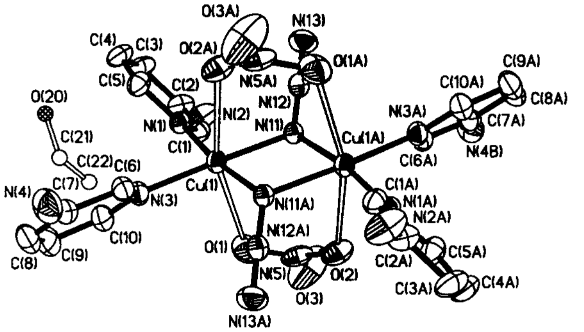


Figure 2. ORTEP drawing (40% probability) with atom labeling scheme of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-ampy})_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (**2**). Atoms of disordered EtOH are represented as spheres of arbitrary size.

(b) $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-ampy})_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (2). The structure of **2** consists of the dinuclear units $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-ampy})_4(NO_3)_2]$ and one solvent ethanol molecule. The copper(II) atoms are bridged by azido ions in an EO fashion. An ORTEP drawing with the atom-labeling scheme is shown in Figure 2. The main bond lengths and angles are given in Table 3. The copper atoms represent 4 + 2 coordination. The Cu(1)−N(1), Cu(1)−N(3), Cu(1)−N(11), and Cu(1)−N(11A) in-plane short distances are 1.993(3), 2.000(3), 2.006(3), and 2.000(3) Å, respectively. Two nitrate ions are up and down relative to the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core, acting also as bridging ligands and completing the 4 + 2 coordination of the copper-

---

(16) Nakamoto, N. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-ampy})_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (**2**)[a]

Copper Environment			
Cu(1)···Cu(1A)	3.011(1)	Cu(1)−N(1)	1.993(3)
Cu(1)−N(11A)	2.000(3)	Cu(1)−N(3)	2.000(3)
Cu(1)−N(11)	2.006(3)	Cu(1)−O(1)	2.512(4)
Cu(1)−O(2A)	2.578(4)		
N(1)−Cu(1)−N(11A)	172.4(1)	N(1)−Cu(1)−N(3)	93.5(1)
N(11A)−Cu(1)−N(3)	93.0(1)	N(1)−Cu(1)−N(11)	91.0(1)
N(11A)−Cu(1)−N(11)	82.5(1)	N(3)−Cu(1)−N(11)	175.5(1)
O(1)−Cu(1)−O(2A)	161.4(1)	N(11)−Cu(1)−O(1)	83.7(1)
N(11)−Cu(1)−O(2A)	83.5(1)	N(1)−Cu(1)−O(1)	98.4(1)
N(3)−Cu(1)−O(1)	96.4(1)	N(1)−Cu(1)−O(2A)	95.2(1)
N(3)−Cu(1)−O(2A)	95.5(1)	O(1)−Cu(1)−N(11A)	84.6(1)
N(11A)−Cu(1)−O(2A)	80.4(1)		
Bridging Ligand			
N(11)−N(12)	1.211(5)	N(12)−N(13)	1.153(5)
N(5)−O(1)	1.263(5)	N(5)−O(2)	1.251(5)
N(5)−O(3)	1.220(6)		
N(12)−N(11)−Cu(1A)	123.3(3)	N(12)−N(11)−Cu(1)	120.9(3)
Cu(1A)−N(11)−Cu(1)	97.5(1)	N(13)−N(12)−N(11)	178.2(4)
O(3)−N(5)−O(2)	119.9(5)	O(3)−N(5)−O(1)	118.8(5)
O(2)−N(5)−O(1)	121.2(4)		

[a] Symmetry code: (A) $-x + 1, -y + 2, -z + 1$.

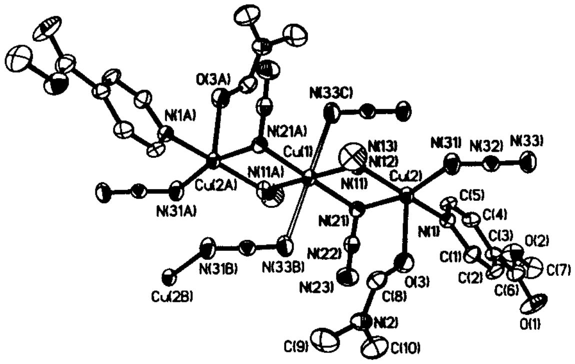


Figure 3. ORTEP drawing (40% probability) with atom labeling scheme of $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (**3**).

(II) atoms; the Cu(1)−O(1) and Cu(1)−O(2A) long distances are 2.512(4) and 2.578(4) Å, respectively. The four atoms of the central square ring ring Cu(1)−N(11)−Cu(1A)−N(11A) are in a plane. The Cu(1)−N(11)−Cu(1A) angle (θ) is 97.5(1)°, and the mean out-of plane deviation of the azido group (τ) is 35.6(2)°. The intradimer Cu−Cu distance is 3.011(1) Å. The minimum interdinuclear Cu−Cu distance is 7.909(2) Å.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (**3**)[a]

Copper Environment			
Cu(1)···Cu(2)	3.088(1)	Cu(1)···Cu(2A)	3.088(1)
Cu(1)···Cu(2B)	5.325(2)	Cu(2)···Cu(2A)	6.176(2)
Cu(1)−N(11)	1.988(3)	Cu(1)−N(11A)	1.988(3)
Cu(1)−N(21)	2.012(3)	Cu(1)−N(21A)	2.012(3)
Cu(1)−N(33B)	2.546(5)	Cu(1)−N(33C)	2.546(5)
Cu(2)−N(11)	2.020(4)	Cu(2)−N(21)	2.044(4)
Cu(2)−N(31)	1.959(4)	Cu(2)−N(1)	2.004(3)
Cu(2)−O(3)	2.311(4)		
N(11)−Cu(1)−N(21)	80.8(2)	N(11)−Cu(1)−N(33B)	92.1(2)
N(21)−Cu(1)-N(33B)	91.5(2)	N(31)−Cu(2)−N(1)	96.2(2)
N(31)−Cu(2)−N(11)	91.1(2)	N(1)−Cu(2)−N(11)	168.2(1)
N(31)−Cu(2)−N(21)	163.5(2)	N(1)−Cu(2)−N(21)	91.4(1)
N(11)−Cu(2)−N(21)	79.3(1)	N(31)−Cu(2)−O(3)	101.1(2)
N(1)−Cu(2)−O(3)	89.3(1)	N(11)−Cu(2)−O(3)	98.4(2)
N(21)−Cu(2)−O(3)	93.5(1)		
Azido and DMF Ligands			
N(11)−N(12)	1.218(5)	N(12)−N(13)	1.144(6)
N(21)−N(22)	1.210(5)	N(22)−N(23)	1.144(5)
N(31)−N(32)	1.190(5)	N(32)−N(33)	1.149(5)
O(3)−C(8)	1.225(6)	C(8)−N(2)	1.310(6)
N(2)−C(9)	1.440(7)	N(2)−C(10)	1.453(7)
Cu(1)−N(11)−Cu(2)	100.8(2)	Cu(1)−N(21)−Cu(2)	99.2(2)
N(12)−N(11)−Cu(1)	126.3(3)	N(12)−N(11)−Cu(2)	122.6(3)
N(22)−N(21)−Cu(1)	120.3(3)	N(22)−N(21)−Cu(2)	120.3(3)
N(13)−N(12)−N(11)	177.7(5)	N(23)−N(22)−N(21)	177.7(5)
N(33)−N(32)−N(31)	177.1(5)	N(32)−N(31)−Cu(2)	125.2(3)
Cu(2)−O(3)−C(8)	132.6(3)	O(3)−C(8)−N(2)	125.7(5)
C(8)−N(2)−C(9)	121.8(5)	C(8)−N(2)−C(10)	120.5(5)
C(9)−N(2)−C(10)	117.3(5)		

[a] Symmetry codes: (A) $-x, -y, -z$; (B) $1 - x, -y, -z$; (C) $x - 1, y, z$.

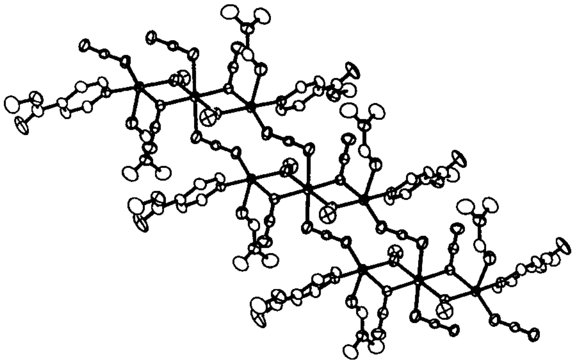


Figure 4. $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (**3**). Two $\mu_{1,3}$-N_3-bridging azido groups are forming a chain structure (oriented along the *c* axis of unit cell) with "stairlike packing" of trinuclear subunits.

(c) $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (3). The structure of **3** consists of the trinuclear unit $[(\text{DMF})(\text{Meinic})(N_3)Cu(\mu_{1,1}\text{-}N_3)_2Cu(\mu_{1,1}\text{-}N_3)_2Cu(\text{Meinic})(N_3)(\text{DMF})]$ linked by semicoordinating end-to-end azido bridges. The neighboring copper(II) atoms are bridged by two azido ions in an EO fashion. An ORTEP drawing with the atom-labeling scheme is shown in Figure 3. The main bond lengths and angles are given in Table 4. The central (Cu(1)) and the terminal (Cu(2) and Cu(2A)) copper atoms represent 4 + 2 and 4 + 1 coordination, respectively. For the central Cu(1) atom, the four short distances are the Cu−N(azido) of the bridging 1,1-azido ligands: 1.988(3) and 2.012(3) Å for Cu(1)−N(11) and Cu(1)−N(21), respectively. Cu(1) is also bonded at long distance to the end-N atoms of two azides coordinated to terminal Cu atoms of neighboring trinuclear units, placed top and bottom of the reference trinuclear unit, forming a chain of trinuclear units with E−E azido bridges (Figure 4). The Cu(1)−N(33) distance is 2.546(5) Å. The minimum intertrinuclear Cu−Cu distance is 5.325(2) Å. The terminal Cu(2) atoms are bonded at short distances to two N atoms of the bridging 1,1-azido ligands, one N atom of one terminal azido ligand, and one N-pyridine atom of the Meinic ligand. The distances Cu(2)−N(11), Cu(2)−N(21), Cu(2)−N(31), and Cu(2)−N(1) are 2.020(4), 2.044(4), 1.959(4), and 2.004(3) Å, respectively. Each Cu(2) atom is also bonded to the O atom of one DMF ligand at a distance of 2.311(4) Å. The Cu(1)−N(11)−Cu(2) angle (θ) is 100.8(2)°, and the Cu(1)−N(21)−Cu(2) angle (θ) is 99.2(2)°. The mean out-of plane deviations of the azido group (τ) are 26.4(4)° for the N11−N(12)−N(13) azido ligand and 38.2(3)° for the N(21)−N(22)−N(23) azido ligand. The four atoms of the central square ring are in a plane. The intradimer Cu−Cu distance is 3.088(1) Å.

Magnetic Results. The variable temperature magnetic susceptibility data for **1**−**3** were recorded between 300 and 2 K. Plots of $\chi_M T$ versus T for **1** and **2** are shown in Figure 5. For **1** the $\chi_M T$ value at room temperature (1.06 cm^3 mol^{-1} K) increases to a maximum at 44 K (1.17 cm^3 mol^{-1} K) as temperature decreases, indicating a strong ferromagnetic coupling, and after the maximum, it decreases to 1.08 cm^3 mol^{-1} K at 2 K. For **2**

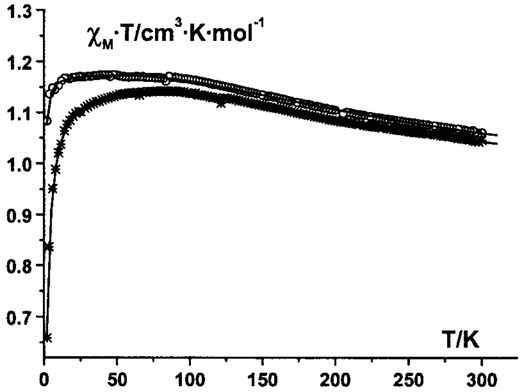


Figure 5. $\chi_M T$ vs T plots for $[Cu_2(\mu_{1,1}\text{-}N_3)_2(4\text{-Etpy})_4(\mu\text{-}NO_3)_2]$ (**1**) (○) and of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(3\text{-ampy})_4(\mu\text{-}NO_3)_2]\cdot C_2H_5OH$ (**2**) (∗). Solid lines show the best fit indicated in the text.

the $\chi_M T$ value at room temperature (1.05 $cm^3\ mol^{-1}$ K) increases to a maximum at 82 K (1.14 $cm^3 mol^{-1} K$) as the temperature decreases, also indicating a strong ferromagnetic coupling, and after the maximum it decreases to 0.66 $cm^3\ mol^{-1}$ K at 2 K. The susceptibility data for **1** and **2** were fitted to the Bleaney−Bowers expression[17] for the magnetic susceptibility of isotropically coupled $S = {}^1/_2$ dinuclear compounds, derived from the Hamiltonian $\mathbf{H} = -\mathbf{J}S_1S_2$: $\chi = \{2Ng^2\beta^2/[k(T - \omega)]\}\{\exp[-J/(kT)]\}$. The Weiss ω parameter was introduced in the formula to take into account possible antiferromagnetic interactions between dinuclear molecules together with zero-field splitting in the $S = 1$ ground state. The results of the best fit, shown as the solid lines in Figure 5, were $J = 230.1(1)\ cm^{-1}$, $g = 2.17(0.01)$, $\omega = -0.17(0.01)$ K for **1** and $J = 223.2(2)\ cm^{-1}$, $g = 2.16(0.01)$, $\omega = -1.40(0.01)$ K for **2**. These calculated J values are the strongest spin triplet ground state−spin singlet state separation reported to date for copper(II) compounds with the symmetrical $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core. According to Ruiz et al.,[3] from density functional calculations there appears to be a clear correlation between the calculated J parameter and the θ angle; the J value decreases from a maximum at about $\theta = 85°$ with increasing θ, eventually reaching an antiferromagnetic regime for $\theta \geq 104°$. The τ angle seems to have a negligible influence on the J value.[3] Also, from the linear trend ($J = -41.94\theta + 4440\ cm^{-1}$) in the θ vs J plot observed by Thomson et al.;[5] the predicted J values are 321.5 and 350.8 cm^{-1} for **1** and **2**, respectively. Note that **1** and **2** have the lowest reported θ angles (98.2(1) and 97.5(1)°, respectively) and the highest J values (230.1(1) and 223.2(2) cm^{-1}, respectively). The τ values are the highest reported so far (31.3(2) and 35.6(2)° for **1** and **2**, respectively); the large J values measured here confirm the negligible effect of τ on J. The Cu−N found distances in **1** and **2** are in the range of the previously reported parameters.

The magnetic susceptibility data, χ_MT versus T for **3** are plotted in Figure 6. For **3** the $\chi_M T$ value of 1.42 $cm^3\ mol^{-1}$ K at room temperature increases slowly to 1.7 $cm^3 mol^{-1} K$ at 6 K as the temperature decreases, and it increases quickly to 1.96 $cm^3\ mol^{-1}$ K at 2 K. The magnetic susceptibility behavior of **3** indicates bulk ferromagnetic coupling. Taking into account the linear structure of **3** (Scheme 1), the fit of the magnetic data was made by using the appropriate equation[18] derived from the Hamiltonian $\mathbf{H} = -\mathbf{J_1}(S_{A1}S_B + S_{A2}S_B) - \mathbf{J_2}S_{A1}\cdot S_{A2}$. The best-fit parameters were $J_1 = 47.3(2)\ cm^{-1}$, $J_2 = -22.5(1)\ cm^{-1}$, $g_A = 2.26(0.02)$, $g_B = 2.07(0.03)$. In **3** the θ angles are 100.8(2)° for Cu(1)−N(11)−Cu(2) and 99.2° for Cu(1)−N(21)−Cu(2). The ferromagnetic coupling in the $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ core ($J_1 = 47.5\ cm^{-1}$) is in accordance with $\theta \leq 104°$. The antiferromagnetic coupling between the terminal Cu(II) atoms is more difficult to explain, but recently, from a theoretical density functional study, Ruiz et al.[19] have predicted a moderate AF coupling between terminal Cu(II) atoms in trinuclear Cu(II) compounds with oxo bridges and ferromagnetic coupling between neighboring Cu(II) atoms. We have not considered the possible AF interaction through 1,3 azido bridges connecting the neighboring trinuclear units because in an octahedral environment the unpaired electronic density on d_{z^2} atomic orbitals of the Cu(II) ions is negligible. The absence of AF interaction between the trimeric units is also confirmed by the $\chi_M T$ vs T plot; no decay of the $\chi_M T$ value is observed even at 2 K.

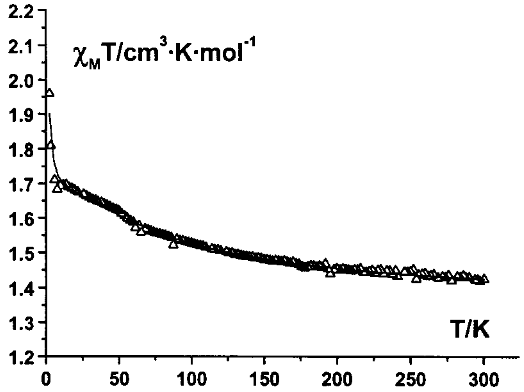
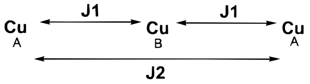


Figure 6. $\chi_M T$ vs T plot for $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(\text{Meinic})_2(\text{DMF})_2]$ (**3**). Solid lines show the best fit indicated in the text.

Scheme 1



Previously to **3**, as far as we know, only the structurally similar complex $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(L)_2]$ was reported,[10] L = hydridotris(3,5-dimethylpyrazolyl)borate. $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(L)_2]$ has θ angles of 101.5(6) and 101.2(6)°. The variable temperature magnetic susceptibility measurements of $[Cu_3(\mu_{1,1}\text{-}N_3)_4(N_3)_2(L)_2]$ in the range 75.5−300 K indicate that $\chi_M T$ is apparently independent of temperature, but taking into account the θ angles and the limited range of temperature in which the magnetic susceptibility was studied, a similar magnetic behavior for this compound cannot be ruled out.

Conclusions

Kahn et al. concluded their previously cited paper[1] with a question: "Can the 1,1-azido group be considered as an almost universal ferromagnetic coupler, or is the stabilization of the parallel spin state only achieved in a limiting range of bridging angle values?" From the density functional study of Ruiz et al.[3] the answer is the second possibility; for $\theta \geq 104°$ it is possible to have AF coupling. Also, Thomson et al., after the magneto−structural study of several dinuclear copper(II) compounds involving a combination of a $\mu_{1,2}$-diazine and a $\mu_{1,1}$-N_3 azide bridges, suggest that the realm of the ferromagnetic coupling ceases for Cu−N−Cu angles greater than 108°.[5,6]

In this paper we have presented the synthesis and the structural and magnetic study of two new symmetrical [Cu-

---

(17) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

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

(19) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P.; Verdaguer, M. *Phys. Rev. B* **2000**, *61*, 54.

($\mu_{1,1}$-N$_3$)$_2$Cu]$^{2+}$ complexes [Cu$_2$($\mu_{1,1}$-N$_3$)$_2$(4-Etpy)$_4$(μ-NO$_3$)$_2$] (**1**) and [Cu$_2$($\mu_{1,1}$-N$_3$)$_2$(3-ampy)$_4$(μ-NO$_3$)$_2$]·C$_2$H$_5$OH (**2**), which present the lowest reported θ angles: 98.3(2) and 97.5(1)° for **1** and **2**, respectively, with the strongest calculated J values of 230.1 and 223.2 cm^{-1} for **1** and **2** respectively. These results are in accordance with the above-mentioned predictions for the lower θ region, but they remain to be confirmed experimentally in the higher θ region. To our knowledge, the copper(II) complex with the symmetrical [Cu($\mu_{1,1}$-N$_3$)$_2$Cu]$^{2+}$ core (or having as the bridge only one $\mu_{1,1}$-N$_3$ ligand and short Cu−N(azido distances)) and θ angles greater than 104−108° has not yet been synthesized.

Acknowledgment. This research was partially supported by CICYT (Grant PB96/0163) and OENB (Grants 6630 and 7967). F. A. Mautner and M. A. S. Goher thank Prof. C. Kratky and Dr. Belaj (University of Graz) for use of experimental equipment.

Supporting Information Available: Three X-ray crystallographic files, in CIF format, including atomic coordinates, thermal parameters, and a complete listing of bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991135C