complex $[Cu_4L_2(\mu_{1,1}\text{-}N_3)_2]\cdot5H_2O$ containing two azido (end-on or EO mode) and two alkoxo bridges, which presents an unusual open cubane core and displays an overall strong antiferromagnetic behavior (H_3L = *N*,*N*′-(2-hydroxylpropane-1,3-diyl)bis-salicylidene-imine).

It is noteworthy that only very few cases of the end-on azido-bridged polynuclear copper(II) complexes reported so far have shown antiferromagnetic coupling.[11,12] In the present complex, the Cu−N(azido)−Cu angles [101.5(1)° and 101.3(1)°] are close to the cutoff angle (104°) for ferromagnetic coupling.[13,14] The Cu−N(azido) bond distance is around 2.04 Å, which is very close to the critical distance for the ferromagnetic to antiferromagnetic crossover.[13,14] Indeed, the evaluation of this interaction yields a small value, while the dominant antiferromagnetic interaction in the complex is associated with the alkoxo bridges.[15,16]

Experimental Section

Caution! Azido complexes of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Spectral Characterization. All reagents and solvents were purchased from commercial sources and used as received. Elemental analyses (C, H, N, S) were carried out on a Perkin-Elmer 2400 series II analyzer. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR device, using the diffuse reflectance technique. X-band EPR spectra were recorded at room temperature and at 77 K on a JEOL RE2X electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. The ligand-field spectrum of the solid compound was recorded in the range 200−2000 nm on a Perkin-Elmer Lambda 900 UV−vis−NIR spectrometer in the diffuse reflectance mode with MgO as a reference.

Synthesis of the Ligand and the Copper Complex. The ligand H_3L was prepared by reaction of salicylaldehyde and 1,3-diamino-2-propanol in methanol by following the standard procedure.[17] The complex was synthesized as follows: to 20 mL of a methanolic solution of $Cu(NO_3)_2\cdot3H_2O$ (0.25 g, 1 mmol) was added 0.15 g (0.5 mmol) of H_3L dissolved in 20 mL of acetone, and the resulting solution was stirred for 20 min. Then, NaN_3 (0.27 g, 4 mmol) dissolved in 5 mL of H_2O was added slowly to the above mixture, and the resulting brown solution was stirred for another hour. The solution was left at room temperature, and dark prismatic crystals appeared after one week; they were collected by filtration and washed with small amounts of methanol (yield: 56%; 141.2 mg). Anal. Calcd for $C_{34}H_{30}Cu_4N_{10}O_6\cdot5H_2O$: C 40.0, H 3.9, N 13.7. Found: C 40.2, H 3.4, N 14.2. IR (solid) ν = 2059.0 (s), 1626.4 (s), 1600.2 (s), 1532.2 (m), 1445.9 (s), 1392.8 (w), 1304.4 (m), 1193.9 (m), 1147.4 (m), 1129.6 (m), 1027.4 (w), 894.0 (w), 755.0 (s), 460.0 (m) cm^{-1}.

Table 1. Selected Distances and Angles for the Complex $[Cu_4L_2(N_3)_2]\cdot5H_2O$

selected distance (Å)				selected angle (deg)	
Cu1−O1	1.905(2)	Cu2−O2	2.285(2)	Cu1−N1−Cu3	101.5(1)
Cu1−O2	1.977(2)	Cu2−O4	1.879(2)	Cu1−O2−Cu2	101.9(1)
Cu1−O5	2.329(2)	Cu2−O5	1.979(2)	Cu1−O5−Cu2	100.4(1)
Cu1−N1	2.057(2)	Cu2−N4	2.060(2)	Cu1−O2−Cu4	108.7(1)
Cu1−N7	1.914(2)	Cu2−N9	1.947(3)	Cu1−O5−Cu3	94.4(1)
				Cu2−N4−Cu4	101.3(1)
Cu3−O5	1.958(2)	Cu4−O2	1.971(2)	Cu2−O2−Cu4	96.0(1)
Cu3−O6	1.885(2)	Cu4−O3	1.874(2)	Cu2−O5−Cu3	111.6(1)
Cu3−N1	2.019(2)	Cu4−N4	2.039(2)		
Cu3−N10	1.922(2)	Cu4−N8	1.909(2)		
Cu1···Cu2	3.316(1)	Cu1···Cu3	3.156(1)		
Cu1···Cu4	3.208(1)	Cu2···Cu3	3.256(1)		
Cu3···Cu4	3.661(2)	Cu2···Cu4	3.170(1)		

Table 2. Crystallographic Data for the Complex $[Cu_4L_2(N_3)_2]\cdot5H_2O$

empirical formula	$C_{34}H_{30}Cu_4N_{10}O_6\cdot5H_2O$
fw	1018.92
cryst syst	monoclinic
space group	$P2_1/a$
a [Å]	26.442(5)
b [Å]	13.302(5)
c [Å]	12.119(5)
β [deg]	93.160(5)
V [Å^3]	4256(3)
Z	4
D_{calcd} [g cm^{-3}]	1.590
linear absorption coeff [mm^{-1}]	2.038
F(000)	2072
cryst size [mm^3]	0.14 × 0.17 × 0.24
index ranges	$-34 \leq h \leq 33$ $0 \leq k \leq 16$ $0 \leq l \leq 15$
θ range for data collection [deg]	1.54−27.5
reflns collected	26806
indep reflns	9415 (R_{int} = 0.0156)
obsd reflns [$I > 2\sigma(I)$]	6987
data/restraints/params	9415/0/511
GOF on F^2 [a]	1.196
final R indices (obsd data)[b]	R_1 = 0.0438, wR_2 = 0.0607
R indices (all data)[b]	R_1 = 0.0627, wR_2 = 0.0616
largest diff peak and hole [e/Å^{-3}]	0.342 and −0.208

[a] GOF $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Crystallographic Data Collection and Refinement. The molecular structure of $[Cu_4L_2(N_3)_2]\cdot5H_2O$ was determined by single-crystal X-ray diffraction methods. Crystallographic and experimental details for the structure are summarized in Table 2. Intensity data and cell parameters were recorded at room temperature (25 °C) on a Bruker AXS Smart 1000 single-crystal diffractometer (Mo Kα radiation) equipped with a CCD area detector. The data reduction

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was performed using the SAINT and SADABS programs.[18] The structure was solved by direct methods using the SIR97 program[19] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program.[20] All non-hydrogen atoms were refined with anisotropic atomic displacements with the exception of the oxygens of the five water molecules. The hydrogen atoms were included in the refinement at idealized geometries (C−H 0.95 Å) and refined "riding" on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2F_o^2 + (0.0069P)^2 + 2.4094P]$ (where $P = (F_o^2 + 2F_c^2)/3$).

Molecular geometry calculations were carried out using the PARST97 program.[21] Drawings were obtained by ORTEP3 in the WinGX suite.[22] All calculations were carried out on a DIGITAL Alpha Station 255 computer.

Results and Discussion

Synthesis. The title complex cannot be obtained in a straightforward preparation procedure by reaction of $Cu(NO_3)_2$, H_3L, and NaN_3 in 1:1:1 molar ratio in MeOH; in fact, no azido groups are present in the resulting product using this procedure (the azido stretch absorption around 2000 cm^{-1} in the IR spectrum of the compound is absent). However, reaction of $Cu(NO_3)_2$, H_3L, and sodium azide in 2:1:8 molar ratio leads to the azido-bridged copper(II) complex in a good yield. The strong absorption of the complex in the 2000−2100 cm^{-1} region of the IR spectrum clearly proves the presence of the azido groups, and also the elemental analysis is consistent with the formula $[Cu_4L_2(\mu_{1,1}\text{-}N_3)_2]\cdot5H_2O$.

Description of the Structure $[Cu_4L_2(\mu_{1,1}\text{-}N_3)_2]\cdot5H_2O$. The complex consists of a distorted cubic unit $Cu_4N_2O_2$ in which the four copper atoms are bridged two by two by nitrogen atoms (N1 and N4) from two azide ions in an end-on fashion and three by three by the alkoxo oxygen atoms (O2 and O5) from two anionic ligands L. An ORTEP drawing with the atomic labeling scheme is shown in Figure 1. Selected distances and angles are given in Table 1.

Among the four metal centers, Cu1 and Cu2 present clear pentacoordination. The basal plane around Cu1 and Cu2 involves one nitrogen atom from a bridging azide group, and an imine nitrogen, a phenolate oxygen, and the alkoxo oxygen of the same organic ligand. Their pentacoordination is completed, in the axial position, by the oxygen of the alkoxo group of the other organic ligand [Cu1−N1 2.057(2) Å, Cu1−N7 1.914(2) Å, Cu1−O1 1.905(2) Å, Cu1−O2 1.977(2) Å, Cu1−O5 2.329(2) Å; Cu2−N4 2.060(2) Å, Cu2−N9 1.947(3) Å, Cu2−O4 1.879(3) Å, Cu2−O5 1.979(2) Å, Cu2−O2 2.285(2) Å]. The geometry around Cu1 and Cu2 can be best described as square-pyramidal ($\tau_1 = 0.215$ and 0.267, where $\tau = 0$ and 1 are for the perfect square pyramidal and trigonal bipyramidal geometries, respectively[23]).

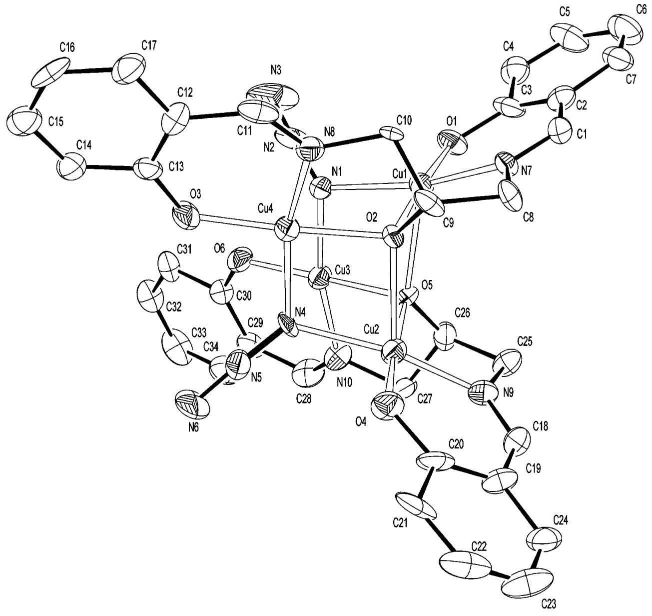

Figure 1. ORTEP view (20% probability) of the molecular complex $[Cu_4L_2(N_3)_2]\cdot5H_2O$ with the atomic numbering scheme. Hydrogens and lattice water molecules are omitted for clarity.

The Cu3 and Cu4 atoms show a planar arrangement in first approximation, consisting of one imino nitrogen atom, a phenolate oxygen, and the alkoxo oxygen from the same ligand, and one nitrogen atom from a bridging azido group [Cu3−N10 1.922(2) Å, Cu3−O6 1.885(2) Å, Cu3−O5 1.958(2) Å, Cu3−N1 2.019(2) Å; Cu4−N8 1.909(2) Å; Cu4−O3 1.874(2) Å, Cu4−O2 1.971(2) Å, Cu4−N4 2.039(2) Å]. The Cu3···N4 and Cu4···N1 axial contacts of 2.721(3) and 2.681(3) Å are very weak when compared with the Cu···N axial distances usually reported for square pyramidal arrangements around copper (so far, following a systematic research on the Cambridge Crystallographic Data File, the longest Cu···N axial distance reported in the literature is 2.653(2) Å for an intermolecular contact in the polymeric compound $(C_{24}H_{30}CuN_4O_8)_n$ [24]). Also, the Cu3 and Cu4 water contacts of 3.2 and 3.1 Å are longer then common coordination distances (see Figure S1a in the Supporting Information). Therefore, the coordination around Cu3 and Cu4 should be regarded as predominantly square planar, and consequently, the $Cu_4N_2O_2$ unit should be considered as an open cubane-like core. The latter consideration seems to be supported also by the Cu···Cu distances found in the cubic unit $Cu_4N_2O_2$. The Cu···Cu separation ranges from 3.156(1) to 3.170(1) Å for the N,O-bridged copper atoms (Cu1···Cu3 and Cu2···Cu4) and from 3.208(1) to 3.256(1) Å for the metal centers bridged by a single oxygen (Cu1···Cu4 and Cu2···Cu3) and is 3.316(1) Å for the O,O-bridged pentacoordinated metal ions (Cu1···Cu2). The Cu3···Cu4 separation of 3.661(2) Å, significantly larger with respect to that found for the nonbridged Cu atoms

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[3.38(1)−3.41(1) Å] in the open cubane Cu_4O_4 framework in the $[Cu_4(hpda)_4](ClO_4)_4\cdot H_2O$ [hpda = *N*-(2-hydroxyethyl)-1,3-propanediamine] complex,[25] further supports an open cubane-like configuration for our $Cu_4N_2O_2$ framework.

The orientation of the salicylideneimine moieties of each ligand L, with respect to the cubane faces, is completely different. The two salicylideneimine portions involved in the square-planar coordination around Cu3 and Cu4 are almost coplanar with the adjacent Cu_2NO face. The other two salicylideneimine moieties, involved in the coordination around Cu1 and Cu3, are opposite to the first ones with respect to the least-squares plane passing through Cu_2O_2, and they form a dihedral angle of nearly 60° with this latter face. They also form an angle of 60° with one another.

Also, C−H···N and C−H···O hydrogen bonds involving C−H groups and azide nitrogens from neighboring complexes or neighboring water molecules contribute to the crystal packing (for geometrical details, see Table S2 and Figure S1b in the Supporting Information). From the analysis of the intermolecular contacts, it appears that the oxygens of the water molecules are involved in hydrogen bonds as donor atoms among each other. These water molecules are also involved in hydrogen bonds as hydrogen donors with the oxygens of the four phenolate ligands [O5s···O3 2.837(4) Å, O5s···O6 2.820(4) Å, O2s···O1 2.797(4) Å, O4s···O4 2.772(4) Å, see Figure S1a in the Supporting Information]. In particular, the water oxygen O5s bridges two ligands probably also contributing to the stability of the complex. The fact that the hydrogens of these water molecules could not be calculated or located in the difference Fourier map prevents a detailed description of the geometrical parameters.

To the best of our knowledge, the title compound represents the first structurally characterized example of a tetranuclear copper(II) complex in which two azide groups and two 2*N*,3*O*-pentadentate ligands (involving an alkoxo oxygen and two imine nitrogens as central donors and two terminal phenolate oxygen donors) are coordinated to give a copper(II) complex with a distorted $Cu_4N_2O_2$ open single-cubane core. The Cu_2NO faces, roughly parallel to each other, are on the same side with respect to the least-squares plane passing through Cu_2O_2. The dihedral angles between the least-squares plane through Cu1Cu2O2O5 and the least-squares planes through Cu1Cu3N1O5 and Cu2Cu4O2N4 are 103.6(1)° and 102.0(1)°, respectively.

The only known example of a copper(II) complex containing $\mu_{1,1}$-azide nitrogens and μ_3-alkoxo oxygens in a cubane-type tetranuclear core is $[Cu_4(M3)_2(\mu_3\text{-}OEt)_2(\mu_2\text{-}N_3)_2(N_3)_2](MeOH)$, where M3 is a deprotonated macrocycle ligand.[26] This compound shows two dimeric units Cu_2O_2 associated in an axial fashion through two $\mu_{1,1}$-azides and two μ_3-alkoxides, to form a $Cu_4N_2O_4$ open "box-kite" arrangement of two fused cubes, each missing one apex. In this dicubane-type complex, the two Cu_2NO faces are on opposite sides with respect to the Cu_2O_2 face, which they share in the tetranuclear core.

In recent years, defective double-cubane structures with simultaneous $\mu_{1,1}$-azide and μ-O bridges similar to $[Cu_4(M3)_2(\mu_3\text{-}OEt)_2(\mu_2\text{-}N_3)_2(N_3)_2](MeOH)$ have been reported in the literature for tetranuclear nickel(II),[27] manganese(II),[28] and cobalt(II) complexes.[28,29] Face-shared dicubane-type structures with two missing vertices containing $\mu_{1,1}$-thiocyanate (or $\mu_{1,1}$-cyanate) and μ_3-O bridges have been found for manganese(II)[30] and cobalt(II)[31] complexes.

However, the different configuration of the tetranuclear dicubane-like core presented by all these cited compounds prevent any significant structural comparison with the open single-cubane complex reported here.

IR Spectroscopy, Ligand-Field, and X-Band EPR Spectra. The IR absorption band of the complex observed at 2059 cm^{-1} indicates the presence of the asymmetric stretch of an azido bridge, which is attributable to an end-on bridging mode.[32] The medium band at 1304 cm^{-1} is assigned to the azido symmetric stretching mode, $\nu_s(N_3)$. The absorption bands of the C=N group in the free ligand appear at 1631 and 1580 cm^{-1}, while these bands shift to 1626 and 1532 cm^{-1} upon coordination with copper.

The ligand-field spectrum of the complex in the solid state (diffuse reflectance) shows 4 bands centered at 268 nm (37.1×10^3 cm^{-1}), 354 nm (28.1×10^3 cm^{-1}), 445 nm (22.4×10^3 cm^{-1}), and 635 nm (15.6×10^3 cm^{-1}) in the range 200−2000 nm. The broad absorption band centered at 354 and 445 nm may due to the charge-transfer transitions of the azido nitrogens and phenolate or alkoxo oxygens to the copper ions.[33] The band centered at 635 nm is assigned to the d−d transitions.

X-band EPR spectra were recorded for the polycrystalline powder of the complex at room temperature and at 77 K, and no signal was obtained, which can be explained by the strong interactions between the copper(II) atoms, as evidenced by the magnetic susceptibility measurements.

Magnetic Susceptibility Measurements. The temperature dependence of the bulk magnetic properties of the title compound is shown in Figure 2. The product of the molar magnetic susceptibility χ_M decreases from ca. 1.54 cm^3 mol^{-1} K at 320 K (value close to the expected value for four uncoupled spin $^1/_2$ with $g = 2$, 1.5 cm^3 mol^{-1} K), first

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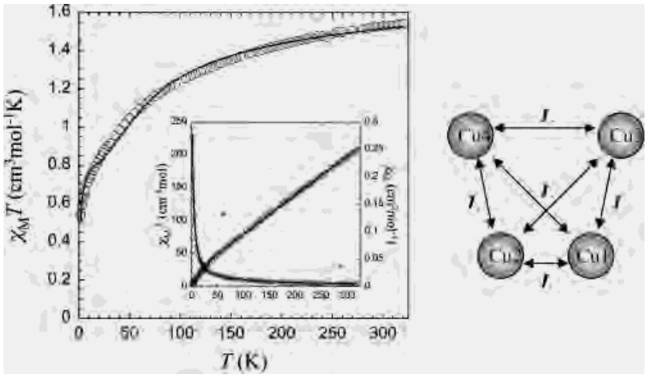

Figure 2. Temperature dependence of the magnetic properties of $[Cu_4L_2(N_3)_2]\cdot 5H_2O$ (left) and magnetic coupling scheme used for the fitting procedure (right), in which J_1 to J_4 represent the interaction parameters for each type of Cu(II) pair. Full lines represent the best fit obtained with the tetranuclear model described in the text.

gradually down to 150 K and then more markedly down to ca. 0.52 cm^3 mol^{-1} K at 2 K. To describe the magnetic properties of the title compound, the Heisenberg spin exchange Hamiltonian $\hat{H} = -2\sum_{i<j} J_{ij}\, \hat{S}_i \cdot \hat{S}_j$ was used, in which J_{ij} represents the exchange constant and the subscripts i and j number the pairwise interacting Cu(II) ions. Assuming that the pairs Cu4−Cu2/Cu1−Cu3 and Cu1−Cu4/Cu2−Cu3 are equivalent, respectively (similar Cu−O−Cu and Cu−N−Cu angles and Cu−O and Cu−N distances), the tetramer core presents a C_2 axis which simplifies the Hamiltonian to $\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) - 2J_2 \hat{S}_1 \cdot \hat{S}_2 - 2J_3(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3) - 2J_4 \hat{S}_3 \cdot \hat{S}_4$, with the numbering scheme given in Figure 2. The resulting energy matrix can be solved[16] and an expression for the molar magnetic susceptibility derived from the van Vleck equation (see Supporting Information). Since the structure is in fact an open cubane, the value of J_4 should be negligible. Indeed, in fitting the experimental data to eq S1 (which also includes a term for the temperature indepedent paramagnetism, TIP), only very small values with large errors are obtained for J_4. Thus, to limit the number of parameters, J_4 was fixed to 0 and g set to 2. It should be noted that a paramagnetic impurity was needed to obtain a correct fit. The resulting best parameters (corresponding to the full lines in Figure 2) were $2J_1/k_B = 10.8$ (7) K (or 7.5 cm^{-1}), $2J_2/k_B = -5.2$ (6) K (or -3.6 cm^{-1}), $2J_3 = -110$ (1) K (or -76.5 cm^{-1}), and TIP $= 3.1(1) \times 10^{-4}$ cm^3 mol^{-1} ($g = 2$).

These values are reasonable and can be rationalized in light of the structural parameters. The triply bridging oxygen atoms O2 and O5 correspond to the apical positions of Cu2 and Cu1, respectively, which are in a square-pyramidal environment. Therefore, no significant spin density is expected on this position, corresponding to the fully occupied d_{z^2} orbital. Thus, although the Cu1−O−Cu2 angles (100.4° and 101.9°) lie in the area for which strong antiferromagnetic interactions have been observed in alkoxo-bridged Cu(II) pairs,[15,34] only very small values would be expected for J_2, in agreement with the result found. On the other hand, the Cu1−O−Cu4 and Cu2−O−Cu3 alkoxo bridges correspond to basal positions. The large angles (108.7° and 111.6°, respectively) should thus produce very strong antiferromagnetic couplings. However, when the carbon carrying the alkoxo oxygen is out of the Cu−O−Cu plane, the extent of this coupling is known to be strongly reduced.[35] This appears also to be the case here, and the value of J_3 is reasonable for a C out of the plane by more than 50°.[35] Due to the long distances (semicoordination) of the azido bridging N-atoms with these Cu(II) atoms (N1−Cu4 2.722(3) Å and N4−Cu3 2.679(3) Å), the participation of an interaction pathway through the azido bridges to J_3 may likely be negligible with respect to the alkoxo pathway. Finally, the Cu2−Cu4 and Cu1−Cu3 pairs contain two different coupling pathways, being an end-on azido and an alkoxo bridge, corresponding to the interaction constant J_1. Previous studies showed that the nature of the coupling between two copper ions with an end-on azido bridge depends on two parameters:[36] (1) the Cu−N(azido)−Cu angle, and (2) the Cu−N(azido) bond distance.[13] If the Cu−N(azido)−Cu angle is in the range 96−104°, which is the case here (101.4° on average), the interaction should be moderately ferromagnetic here. It must be noted that such findings have been confirmed in almost all of the end-on azido-bridged Cu(II) multinuclear complexes reported so far, irrespective of their nuclearity,[13,37] with only very few exceptions.[11] Regarding the alkoxo-bridge in these pairs, the Cu−O−Cu angles should also produce weak ferromagnetic coupling.[35] Therefore, both pathways are in agreement with the value found for J_1. However, since the O2 and O5 oxygen atoms correspond to the apical position of, respectively, Cu2 and Cu1, the ferromagnetic coupling found here with $2J_1/k_B = 10.8$ K is most likely originating from the end-on azido bridge. Overall, the measure of the different coupling pathways obtained for the title compound is in very good agreement with its structural features. The dominant coupling corresponds to a widely open alkoxo bridge, whose strength is weakened by the constrained geometry of the alkoxo group (C atom out of the Cu−O−Cu plane), the resulting ground state of the tetranuclear complex being $S = 0$.

Concluding Remarks

The synthesis and structural and magnetic characterization of a novel tetranuclear copper(II) complex with alkoxo and end-on azido bridges have been presented. The originality of the open cubane structure lies in the fact that (1) O2 and O5 alkoxo ligands as μ_3-bridging groups involve two short and one long Cu−O distances, and (2) two azido ligands with a $\mu_{1,1}$-N_3 mode bridge copper(II) atoms (Cu1 and Cu3, and Cu2 and Cu4) in the cubane structure. The “open” cubane is due to the long distances between N4 and Cu3, and N1 and Cu4. The weak intermolecular hydrogen bonds

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involving C−H groups and azide nitrogens from neighboring complexes, or oxygens from crystallization water molecules, contribute to the crystal packing.

An overall antiferromagnetic behavior is observed, as a result of dominant antiferromagnetic interactions through alkoxo-bridges. The end-on azido bridge yields a weak ferromagnetic interaction, as expected for the Cu−N(azido)−Cu angles and Cu−N(azido) distances in the complex.

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Supporting Information Available: Additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC-239421 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat) + 44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.]

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