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Trinuclear N,N-Bridged Copper(II) Complexes Involving a Cu_3OH Core: $[Cu_3(\mu_3\text{-}OH)L_3A(H_2O)_2]A\cdot(H_2O)_x$ {L = 3-Acetylamino-1,2,4-triazolate; A = CF_3SO_3, NO_3, ClO_4; $x = 0, 2$} Synthesis, X-ray Structures, Spectroscopy, and Magnetic Properties

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The reaction of Haat [Haat = (3-acetylamino-1,2,4-triazole)] with aquated $Cu(CF_3SO_3)_2$, $Cu(NO_3)_2$, and $Cu(ClO_4)_2$, respectively, in water results in the trinuclear complexes $[Cu_3(OH)(aat)_3(CF_3SO_3)(H_2O)_2](CF_3SO_3)$ (**1**), $[Cu_3(OH)(aat)_3(NO_3)(H_2O)_2](NO_3)\cdot(H_2O)_2$ (**2**), and $[Cu_3(OH)(aat)_3(ClO_4)(H_2O)_2](ClO_4)$ (**3**). The synthesis, X-ray structure, and magnetic and spectroscopic properties of the three title complexes are described. The cation of the three complexes is trinuclear with a Cu_3OH skeleton which has the N−N diazine grouping of a triazole ring as bridge between each pair of copper atoms. The Cu_3OH units have an average Cu−O distance of 1.991(6) (**1**), 2.000(6) (**2**), and 2.007(6) (**3**) Å, an average Cu−Cu′ distance of 3.355(2) (**1**), 3.341(1) (**2**), and 3.371(3) (**3**) Å, and an average Cu−O−Cu′ angle of 114.6(3)° (**1**), 112.4(2)° (**2**), and 115.4(3)° (**3**). The existence of the Cu_3OH fragment is confirmed by a pseudotetrahedral oxygen environment, by detection of the OH hydrogen atom, and by stoichiometry. In the trinuclear unit the metal ions show, in the first approximation, a pseudo-square-planar pyramidal environment forming a CuN_2O_3 chromophore; three of the basal positions are occupied by N,N,O aat ligand atoms, the fourth one is occupied by the oxygen of the central OH group, and the apical site is occupied by an oxygen atom from a water molecule in the case of two of the copper(II) atoms and by an oxygen atom from the coordinating anion in the case of the third metal ion. The three compounds exhibit strong antiferromagnetic interaction, with similar J constants [$J = -197.7$ (**1**), $J = -190.9$ (**2**), $J = -198.2$ (**3**) cm^{-1}], reaching complete spin coupling at ca. 75 K (**1**)/55 K (**2**)/95 K (**3**). At very low temperature the magnetic moment (magnetic susceptibility) falls below that expected for one unpaired electron. Magnetic parameters are discussed on the basis of the structural results and compared with those reported in the literature for related trimeric Cu(II) compounds with N−O or N−N peripheral bridges. Solid state EPR spectra of the three complexes recorded at liquid N temperature show axial signals. Crystal data: $C_{14}H_{20}Cu_3F_6N_{12}O_{12}S_2$ (**1**) ($M_w = 917.16$) crystallizes in the monoclinic space group, $P2_1/c$, $Z = 4$, with cell dimensions $a = 13.080(2)$ Å, $b = 17.202(2)$ Å, $c = 13.840(2)$ Å, $\beta = 92.40(1)°$, and $V = 3111.3(7)$ Å^3, $D_{calcd} = 1.958$ Mg m^{-3}; the final agreement values were R1 = 0.0582 and wR2 = 0.1462 for 7107 unique reflections. $C_{12}H_{24}Cu_3N_{14}O_{14}$ (**2**) ($M_w = 779.07$) crystallizes in the triclinic space group, $P\bar{1}$, $Z = 2$, with cell dimensions $a = 9.647(2)$ Å, $b = 9.985(2)$ Å, $c = 15.314(2)$ Å, $\alpha = 84.080(10)$, $\beta = 87.694(10)$, $\gamma = 65.030(10)°$, and $V = 1330.1(4)$ Å^3, $D_{calcd} = 1.945$ Mg m^{-3}; the final agreement values were R1 = 0.0397 and wR2 = 0.0950 for 7728 unique reflections. $C_{12}H_{20}Cl_2Cu_3N_{12}O_{14}$ (**3**) ($M_w = 817.92$) crystallizes in the monoclinic space group, $P2_1/a$, $Z = 4$, with cell dimensions $a = 14.238(5)$ Å, $b = 16.387(6)$ Å, $c = 11.678(4)$ Å, $\gamma = 90.45(2)°$, and $V = 2724.6(18)$ Å^3, $D_{calcd} = 1.994$ Mg m^{-3}; the final agreement values were R1 = 0.0616 and wR2 = 0.1279 for 4038 unique reflections.

Introduction

Trinuclear copper(II) compounds of different kinds have been extensively studied; those of the triangular type have generated great interest, especially concerning their magnetic, structural, and redox characteristics, in relation to their role in the active site of multicopper oxidases and in homogeneous catalysis.[1−4] In the recently reported crystal structure of the oxidized ascorbate oxidase (resolution 2.5 Å) an angled triangular array of copper atoms has been detected with Cu−Cu separations lying in the range 3.66−3.90 Å at an average distance of 3.7

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Å.[5] It seems thus of importance to investigate low-molecular-weight trinuclear copper(II) compounds that model those active sites.

μ-Hydroxo or μ-oxo ions have generally been observed as central bridging ligands. The existence of the M_3O core held by peripheral bridging ligands is well documented in the chemistry of, e.g., iron(II−III) and chromium(III)[6] but not in that of copper(II). Actually, only a few complexes with a $Cu_3O(H)$ core held by pheripheral bridging ligands have been described so far; these reports involve *N,O*-oximate[1,7−10] or ketonic oxygen bridges;[11] to our knowledge, in the literature only three complexes containing a N,N bridge are known in which the bridge belongs to a pyrazole ring. Two of the three latter compounds[12a,13] were synthesized by *oxidation* of a Cu(I) compound in the presence of the appropriate ligand; the third one[12b] is a hexacopper(II) complex made up of two trimeric units in which the trinuclear $[Cu_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ core involved is the same previously identified in the other two compounds. This paper describes a new example of N,N-bridged triangular copper(II) species, the most remarkable differences with respect to the analogous pyrazole derivatives being that (a) the N,N bridging is the N1,N2 part of a 1,2,4-triazole ring and (b) the triazole ring belongs to a chelating ligand, in such a way that the square-planar arrangement around the copper(II) is completed by a donor atom (an oxygen) provided by the *same* bridging ligand; in addition, the complexes were obtained directly from the corresponding copper(II) salts (which means that the identification problem of the μ-hydroxo or μ-oxo ligand does not occur). It should be noted that cyclic trinuclear compounds containing a triazole ligand had already been obtained before. Vreugdenhil[14] has described related cyclic trimeric isostructural compounds with the formula $[Cu_3(\mu_3\text{-OH})(hppt)_3(A)_2](H_2O)_x$ [hppt = 3-(2-hydroxyphenyl)-4-phenyl-1,2,4-triazole; A = NO_3, ClO_4, CF_3SO_3, x = 4, 2, 3]. The crystal structure of the nitrate complex was solved, although it showed some disorder problems. Vreugdenhil's results will be compared with ours in Results and Discussion.[46]

The present work stems from our study on the reactivity of copper(II) salts with Haat. The ligand Haat (3-acetylamino-1,2,4-triazole) belongs to the group of the 1,2,4-triazole derivatives, studied as precursors of compounds with importance in medicine, biology, and industry.[15] Numerous papers on their coordination chemistry have shown that they can lead to a wide variety of compounds depending upon the nature of the substituent; so, mononuclear, dinuclear, linear trinuclear, and tetranuclear complexes can be found described in the literature.[16−19] The ligand Haat is an especially versatile ligand due to the acetylamino substituent, which contains donor atoms itself, and to the possibility of dehydronation (it possesses two potential acidic hydrogens), which enlarges the coordination ability. Until now, only mononuclear compounds of Haat had been reported: the series $[M(Haat)_2(H_2O)_2]A{\cdot}(H_2O)_x$ [M = Cu(II), Ni(II), or Co(II); A = Cl, Br, or SO_4][16,17] and the couple of linkage isomers $[Cu(Haat)_2(N\text{-NCS})_2]$ and $[Cu(Haat)_2(S\text{-NCS})_2]$,[18] all of them containing the neutral ligand.

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This paper deals with the synthesis, structure, spectroscopy, and magnetic properties of three cyclic trimers, of formula $[Cu_3(\mu_3\text{-}OH)(aat)_3A(H_2O)_2]A\cdot(H_2O)_x$ [A = NO_3, CF_3SO_3, ClO_4; x = 0, 2], where aat stands for the former ligand but monodehydronated. The coordination behavior of the ligand will be compared with that described for the mononuclear compounds.[16−18] The relation between structure and magnetic parameters in the three complexes will be discussed and compared with the data available in the literature for similar cases.

Experimental Section

Materials. The ligand Haat has been synthesized as indicated by van den Bos[20] and recrystallized from boiling water. (In the previous literature (refs 16−18), the ligand 3-acetylamino-1,2,4-triazole was abbreviated as aat; in the present paper, aat refers to the same ligand but monodehydronated (L = 3-acetylamino-1,2,4-triazolate); so that, from now we will refer to the non-dehydronated ligand as Haat). **CAUTION**! Perchlorate derivatives may detonate upon scraping or heating.

Synthesis of $[Cu_3(OH)(aat)_3(CF_3SO_3)(H_2O)_2](CF_3SO_3)$ (1). Solid Haat (2 mmol) was added to an aqueous solution of $Cu(CF_3SO_3)_2$ (4 mmol in 20 mL) (molar ratio Haat:Cu = 2:1). After stirring for ca. 20 min, the resulting solution was filtered and allowed to stand at room temperature. Within ca. 20 days dark blue irregularly shaped single crystals appeared; they were isolated by filtration and washed with water. (Yield: ca. 70%.)

Synthesis of $[Cu_3(OH)(aat)_3(NO_3)(H_2O)_2](NO_3)\cdot(H_2O)_2$ (2). Solid Haat (2 mmol) was added to an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (4 mmol in 40 mL) (molar ratio Haat:Cu = 2:1). After stirring for ca. 30 min, the resulting solution was filtered and allowed to stand at room temperature. Within ca. 20 days, dark blue prismatic shaped single crystals appeared; they were collected on a filter paper and washed with water. *Note*: different mixtures of Haat and $Cu(NO_3)_2\cdot 3H_2O$, always in the ratio 2:1 but with different degrees of dilution, had to be used in order to obtain *only* crystals of **2** as, in the first trials, a light blue microcrystalline product was formed from the starting solution together with crystals of **2**. This light blue complex is infrared isostructural with previously isolated monomeric Haat−copper(II) compounds.[16,17] In the case of **1**, however, a light blue impurity was seldom detected. (Yield: ca. 50%.)

Synthesis of $[Cu_3(OH)(aat)_3(ClO_4)(H_2O)_2](ClO_4)$ (3). Solid Haat (2 mmol) was added to an aqueous solution of $Cu(ClO_4)_2\cdot 6H_2O$ (4 mmol in 25 mL) (molar ratio Haat:Cu = 2:1). After stirring for ca. 30 min, the resulting solution was filtered and allowed to stand at room temperature. From this solution were obtained crystals of several different shapes: first, big flattened light blue crystals (as it happens with synthesis of **2**, these light blue crystals are infrared isostructral with the monomeric Haat−copper(II) compounds);[16,17] then, among those crystals, other smaller, violet ones could be observed; later on, the former crystals redissolved and blue needles appeared; only after ca. 2 months did elongated prismatic dark blue crystals of **3** start to be formed. Within ca. 5 months crystals of **3** were the main product present in solution. They were collected by filtration and washed with water. (Yield: ca. 60%.)

Analysis. Calcd for $C_{14}H_{20}Cu_3F_6N_{12}O_{12}S_2$ (**1**) (M_w = 917.13): C, 18.3; H, 2.2; N, 18.3; S, 7.0; F, 12.4; Cu, 20.8.7. Found: C, 18.3; H, 2.2; N, 18.3; S, 7.1; F, 12.3; Cu, 20.8. Calcd for $C_{12}H_{24}Cu_3N_{14}O_{14}$ (**2**) (M_w = 778.69): C, 18.5; H, 3.1; N, 25.2; Cu, 24.5. Found: C, 18.5; H, 3.1; N, 25.3; Cu, 24.3. Compound **3** was not analyzed other than by X-ray analysis, shown below.

Physical Measurements. Elemental analyses were performed by the Microanalytical Laboratory of University College of Dublin, Ireland. Infrared spectra were obtained with a Perkin-Elmer model 580B IR spectrophotometer in the region 4000−180 cm^{-1} as KBr pellets and in Nujol. Ligand field spectra were registered in the region 28000−4000 cm^{-1} on a Perkin-Elmer 330 UV−vis spectrophotometer, by the use of the diffuse-reflectance technique with MgO as a reference. EPR spectra on powdered and solution samples were recorded at X-band frequencies on a JEOL JES-RE2X ESR spectrometer using an ESR900 continuous-flow cryostat. NMR spectra were obtained on a Bruker S4 200 spectrometer. Magnetic susceptibilities of solid compounds were measured from 290 to 4 K with a fully automatized pendulum type magnetometer (MANIC DSM8) equipped with a continuous helium flow cryostat and Drusch EAF 16UE electromagnet operating at ca. 15000 G. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal tables. The TIP correction was -100×10^{-6} cm^3 mol^{-1} (per copper atom). Magnetic data were fitted to the theoretical expressions by means of a subroutine, using the REGRES computer program.[21] All the parameters (J and g) were varied independently during the fitting procedure. This routine minimizes the function $R = \sum_i[(\chi_i^{obs} - \chi_i^{calc})^2/(\chi_i^{obs})^2]$.

Crystallography. X-ray Data Collection, Structure Determination, and Refinement of Complexes 1, 2, and 3. Irregularly (**1**), prismatic (**2**), and elongated prismatic (**3**) shaped crystals, dark blue (**1**, **2**) and blue (**3**) colored, were selected and sealed in glass capillaries. The crystallographic data are summarized in Table 1. Accurate unit-cell parameters were determined by least-squares refinement of the setting angles of 25 (**1**, **2**) and 30 (**3**) randomly distributed and carefully centered reflections with θ in the ranges 10−12° (**1**, **2**) and 19−31° (**3**). The data collection was performed on CAD-4 Enraf Nonius (**1**, **2**) and Siemens AED (**3**) diffractometers by the $\omega/2\theta$ (**1**, **2**) and $\theta/2\theta$ (**3**) scan modes, at 293 K. One standard reflection was monitored every 100 measurements, and no significant decay was noticed over the time of data collection for the three compounds. The individual profiles have been analyzed following the method of Lehmann and Larsen.[22] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied for **3** (maximum and minimum values for the transmission factors were 1.0 and 0.652).[23] The three structures were solved by direct methods (SIR92)[24] and refined first isotropically and then anisotropically by full-matrix least-squares using the SHELXL-97 program,[25] for all the non-hydrogen atoms apart from the methyl carbons C(14), C(24), C(34) and the oxygen atoms of the perchlorate anions for **3**. For all three compounds, the hydrogen atoms were placed at their geometrically default-distance calculated positions and refined riding on their parent atoms, apart from those of the water molecules that were located in the ΔF maps and refined isotropically.

All calculations were carried out on the ENCORE 91 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma. The programs Parst,[26] ORTEP,[27] and PLUTO[28] were also used. The final atomic coordinates are provided in the Supporting Information.

Results and Discussion

Ligands and Complexes. The compounds described in the present study are clearly different from those previously synthesized with the same ligand [Haat], both in the stoichiometry and in the coordination mode exhibited by the ligand. In the two kinds of monomers reported, the *neutral* ligand forms a six-membered chelate ring with the metal through the donor atoms O^1 and N^3. In the trimers, where the ligand is *dehydronated* by loss of the active hydrogen of the triazole,[17] the six-membered chelate ring is formed with O^1 and one of the two

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Table 1. Crystal Data and Structure Refinement for Compounds **1**, **2**, and **3**[a]

	1	**2**	**3**
empirical formula	$C_{14}H_{20}Cu_3F_6N_{12}O_{12}S_2$	$C_{12}H_{24}Cu_3N_{14}O_{14}$	$C_{12}H_{20}Cl_2Cu_3N_{12}O_{14}$
fw	917.16	779.07	817.92
temp (K)	293(2)	293(2)	293(2)
wavelength (λ)	0.71073	0.71073	1.54184
crys syst, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/a$
unit cell dimens			
a (Å)	13.080(2)	9.647(2)	14.238(5)
b (Å)	17.202(2)	9.985(2)	16.387(6)
c (Å)	13.840(2)	15.314(2)	11.678(5)
α(deg)		84.080(10)	
β(deg)	92.40(1)	87.694(10)	90.45(2)
γ(deg)		65.030(10)	
vol (Å^3)	3111.3(7)	1330.1(4)	2724.6(18)
Z, calcd density (Mg/m^3)	4, 1.958	2, 1.945	4, 1.994
abs coeff (mm^{-1})	2.277	2.469	5.331
F(000)	1828	786	1636
cryst size (mm)	0.15 × 0.20 × 0.28	0.21 × 0.30 × 0.35	0.18 × 0.22 × 0.37
θ range for data collection (deg)	2.37−27.47	2.26−29.97	3.79 to 59.99
index ranges	$-16 \le h \le 16, 0 \le k \le 22, 0 \le l \le 17$	$-13 \le h \le 13, -13 \le k \le 14, 0 \le l \le 21$	$-15 \le h \le 15, 0 \le k \le 18, 0 \le l \le 13$
reflns collected/unique	7107/7107	7728/7728	4252/4038
refinement meth		full-matrix least-squares on F^2	
data/restraints/params	7107/342/443	7728/8/412	4038/0/336
goodness-of-fit on F^2	0.963	1.027	0.694
final R indices [$I > 2\sigma(I)$] (R1, wR2)	0.0582, 0.1462	0.0397, 0.0950	0.0616, 0.1279
R indices (all data) (R1, wR2)	0.1960, 0.2086	0.1090, 0.1256	0.1647, 0.1416
extinction coeff	0.0012(3)		
largest diff peak and hole (e Å^{-3})	0.700 and −0.627	0.766 and −0.916	0.637 and −0.521

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$, R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

N-diazinic atoms [N^1], the second N-diazinic atom [N^2] interacting with the other metal ion; so, the dehydronated aat acts as a tridentate chelating and bridging ligand.

It is clear that the *dehydronation* enlarges the coordination properties of the ligands. On the other hand, as widely proved,[14,19] in the triazole ligand derivatives also the *length* of the chelating substituent on the ring is a decisive factor. In this sense, complexes **1**, **2**, and **3** support Vreugdenhil's suggestion that cyclic trinuclear compounds as obtained with hppt [3-(2-hydroxyphenyl)-4-phenyl-1,2,4-triazole][14] most likely can only exist with triazole ligands that can form *six-membered* chelating rings.[47] In comparable trinuclear compounds with *N*,*O*-oximate bridging ligands, however, the chelating ring formed consists only of *five* members.[1] Baral et al.[10] already pointed out that in the latter type of ligand the presence of two carbon atoms away from a potentially donor nitrogen atom would be a general feature of the systems that form this kind of complex with the $Cu_3O(H)$ core.

Description of the Structures. The crystal structures of the trimers are built up by $[Cu_3(\mu_3\text{-OH})(aat)_3A(H_2O)_2]^+$ [A = CF_3SO_3, NO_3, ClO_4] cations and one uncoordinated (in a first approach) A anion per cation, required by stoichiometry. In the case of the nitrate complex, there are two extra crystallization water molecules in the lattice. The cyclic trinuclear units of copper(II) are centered about a pseudo-3-fold axis passing through the hydroxyl OH bond, so that the three copper atoms fall at the corners of an almost equilateral triangle. The average Cu−Cu′ distances are 3.355(2) Å (for **1**), 3.341(1) Å (for **2**), and 3.371(1) Å (for **3**). Each unit is chiral, having only pseudo-C_3 symmetry. Figures 1 (**1**), 2 (**2**), and 3 (**3**) show ORTEP drawings of the coordination polyhedra of the three compounds, respectively, with the labeling systems used. Selected bond lengths and bond angles are listed in Table 2.

In the trimeric units the copper atoms are held together by two distinct bridging systems: (i) the oxygen atom of the tridentate hydroxy group, placed out of the plane defined by the Cu_3 triangle by 0.473(6) Å (**1**), 0.564(3) Å (**2**), and 0.433(6) Å (**3**), with an average distance from each of the copper atoms of 1.991(6) Å (**1**), 2.000(6) Å (**2**), and 2.007(6) Å (**3**); and (ii) three pseudo-symmetry-related aat molecules each of which behaves both as bidentate chelate to one of the copper atoms (via the O carbonyl and the N^1 triazole atom) and as a Cu−Cu bridge (via the N^1,N^2-diazinic group).

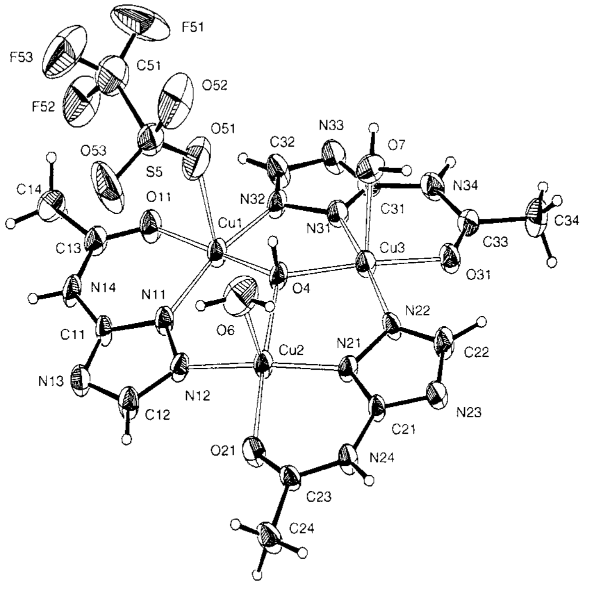

Figure 1. ORTEP representation of one isomer of $[Cu_3(OH)(aat)_3(CF_3SO_3)(H_2O)_2]^+$ (**1**) showing the atom-labeling scheme.

(a) The Copper Environment. The geometry at each copper(II) ion is best described as a distorted (4 + 1) (NN′OO′ + O″) square-based pyramid. The four atoms constituting the basal plane are the O carbonyl atom and a N triazole atom from one

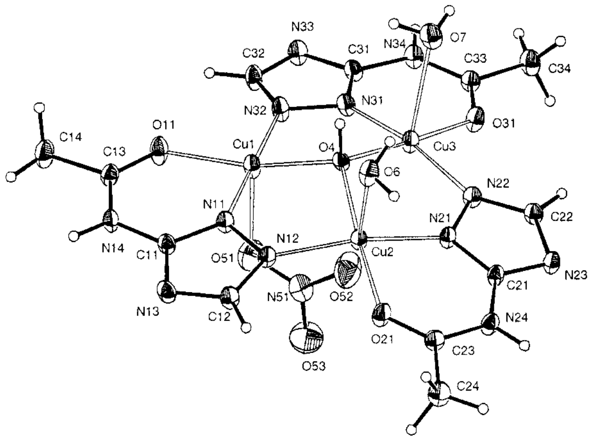

Figure 2. ORTEP representation of one isomer of $[Cu_3(OH)(aat)_3(NO_3)(H_2O)_2]^+$ (**2**) showing the atom-labeling scheme.

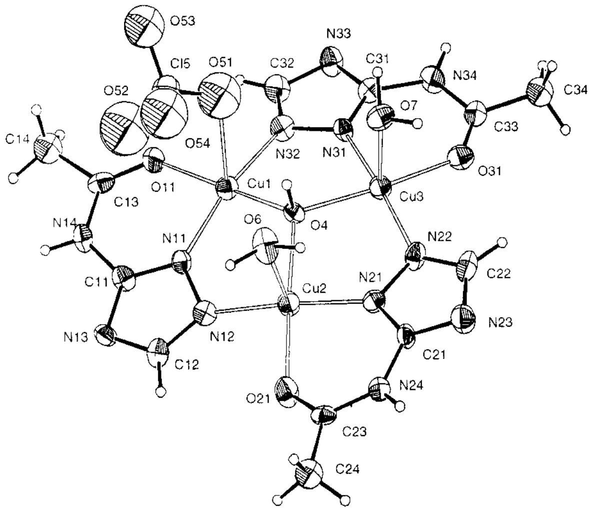

Figure 3. ORTEP representation of one isomer of $[Cu_3(OH)(aat)_3(ClO_4)(H_2O)_2]^+$ (**3**) showing the atom-labeling scheme.

aat ligand, a N triazole atom from the adjacent aat molecule, and the O atom from the central hydroxy group. The three axial sites are occupied by one O triflate (**1**)/nitrate (**2**)/perchlorate (**3**) atom and two O water atoms. Moreover, in all three compounds a sixth position of coordination is achieved for Cu(2) by an O anion atom at semibonding distances. Notice that, unlike the reported trinuclear copper(II) complexes,[1,7−13] which contain always the μ_3-OH group trans to N atoms, the present trimers show the hydroxyl group trans to O atoms (as the compound described by Vreugdenhil).[14,48] In the basal plane, the average bond distances (Å) are Cu−N(1) = 1.905(6) (**1**)/1.912(3) (**2**)/1.902(9) (**3**), Cu−N(2) = 1.949(7) (**1**)/1.945(3) (**2**)/1.949(9) (**3**), Cu−O(1) = 1.989(6) (**1**)/1.985(3) (**2**)/1.970(8) (**3**), and Cu−O(H) = see above. The Cu−N distances are shorter than the Cu−O ones, as expected. All these distances are normal when compared with those of the literature.[1,12−14] As for the axial donor atoms, the two copper−O_{water} bond lengths are similar in each compound and the average values are comparable in **1** and **3** [2.29(8) vs 2.308(7) Å] and significantly elongated in **2** [2.425(4) Å]; the corresponding copper−O_{anion} distances, similar in **1** and **2** [2.416(8) and 2.340(4) Å], are significantly shorter than the corresponding distance in **3** [2.717(13) Å]. The last bond length confirms the scarce basic character of the perchlorate anion.

As indicated, in the three compounds Cu(2) completes its coordination to octahedral (highly tetragonally distorted); the sixth position is occupied by O(63^I) (I: $x, -y + {}^1/_2, +z - {}^1/_2$) (from a “noncoordinating” triflate) in **1**, by O(52) (from the same coordinating nitrate which binds Cu(1) in **2**, and by O(81) (from the “noncoordinating” perchlorate) in **3**, with distances of 2.67(1), 2.88(1), and 2.78(1) Å, respectively. In the case of **3**, the Cu(1)−O(51) distance is comparable to the Cu(2)−O(81) one and could also be regarded as a semibonding interaction; so, with this criterion, in **3** Cu(1) is coordinated in an almost square-planar manner.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, and **3**

complex	1	2	3
Cu(1)−N(11)	1.897(6)	1.908(3)	1.898(9)
Cu(1)−N(32)	1.930(7)	1.938(3)	1.941(9)
Cu(1)−O(11)	1.967(5)	1.986(3)	1.963(7)
Cu(1)−O(4)	1.977(5)	2.034(3)	1.963(6)
Cu(1)−O(51)	2.416(8)	2.340(4)	2.717(13)
Cu(2)−N(21)	1.906(6)	1.919(3)	1.889(9)
Cu(2)−N(12)	1.955(6)	1.943(3)	1.928(9)
Cu(2)−O(4)	1.998(5)	1.997(2)	2.004(6)
Cu(2)−O(21)	2.002(5)	1.988(3)	1.961(8)
Cu(2)−O(6)	2.306(8)	2.421(4)	2.294(7)
Cu(3)−N(31)	1.912(6)	1.910(3)	1.920(8)
Cu(3)−N(22)	1.963(6)	1.953(3)	1.978(8)
Cu(3)−O(31)	1.999(6)	1.981(3)	1.987(8)
Cu(3)−O(4)	2.008(5)	1.999(2)	2.014(6)
Cu(3)−O(7)	2.274(7)	2.430(4)	2.322(7)
N(11)−Cu(1)−O(11)	88.3(2)	87.43(12)	88.7(3)
N(32)−Cu(1)−O(11)	91.5(2)	93.02(12)	94.2(4)
N(11)−Cu(1)−O(4)	89.3(2)	88.64(12)	88.9(3)
N(32)−Cu(1)−O(4)	92.1(2)	90.79(12)	89.9(3)
N(11)−Cu(1)−O(5)	100.9(3)	90.02(14)	106.2(4)
N(32)−Cu(1)−O(5)	95.1(3)	90.46(15)	87.5(4)
O(11)−Cu(1)−O(51)	92.9(3)	89.85(14)	97.3(4)
O(32)−Cu(1)−O(51)	82.8(3)	108.30(12)	76.7(3)
N(21)−Cu(2)−O(4)	89.2(2)	89.67(11)	89.9(3)
N(12)−Cu(2)−O(4)	90.7(2)	91.43(12)	91.1(3)
N(21)−Cu(2)−O(21)	87.0(2)	87.61(12)	87.7(4)
N(12)−Cu(2)−O(21)	93.2(2)	91.80(12)	91.6(4)
N(21)−Cu(2)−O(6)	93.3(3)	98.38(13)	91.6(3)
N(12)−Cu(2)−O(6)	95.4(3)	95.89(13)	96.9(3)
O(4)−Cu(2)−O(6)	85.5(3)	91.71(11)	82.7(3)
O(21)−Cu(2)−O(6)	93.6(3)	86.35(12)	95.0(3)
N(31)−Cu(3)−O(31)	87.3(3)	87.17(12)	86.7(3)
N(22)−Cu(3)−O(31)	92.9(2)	91.87(12)	94.8(3)
N(31)−Cu(3)−O(4)	89.0(2)	89.47(12)	87.2(3)
N(22)−Cu(3)−O(4)	89.8(2)	91.51(12)	91.1(3)
N(31)−Cu(3)−O(7)	92.6(3)	91.61(13)	100.4(3)
N(22)−Cu(3)−O(7)	94.7(3)	101.47(13)	87.2(3)
O(31)−Cu(3)−O(7)	98.0(3)	88.53(12)	95.7(3)
O(4)−Cu(3)−O(7)	89.0(2)	91.09(11)	86.7(3)

When the angles of the coordination polyhedron are considered, the distortion of the metal environment is also evident (see Table **2**). In the basal plane, in general, the angle O(1)−Cu−N(2), where the coordinating atoms are from different ligands, exhibits the highest values (from 94.8(3)° to 91.5(2)°), and the angle O(1)−Cu−N(1), the smallest (from 86.7(3)° to 88.7(3)°).

The four atoms that define each of the three basal planes around the metal ions deviate significantly from planarity (only the O4 N22 N31 O31 atoms of **1** can be considered perfectly coplanar), their main deviation from the least-squares plane passing through their positions being 0.195(7) (**1**), 0.180(4) (**2**), and 0.215(9) (**3**) Å. The copper atoms lie not in the basal plane but slightly out of it at the following distances: 0.072(2), 0.055(2), and 0.125(2) Å in **1**; −0.186(1), 0.085(1), and 0.092(1) Å in **2**; 0.029(2), 0.034(2), and 0.071(2) Å in **3**.

(b) The μ_3-OH and N−N Bridges. The presence of the ligand OH^- has been confirmed, following the criteria described

Table 3. Comparison of Structural Parameters Concerning the μ_3-OH and N−N/N−O Bridges in $Cu_3N_6(OH)/Cu_3N_3O_3(OH)$ Trinuclear Clusters (Order: Decreasing O(H)···Cu_3 Distance/Increasing Cu−O(H)−Cu′ Angle, and Compounds of This Work at the End)

param	**E**[a] N−O_{i-o}[b]	**F** N−O_{i-o}	**D** N−N_{pz}	**C** N−N_{pz}	**A** N−N_{tz}	**B** N−N_{pz}	**2** N−N_{tz}	**1** N−N_{tz}	**3** N−N_{tz}
Cu(1)−O(H)−Cu(2)/°							111.5(2)	115.4(3)	115.8(3)
Cu(1)−O(H)−Cu(3)/°							111.6(2)	114.7(2)	117.1(3)
Cu(2)−O(H)−Cu(3)/°							114.2(2)	113.6(2)	113.4(3)
Cu−O(H)−Cu′/° (av)	108.8(3)	111.1(3)	109.6(2)	111.2(9)	112.1(3)	114.5(1)	112.4(2)	114.6(3)	115.4(3)
O(H)···Cu_3 plane/Å	0.695	0.60		0.605	0.576(8)	0.478	0.564(3)	0.473(6)	0.433(6)
Cu−O(H)/Å (av)	1.964(6)	1.967(6)	1.992(4)	2.00(2)	2.013(7)	1.994(3)	2.000(6)	1.991(6)	2.007(6)
Cu−Cu′/Å (av)		3.245(2)	3.251(1)	3.303(4)	3.341(2)	3.351(7)	3.341(1)	3.355(2)	3.371(3)
Cu−N/O/Å (av)[c]	1.958(8) 1.955(6)	1.969(8) 1.935(6)	1.957(4)	1.95(2)	1.95(1)	1.945(4)	1.928(3)	1.927(7)	1.926(9)
N−N′/O/Å (av)[c]	1.343(8)		1.356(8)		1.38(1)	1.357(6)	1.369(4)	1.374(8)	1.378(1)
$-J^d/cm^{-1}$	244		140		191.2	200(ca.)	190.9	197.7	198.2
ref	9	1	13	12b	14	12a	t.w.	t.w.	t.w.

[a] **A** = $[Cu_3(\mu_3\text{-OH})(hppt)_3(NO_3)_2](H_2O)_4$ [hppt = 3-(2-hydroxyphenyl)-4-phenyl-1,2,4-triazole]; **B** = $[Cu_3(\mu_3\text{-OH})(pz)_3(NO_3)(Hpz)_2](NO_3)\cdot H_2O$; **C** = $[Cu_3(\mu_3\text{-OH})(pz)_3(\mu_4\text{-}NO_3)(Hpz)_3]_2(\mu\text{-}NO_3)_2$; **D** = $[Cu_3(\mu_3\text{-OH})(pz)_3(py)_2Cl_2]$; **E** = $[Cu_3(\mu_3\text{-OH})L_3(ClO_4)]ClO_4$ [HL=3-(phenylimino)butanone 2-oxime]; **F** = $[Cu_3(\mu_3\text{-OH})L_3(ClO_4)_2(H_2O)]$ [HL = 3-(benzilimino)butanone 2-oxime]; **1**, **2**, and **3**, this work. [b] i−o = imino-oximato, pz = pyrazole, tz = triazole. [c] Distances in the nine-membered {Cu−N−N′/O}$_3$ ring: Cu−N and N−N′ in pz, tz; Cu−N/Cu−O and N−O in i−o ligands. [d] Defined as in ref 13; the reported values of *J* from the literature have been modified according to the definition used in this paper (see eq 1).

in the literature,[9,13] by (a) the location of the hydrogen atom at the expected position in the final difference Fourier map, (b) the electroneutrality of the crystal, and (c) the refined Cu−O(H) distances and Cu−O(H)−Cu′ angles, which, on the basis of the trends observed in similar structures,[13] agree well with a roughly tetrahedral/pseudotetrahedral sphere of Cu, Cu, Cu, H ligands around the oxygen.

Table 3 displays the structural parameters concerning the μ_3-OH bridge as well as the Cu−Cu, Cu−N, and N−N distances of the nine-membered {Cu−N−N}$_3$ ring, for several triangular copper(II) compounds with the Cu_3OH core. It includes the four compounds so far described with N,N peripheral bridges:[49] **A**, a *triazole* derivate (its study has not been reported in a journal,[14] but the corresponding data have been added in the table because of its obvious interest); **B**, **C**, and **D**, three *pyrazole* derivatives; the compounds of the present work, **1**, **2**, and **3**, with a N−N *triazole* bridge; and two complexes with N,O bridges, **E** and **F**, added for comparison purposes (and selected for being the two most similar ones to **1**, **2**, and **3)**.

Comparison of the data of Table 3 illustrates the above-mentioned trend: a larger average Cu−O(H)−Cu′ angle (**3** > **1** > **2**) corresponds to a larger sp^2 character of the O(H) atom and so to a higher Cu_3O planarity (and obviously a shorter O···Cu_3 plane distance (**3** < **1** < **2**)). One could expect that a shorter O(H)···Cu_3 plane distance (or a more *oxo* character of the oxygen) would be followed by a shorter Cu−O(H) bond length, but this distance is almost equal in the three compounds and also in the literature compounds **A**, **B**, **C**, and **D**. The slightly shorter bond in compounds **E** and **F** must be due to the presence of a different peripheral bridge. On the other hand, Table 3 also shows that the nonbonding distances between adjacent Cu atoms are comparable to those observed in the other Cu_3 systems; higher planarity gives longer Cu−Cu′ distances (**3** > **1** > **2**), indicative of a slightly expanded nine-membered ring.

Spectroscopic and Magnetic Measurements. (a) IR Spectra. A search revision indicates that distinguishing the μ_3-OH group from the corresponding ν(O−H) IR band is not unambiguous.[1,11a,12a,13,29] In certain cases this is contradictory,[1,13] although its absence or presence is considered an important point to discriminate between OH^- and O^{2-} groups. The main problem is that the referred compounds very often contain also coordinating and noncoordinating water molecules.[1] Besides, the possible H-bonds in which the hydroxy group and/or the water molecules may be involved (and that are often neglected) make the assignment even more ambiguous. These limitations being taken into account, the following attempt at assigning the mentioned bands has been made: in the case of the triflate trimer (compound **1**), a clearly defined band is observed in the expected region with two maxima at 3505 and 3485 cm^{-1}, that can be attributed to the hydroxo group and to the two coordinating water molecules, respectively (the X-ray structure shows that the hydroxy group and one of the two water molecules are not involved in any strong H-bond). The nitrate trimer (compound **2**), with two additional noncoordinating water molecules and a complex H-bond network, only displays a broad band with a shoulder over 3440 cm^{-1} and a maximum around 3386 cm^{-1}, the latter presumably due to the “free” water. As for the perchlorate trimer (compound **3**), the IR spectrum shows a broad but well-defined single band with the maximum at 3420 cm^{-1}, that must include both the $\nu(O-H)_{\nu 3-OH}$ and $\nu(O-H)_{coord.H_2O}$ vibrations, in agreement with the weak H-bond contacts that these groups form.

Bands in agreement with both coordinated and noncoordinated anions could be observed (in cm^{-1}):[30−32] for the nitrate compound, $\nu_{as}(NO_3)$ = 1384 vs (and unusually sharp), 1310 m; $\nu_{sym}(NO_3)$ = 1021 m;[30,32] for the triflate compound, $\nu_{as}(CF_3)$ = 1280, 1250 vs; $\nu_{sym}(CF_3)$ = 1230, 1210 s; $\nu_{as}(SO_3)$ = 1170, 1150 s; $\nu_{sym}(SO_3)$ = 1035 s, 980 m;[33] for the perchlorate compound, 1190 vs; 1160−1090 vs, sp; 975 m; 650 s; 455, 445 m.[1,10,32,34]

Table 4 lists the most relevant IR bands of the Haat ligand together with the corresponding bands of the Haat mononuclear complexes and those of the now reported *aat* trinuclear complexes.[16−18,35] It shows that the IR spectra can be used as a diagnostic tool of the coordination mode of the ligand.

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Table 4. Selected IR Ligand Bands (cm^{-1})

compound	ν(C=O)	ν(C=N) + δ(N−H)		ref
Haat	1685 s[a]	1622 s,	1556 s	17
Haat mononuclear compd	1660−1649, 1640−1634 (sp) s	1605−1609 s,	1535−1545 vw	17, 18
aat trimeric compd:				
1	1640s	1590 s,	1525 s	this work
2	1641 m−s	1583 s,	1519 s	this work
3	1645, 1635 (sp) s	1585 s,	1525 s	this work

[a] s = strong, v = very, w = weak, sp = split or doublet.

(b) Ligand Field Spectra. The reflectance electronic spectra of all the complexes display a single band at 675 nm (14800 cm^{-1}), indicating the similarity of the chromophores around the different Cu(II) ions. Electronic spectra in DMSO, methanolic, and aqueous solutions have also been recorded; the observed ligand field band is in agreement with the fact that the trimers remain intact in those solution media.

(c) Magnetic Susceptibility Measurements. The temperature dependence of $\chi_M T$ for complexes **1**, **2**, and **3** is given in Figure 4, plots a, b, and c. At room temperature $\chi_M T$ is very low (0.86 (**1**), 0.90 (**2**), and 0.81 $cm^3\ mol^{-1}$ K (**3**)) with respect to the value expected for three independent Cu(II) ions. As the T is lowered $\chi_M T$ decreases, reaching values of 0.43−0.44 $cm^3\ mol^{-1}$ K at ca. 75 (**1**), 55 (**2**), and 95 K (**3**), which correspond to the spin-only value of 0.437 $cm^3\ mol^{-1}$ K for one unpaired electron with $g = 2.17$. This behavior indicates a quite strong antiferromagnetic interaction between the Cu(II) ions, with an unpaired electron per Cu_3 unit in the ground state. $\chi_M T$ keeps on decreasing below the former indicated temperatures, reaching values of 0.22 (**1**), 0.23 (**2**), and 0.26 $cm^3\ mol^{-1}$ K (**3**) at 4.7 K; this situation has been observed in similar compounds.[3e,9,12a,13]

From the known structures of **1**, **2**, and **3**, and considering that the three metals are structurally almost equivalent and so that $J_1 = J_2 = J_3 = J$, the spin Hamiltonian in eq 1 will describe the interactions of the spins:[9,11a,36−38]

$$H = -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_1 \cdot S_3) \qquad (1)$$

From this Hamiltonian, a solution of the magnetic susceptibility may be derived as follows:

$$\chi_M = (N\beta^2 g^2/4kT)[1 + 5\exp(3J/2kT)]/[1 + \exp(3J/2kT)] \qquad (2)$$

where N, g, β, k, and T have their usual meanings. Due to the above-mentioned experimental variation of $\chi_M T$ at low temperatures, the inclusion of an additional Weiss-like parameter Θ, which would account for possible intertrimer magnetic interaction (T replaced by $T - \Theta$ in eq 2) was considered necessary.

Variable-temperature magnetic susceptibility data for **1**, **2**, and **3** were analyzed with the theoretical expression which results from the modified eq 2; fitting was performed on $\chi_M T$. The experimental data are plotted in Figure 4, panels a, b, and c, respectively, along with the best fitted curve. The results of the fittings (Tables 3 and 5, Figure 4) indicate that the magnetic interaction is of similar strength in the three compounds as the J values can be considered equal. This is in principle reasonable given the fact that the bridging between pairs of copper atoms is equivalent and the unpaired electrons are in the same type of orbitals. [Attempts at getting a better fit by using an equation with two different J values (so treating the system as an isosceles triangle) were also performed.[9,13,38] The J and J' values obtained, very similar, did not significantly differ from those obtained with only one J value, and the goodness of the fitting did not improve.]

The coupling parameters thus obtained have been compared with those reported for analogous compounds as a function of certain structural features (Tables 3 and 5). Magnetostructural correlations for trimers with the $Cu_3O(H)$ moiety have already been described in relation to the two potential bridges: the tridentate central oxygen and the bidentate N,N peripheral ligand; the authors established, on the one hand, that the more flattened is the $Cu_3O(H)$ bridge the stronger is the magnetic interaction,[9] and, on the other hand, that higher coplanarity of the coordination planes around each copper atom is followed by a larger spin coupling constant;[9,13] in addition, in oxime-bridged trimeric compounds, a direct relationship between both former structural features has been observed due to the fact that in the Cu_3O complexes there is a higher degree of coplanarity of the principal ligand planes than in the Cu_3OH analogous complexes.[9]

The previous correlations were established considering only oxime-type compounds, or both oxime compounds with N,O peripheral bridges and azole compounds with N,N peripheral bridges at the same time. Since the two types of bridges are not strictly comparable (see later), in this work we will focus on compounds with N,N bridges. Tables 3 and 5 compile structural parameters concerning both central and pheripheral bridges, respectively, for the above referred triangular copper(II) compounds with Cu_3OH core. So, as for the central bridge, if larger Cu−O(H)−Cu′ angles/shorter O(H)···Cu_3 plane distances imply higher J values, the correlation showed in Table 3 is quite good, but J_3 should be higher. With respect to the coplanarity of the pheripheral ligands (Table 5), again, it is difficult to derive conclusions due to the scarcity of data; in general terms, the J values of the present work are also in the expected range although J_3 should be higher than J_1. Compound **E**, with a N,O oximato bridge, does not follow the correlation (the N,O bridge seems to be more efficient than the N,N bridge in the magnetic exchange interaction). In our opinion, the observations made on **1**, **2**, and **3** suggest, first, that the two above-described criteria are not totally equivalent when discussing magnetostructural correlations since the axial ligand may push the copper atom out of the basal plane; second, that these two coplanarity criteria cannot fully explain the magnitude of the magnetic exchange: despite the structural differences in coplanarity, **1**, **2**, and **3** exhibit essentially identical J values.

A different approach to the problem could be carried out by taking into account the more studied N_2 diazine doubly bridged Cu(II) compounds. For the (quasi) planar doubly triazole- or pyrazole-bridged systems, general agreement exists that the dominant pathway for the antiferromagnetic exchange is provided by σ bonding between copper $d_{x^2-y^2}$ and bridging ligand

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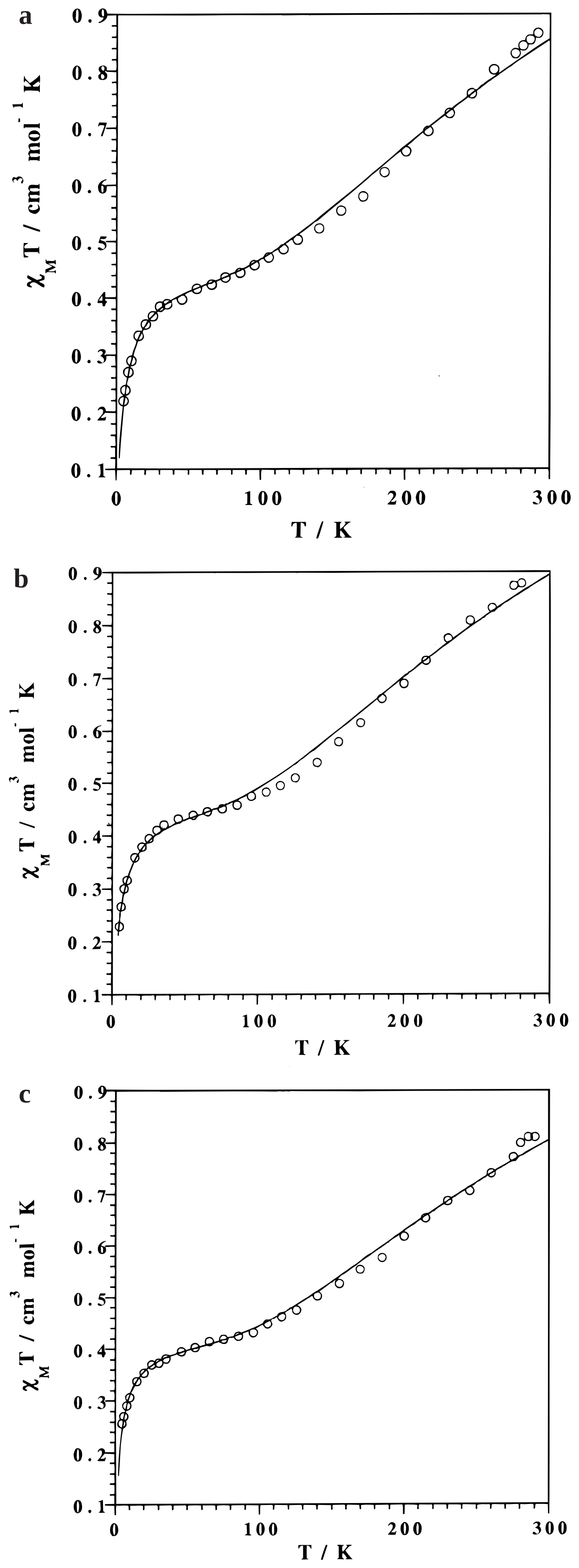

Figure 4. Plot of $\chi_M T$ (cm^3 mol^{-1} K) vs T (K) in the range 4.5−300 K for **1** (a), **2** (b), and **3** (c): ○, experimental data; solid line, best fitting curve (magnetic parameters for **1**, $-J = 197.7$ cm^{-1}; $\Theta = -5.1$ K; $g = 2.15$; $R = 4.2 \times 10^{-4}$; for **2**, $-J = 190.9$ cm^{-1}; $\Theta = -4.5$ K; $g = 2.20$; $R = 5.7 \times 10^{-4}$; for **3**, $-J = 198.2$ cm^{-1}; $\Theta = -3.2$ K; $g = 2.08$; $R = 4.1 \times 10^{-4}$).

orbitals;[39] from this analysis, a correlation between J and the bridging angles has been proposed.[40,41] For **1**, **2**, and **3** the six N−Cu−O(H) angles are similar with values ranging from 89.0° to 92.1°; following the mentioned criteria, this would be consistent with the similarity between the J values. Moreover, the magnitude of the exchange integral would be of the expected order.[41] (This simplification considers the N−N bridge the main way of the superexchange, although the central bridge can attenuate or enhance the interaction, as described in asymmetric dinuclear systems).[42] However, the six N−Cu−O(H) angles of **D**, a pyrazole derivative, are comparable and its J value is clearly lower. So, the value of the bridging angles by itself cannot be used either to predict the trend in the exchange interaction. On the other hand, it has been observed that electronic factors which vary depending on the nature of the heterocyclic ring containing the bridge influence the magnetic exchange phenomena:[39] literature $-J$ values range from 302 to 428 cm^{-1} for pyrazolate[40] and 72−236 cm^{-1} for triazolate[41] dinuclear compounds. It seems that also in the case of the cyclic trimers, when trying to correlate structural and magnetic properties, a distinction should be done in function of the nature of the ring which affords the bridge.

Another question which remains unsolved is how to rationalize the magnetic behavior below 75 (**1**), 55 (**2**), and 95 K (**3**). The experimental observation that the magnetic moment drops below the value expected for one unpaired electron suggests that other kinds of antiferromagnetic interactions are operative; in fact, the Θ values that result from the fitting [−5.1 (**1**), −4.5 (**2**), −3.2 K (**3**)] are significantly large. But, on the basis of the crystallographic data available (room temperature) the potential way for the intertrimer exchange is not clear; the shortest intertrimeric Cu···Cu′ distances, longer than 6 Å [6.538(2) (**1**), 6.037(1) (**2**), 6.421(3) Å (**3**)],[50] exclude, at least in principle, any interaction between spins of different trinuclear entities. Some tentative explanations (lattice-driven phase transitions, antisymmetric exchange, ...) were suggested for a similar case by Angaroni et al.[13] Our hypothesis is that an antisymmetric exchange phenomenon[43] is operating; a detailed study of it is in progress.

(d) EPR Spectra. The X-band EPR spectra of complexes **1**, **2**, and **3** were recorded on powder samples at room and liquid nitrogen temperatures. The magnetic exchange properties of the triangular Cu(II) species resulting from the antiferromagnetic interactions very often cause no EPR signals to be observed at room temperature (apparently, because relaxation phenomena hamper the observation)[12a] and only badly resolved spectra at low temperatures.[1,12a,14] In the present case, the room temperature spectrum of **3** is almost silent but those of **1** and **2** exhibit signals (with an axial pattern for **1** and an isotropic pattern for **2**). The spectra for the three complexes at liquid nitrogen temperature are typical for $S = {}^1/_2$ spin systems, in agreement with the observation that at this temperature complete spin coupling has already been reached, as shown in the previous part. Following the literature[11a] for a trinuclear complex of this type at low temperatures two doublets should be observed; however, it is not unreasonable to think that the two doublet

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Table 5. Dihedral Angles (deg) between the Least-Squares Planes Defined by CuL_4 Square-Planar Coordination. Coplanarity of Principal Ligand Planes, Defined by [O(H), N(1), N(2), O(1)] (as Butcher et al.[9] and Angaroni et al.[13])

compd	Cu(1)−Cu(2)	Cu(1)−Cu(3)	Cu(2)−Cu(3)	av	$-J^a$	ref
1	19.9(2)	24.4(2)	31.7(2)	25.3(2)	197.7	this work
2	23.1(1)	23.3(1)	24.4(1)	23.6(1)	190.9	this work
3	17.4(3)	19.4(2)	26.6(2)	21.1(2)	198.2	this work
E	40.3	28.5	31.1	33.0	244	9
B	35	24	23	27	200 (ca.)	12a
A[b]	25.0(3)	27.3(3)	26.4(2)	26.2(3)	191.2	14
D	54	27	27	36	140	13

[a] The reported values of *J* from the literature have been modified according to the definition used in this paper (see eq 1). [b] Planes data calculated in this work.[26]

states would have very similar *g* values so that the two expected spectra would merge into one. In practice, the three compounds display an axial spectrum giving *g* values of $g_{\|} \simeq 2.31$, $g_{\perp} = 2.08$ (**1**); $g_{\|} = 2.29$, $g_{\perp} \simeq 2.03$ (**2**); $g_{\|} = 2.08$, $g_{\perp} = 2.06$ (**3**); the fine structure (although badly resolved in **1**) can be appreciated, and the calculated hyperfine coupling constant values ($A_{\|} \simeq 152$ (**1**), $A_{\|} \simeq 135-140$ (**2**); $A_{\|} = 143 \times 10^{-4}$ cm^{-1} (**3**)) are in agreement with the square-pyramidal (C_{4v}) geometry around each copper.[44] The averaged $\langle g \rangle$ values (2.16, 2.11, and 2.07, for **1**, **2**, and **3**, respectively) are quite close to those obtained by the fitting procedure of the magnetic susceptibility data for **1** and **3** (2.15, 2.20, and 2.08, for **1**, **2**, and **3**, respectively, Figure 4); they also show the same tendency of a slightly lower value for **3** when compared with **1** and **2**. The different EPR behavior of **3** with respect to **1** and **2** could be connected with its long axial $Cu-O_{anion}$ distance (2.717 compared with 2.416 and 2.340 Å). In addition, the liquid nitrogen temperature spectrum of **2** exhibits a broadening centered at about 4.2 (1450−1500 G), which must be due to $\Delta m = 2$ transitions.[11a]

(e) NMR spectra. As mentioned above, the room-temperature EPR spectrum of **3** is almost silent. It is known that systems showing no EPR spectrum may show interesting NMR spectra (and the reverse);[12a,45] therefore we have tried to obtain NMR spectra of the title compounds in solution. Solutions of **1**, **2**, and **3** in dmso-d_6, D_2O, and D_3OD indeed showed signals that could be attributed to protons of the aat within the trimeric compound. To be noted the *paramagnetic* shift of the *aromatic* and *methyl H atom* signals, which appear, for instance, at ca. 23.0 ppm (expected around 7.8 ppm) and 8.1 ppm (expected at ca. 2.1 ppm), respectively, in a dmso-d_6 solution of the triflate compound.

Attempts at replacing the coordinating axial water by 4-picoline in both dmso-d_6 and D_3OD solutions were not successful, as easily followed by NMR (no shifts of any 4-picoline protons observed).

Concluding Remarks

The results described in this paper show that the ligand Haat, an interesting new asymmetric triazole derivative with a chelating substituent, in its deprotonated form aat is capable of coordinating as a bridging ligand to give rise to trinuclear Cu(II) complexes of the triangular type, by reaction with three different copper(II) salts. The three complexes obtained, very symmetrical (the most symmetrical reported among the triangular non-oximate type), basically only differ in the coordinating anion. A quite strong antiferromagnetic interaction ($-J =$ ca. 200 cm^{-1}) has been found in the three cases. In spite of differences observed in coplanarity of the ligand planes, the three compounds exhibit almost equal spin exchange constants, so that they are suitable materials for a detailed study of the intramolecular magnetic-exchange mechanism.

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Supporting Information Available: Tables of final atomic coordinates for the non-hydrogen atoms (Tables SI, SII, SIII) and for the hydrogen atoms (Tables SIV, SV, SVI), complete list of bond distances and angles (Tables SVII, SVIII, SIX), anisotropic thermal parameters (Tables SX, SXI, SXII), and list of possible hydrogen bonds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) Just before submission of this work, the authors obtained knowledge of a recently published paper (*J. Struct. Chem.* **1997**, *38*, 441) by A. V. Virovets, N. V. Podberezskaya, and L. G. Lavrenova, describing the X-ray structure of a trinuclear triazole copper(II) compound; it represents the first reported compound of this type with a triazole derivative. The structure, however, presents strong disorder problems, and an unambiguous choice between the formulas $(H_3O)[(\mu_3\text{-}OH)(\mu,\eta^2\text{-}L)_3Cu_3Cl_6]$ and $[(\mu_3\text{-}OH)(\mu,\eta^2\text{-}L)_2(\mu_2,\eta^2\text{-}LH)Cu_3Cl_6]\cdot H_2O$ (L = 3,5-dimethyl-4-amino-1,2,4-triazole) was impossible. As the disorder prevents any comparison with our structures, this compound will not be included in our study.

(47) The compound described by Virovets et al. contains a nonchelating triazole ligand.

(48) In Virovets et al.'s compound there is probably a Cl^- in that position.

(49) Apart from the compound reported by Virovets et al.

(50) The shortest "intermolecular" Cu···O′ (coordinating anion) distances are 4.396(9) (**1**), 4.927(5) (**2**), and 4.95(2) Å (**3**); so the coordinating anions do not bridge $Cu_3O(H)$ units, which is different from the situation observed in compounds of refs 9, 12a,b, and 14.

(51) *Note*: The Cambridge Crystallographic Structure Data Base was used in the literature research [Allen, F. H.; Kennard, O.; Taylor, R. Systematic Analysis of Structural Data as a Research Technique in Organic Chemistry. *Acc. Chem. Res.* **1983**, *16*, 146].