Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties of an Unprecedented Three-Dimensional Cu^{II} Coordination Compound of 1,2-Bis(1,2,4-triazol-4-yl)ethane

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A novel three-dimensional copper(II) compound of the formula $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6\cdot H_2O$ (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane) has been synthesized. The structure has been solved at 150 K by single-crystal X-ray analysis. The compound $[C_{30}H_{44}Cu_3N_{30}O_2\cdot 6(ClO_4)\cdot H_2O]$ crystallizes in the triclinic space group *P*1bar with $a = 12.488(1)$, $b = 13.195(1)$, $c = 19.756(2)$ Å, $\alpha = 78.959(8)$, $\beta = 84.553(8)$, $\gamma = 63.869(7)°$, $V = 2868.4(5)$ Å^3, $Z = 2$ (trinuclear Cu^{II} units), 6484 reflections $[I > 4\sigma(I)]$, $R_F = 0.0581$, $wR_2 = 0.1214$. The structure of this coordination polymer consists of a three-dimensional network built up from linear trinuclear Cu^{II} cations of formula $[Cu_3(btre)_5(H_2O)_2]^{6+}$. This crystallographically independent unit comprises a linear array of three Cu^{II} ions linked by triple N1,N2-1,2,4-triazole bridges, yielding Cu1–Cu2 = 3.893(1) Å and Cu2−Cu3 = 3.889(1) Å. These linear trinuclear Cu^{II} units are linked by various pathways involving tridentate and tetradentate bridging btre ligands, which yields an unprecedented three-dimensional network. The Cu^{II} ions are weakly antiferromagnetically coupled with $J = -1.01(2)$ cm^{-1} (based on the Hamiltonian: $\mathbf{H} = -J[S_{Cu1}\cdot S_{Cu2} + S_{Cu2}\cdot S_{Cu3}]$ using the expression for the molar magnetic susceptibility S = 1/2 of a linear trinuclear system). The nature and the magnitude of the antiferromagnetic exchange have been discussed on the basis of the structural features.

Introduction

Polynuclear coordination compounds containing derivatives of 1,2,4-triazole have been of increasing interest during the last decade. Several studies have dealt with the search for magneto-structural correlations for transition metal(II) compounds containing N1,N2-1,2,4-triazole bridges.[1−10] On the other hand, polynuclear (1,2,4-triazole)iron(II) compounds have been found to yield spin-crossover materials exhibiting cooperative behavior.[11−33]

The capability of the 1,2,4-triazole ligand to form a bridge between metal(II) ions by establishing the N1,N2 coordination mode makes them very useful for obtaining polynuclear coordination compounds in which the (paramagnetic) transition metal(II) ions are maintained at relatively short distances. Substituents have been attached to the N4 of the 1,2,4-triazole in order to prevent coordination at this position. Consequently, in coordination compounds, the ligand will be incorporated in its neutral form. Earlier studies dealt with 4-amino-1,2,4-triazole, of which mostly linear chain compounds have been obtained, where the metal(II) ions are linked by triple N1,N2-1,2,4-triazole bridges.[11b,12,13,16−20,23−29] This has been confirmed by an X-ray crystallographic study for $[Cu(4\text{-amino-}1,2,4\text{-triazole})_3](ClO_4)2\cdot 0.5H_2O$.[34] Using alkyl[21,30,31,35] or hydroxyalkyl substituents[8,22,32,33] of different sizes, this triply bidentate N1,N2 bridging of the 4-substituted 1,2,4-triazole ligand has again uniquely been found. In the absence of coordinating anions, this yields linear trinuclear compounds[21,30,31,35] or infinite linear chains.[8,21,22,32,33] On the other hand, taking 4-phenyl-substituted derivatives under the same experimental conditions only led to the formation of linear trinuclear species having triple N1,N2-1,2,4-triazole bridges.[36]

Surprisingly, with 4,4′-bis(1,2,4-triazole) (abbreviated as btr) this N1,N2 bridging coordination mode has not yet been observed. Instead, the ligand has been found to link transition metal(II) ions using N1 and N1′ − the nitrogen atoms originating from the two different 1,2,4-triazole rings − resulting in one-,[37] two-,[38−41] and three-dimensional[42] networks. The occurrence of solely this N1,N1′ bidentate coordination mode may be related to the observation that this coordination of btr is possible while keeping its geometric conformation close to that what has been found for the free ligand, i.e. with fairly perpendicular 1,2,4-triazole rings.[43] Furthermore, charge distribution efficiency considerations may favor a wide separation of the twofold positively charged transition metal(II) ions, which is indeed realized by this N1,N2′ bidentate coordination.

The purpose of this study is to investigate the way in which a more flexible linkage between the 1,2,4-triazole moieties, as compared to the direct N4−N4′ bond in btr, will influence the coordination mode of the ligand, and thus the type of compound to be formed. Therefore, we have

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[‡] We are very sad that Olivier suddenly passed away on December 8, 1999. We will never forget him and dedicate this paper to him.

selected 1,2-bis(1,2,4-triazol-4-yl)ethane (abbreviated as btre). In this paper we describe the structure of a new type of polynuclear copper(II) compound together with its spectroscopic and magnetic properties.

Results and Discussion

Description of the Structure of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6·H_2O$

The structure of this coordination polymer consists of a three-dimensional network built up from linear trinuclear Cu^{II} cations of formula $[Cu_3(btre)_5(H_2O)_2]^{6+}$ (see Figure 1). This crystallographically independent unit comprises a linear array of three Cu^{II} ions linked by triple N1,N2-1,2,4-triazole bridges. Ligands labeled 3 and 4 have an inversion center at the middle of the ethylene linkage. One noncoordinating water molecule, as well as six free perchlorate anions complete the asymmetric unit. Selected bond lengths and bond angles are given in Tables 1 and 2. These linear trinuclear Cu^{II} units are linked via various pathways involving tridentate (ligands marked 1, 2, 5 and 6) and tetradentate (ligands marked 3 and 4) bridging btre ligands, yielding an unprecedented three-dimensional network (see Figure 2). The structure is additionally stabilized by hydrogen bonding involving coordinating as well as noncoordinating water molecules.

Table 1. Bond lengths [Å] for $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6·H_2O$; estimated standard deviations in the last significant digits are given in parentheses

Cu1−O1	2.449(5)
Cu1−N101	1.994(6)
Cu1−N202	2.369(5)
Cu1−N301	2.070(6)
Cu1−N511[a]	1.997(6)
Cu1−N111[b]	2.020(6)
Cu2−N102	2.359(5)
Cu2−N201	2.015(6)
Cu2−N302	1.996(5)
Cu2−N401	1.988(5)
Cu2−N501	2.045(5)
Cu2−N601	2.454(5)
Cu3−O2	2.557(5)
Cu3−N402	2.056(6)
Cu3−N502	2.279(5)
Cu3−N602	1.986(6)
Cu3−N211[c]	1.985(7)
Cu3−N611[d]	2.030(6)

Marked atoms are generated by symmetry operations: [a] −1 + *x*, *y*, *z*. − [b] 1 − *x*, 1 − *y*, 2 − *z*. − [c] 1 + *x*, *y*, *z*. − [d] 2 − *x*, −*y*, 1 − *z*.

Within the trinuclear Cu^{II} unit, three btre ligands link each pair of adjacent copper(II) ions via nitrogen atoms N1 and N2. The central ion, Cu2, is in a strongly distorted octahedral environment formed by six N-donating btre ligands. The coordination plane is formed by four nitrogen donor atoms at 1.988(5)−2.045(5) Å, whereas two btre li-

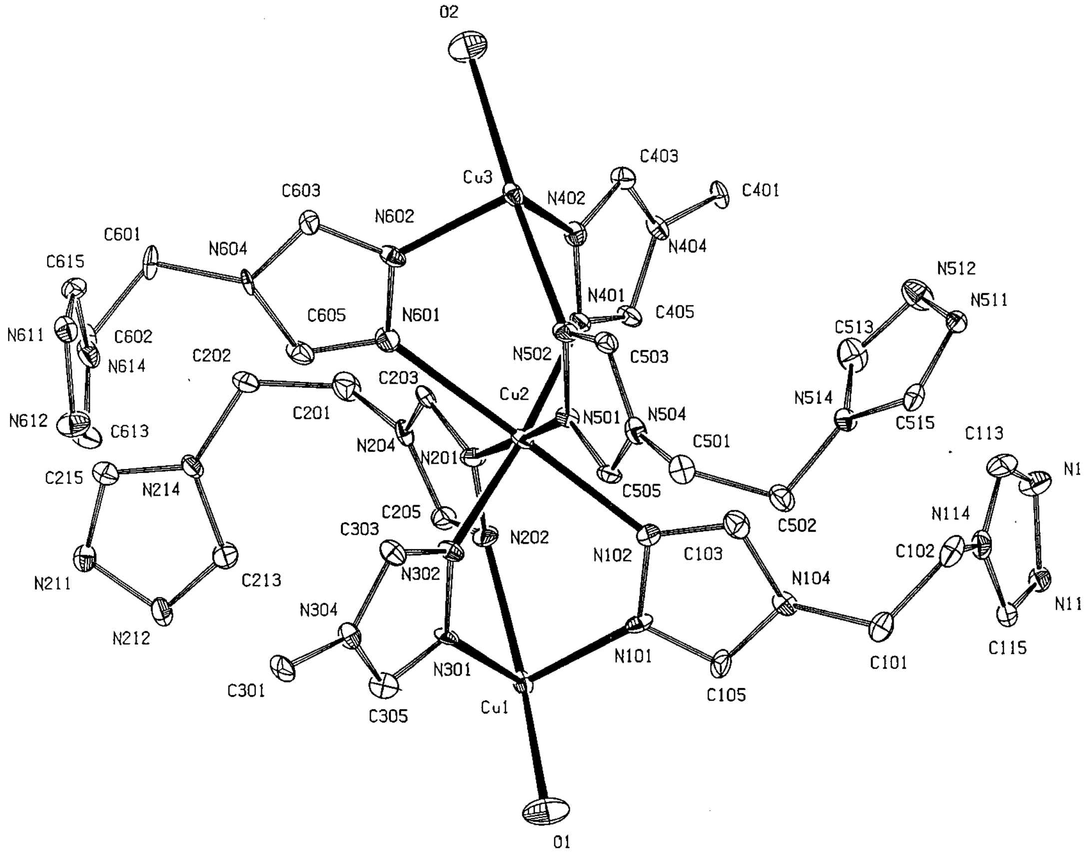

Figure 1. Atomic displacement ellipsoid drawing[57] (50% probability level) and atomic labeling system showing the asymmetric unit of $[Cu_3(btre)_5(H_2O)_2](ClO_4)$6·H2O; hydrogen atoms, noncoordinating counter ions, and water molecules have been omitted for clarity

Table 2. Bond angles [°] for $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$; estimated standard deviations in the last significant digits are given in parentheses

O1−Cu1−N101	89.2(2)	O2−Cu3−N402	84.3(2)
O1−Cu1−N202	163.2(2)	O2−Cu3−N502	171.1(2)
O1−Cu1−N301	78.4(2)	O2−Cu3−N602	90.9(2)
O1−Cu1−N511[a]	89.0(2)	O2−Cu3−N211[c]	87.2(2)
O1−Cu1−N111[b]	93.7(2)	O2−Cu3−N611[d]	89.9(2)
N101−Cu1−N202	87.2(2)	N102−Cu2−N201	89.3(2)
N101−Cu1−N301	92.5(2)	N102−Cu2−N302	88.8(2)
N101−Cu1−N511[a]	175.8(2)	N102−Cu2−N401	96.0(2)
N101−Cu1−N111[b]	89.8(2)	N102−Cu2−N501	92.6(2)
N202−Cu1−N301	85.4(2)	N102−Cu2−N601	179.3(2)
N202−Cu1−N511[a]	95.6(2)	N202−Cu1−N111[b]	102.7(2)
N301−Cu1−N511[a]	90.9(2)	N201−Cu2−N401	88.0(2)
N301−Cu1−N111[b]	171.7(2)	N201−Cu2−N501	178.1(2)
N511[a]−Cu1−N111[b]	86.6(2)	N201−Cu2−N601	90.0(2)
N402−Cu3−N502	86.9(2)	N302−Cu2−N401	174.4(2)
N402−Cu3−N602	92.8(2)	N302−Cu2−N501	90.7(2)
N402−Cu3−N211[c]	88.0(2)	N302−Cu2−N601	90.9(2)
N402−Cu3−N611[d]	173.2(2)	N401−Cu2−N501	91.9(2)
N502−Cu3−N602	90.1(2)	N401−Cu2−N601	84.3(2)
N502−Cu3−N211[c]	88.0(2)	N501−Cu2−N601	88.1(2)
N502−Cu3−N611[d]	98.9(2)	N602−Cu3−N211[c]	177.8(2)
N602−Cu3−N611[d]	90.7(2)	N211[b]−Cu3−N611[d]	88.3(2)
Cu1−N101−N102	126.9(4)	Cu2−N501−C505	129.3(4)
Cu1−N101−C105	125.3(5)	Cu3−N502−N501	127.0(4)
Cu2−N102−N101	123.1(4)	Cu3−N502−C503	126.2(4)
Cu2−N102−C103	129.8(4)	N512−N511−Cu1[c]	120.1(4)
C115−N111−Cu1[b]	129.2(4)	C515−N511−Cu1[c]	131.8(5)
N112−N111−Cu1[b]	121.4(4)	Cu2−N602−N601	123.3(4)
Cu2−N201−N202	125.9(4)	Cu2−N601−C603	128.5(4)
Cu2−N201−C203	126.4(4)	N612−N611−Cu3[d]	121.4(4)
Cu1−N202−N201	121.6(4)	Cu1−N202−C205	129.3(4)
N212−N211−Cu3[a]	117.1(4)	C615−N611−Cu3[d]	126.8(4)
C215−N211−Cu3[a]	134.9(4)	Cu1−N301−N302	128.7(4)
Cu1−N301−C305	125.3(4)	Cu2−N302−N301	127.3(3)
Cu2−N302−C303	124.2(4)	Cu2−N401−N402	129.2(3)
Cu2−N401−C405	123.3(4)	Cu3−N402−N401	127.6(4)
Cu3−N402−C403	125.1(4)	Cu2−N501−N502	123.5(4)

Marked atoms are generated by symmetry operations: [a] $-1 + x$, y, z. − [b] $1 - x$, $1 - y$, $2 - z$. − [c] $1 + x$, y, z. − [d] $2 - x$, $-y$, $1 - z$.

gands coordinate at significantly longer distances [2.359(5) and 2.454(5) Å to N102 and N601, respectively]. The coordination geometry about this Cu^{II} ion very closely resembles those of the Cu^{II} ions in the linear chain compounds $[Cu(4\text{-amino-}1,2,4\text{-triazole})_3](ClO_4)_2 \cdot 0.5H_2O$[34] and $[Cu(hyetrz)_3](ClO_4)_2 \cdot 3H_2O$ [hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole].[8] It is, however, in contrast to the geometry of the central Cu^{II} ion in the linear trinuclear compound $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$ (metz = 3-methyl-4-ethyl-1,2,4-triazole),[42][44] where it appears that the dynamic Jahn−Teller distortion results in a completely regular octahedral coordination about the Cu^{II} ion octahedron, with six relatively short Cu−N distances of 2.14(5) Å.

The terminal copper(II) ions, Cu1 and Cu3, are linked to Cu2 via triple N1,N2-1,2,4-triazole bridges, resulting in a Cu1−Cu2 distance of 3.893(1) Å and a Cu2−Cu3 distance of 3.889(1) Å. This compares rather well to the Cu−Cu distances of 3.853(2) Å and 3.829(2) Å encountered in $[Cu(hyetrz)_3](ClO_4)_2 \cdot 3H_2O$.[8] However, it should be noted that the Cu−Cu distances observed in the present coordination polymer are significantly longer than the 3.719(7) Å for Cu^{II} ions linked by triple μ-N1,N2-1,2,4-triazole bridges in the linear trinuclear compound $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$.[42][44] This may be related to the dynamic Jahn−Teller effect involving the central Cu^{II} ion in the metz compound.

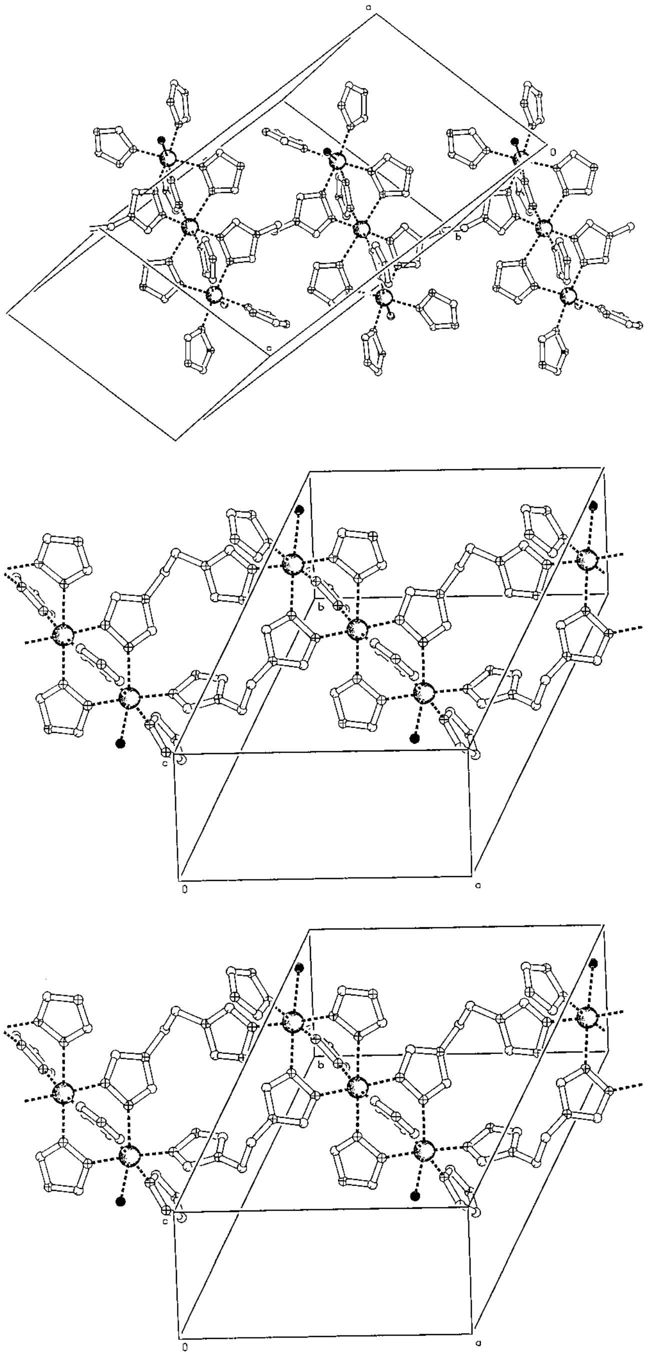

Figure 2. PLUTON[57] drawing showing the structure of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$: (a) (1 −1 1) chain of trinuclear Cu units linked by ligands 3 and 4; (b) (1 0 0) chain of trinuclear Cu units linked by ligands 2 and 5; (c) (1 −1 −1) chain of trinuclear Cu units linked by ligands 1 and 6

As has also been observed in $[Cu(hyetrz)_3](ClO_4)_2 \cdot 3H_2O$,[8] that in order to establish the linkage of Cu^{II} ions in Jahn−

Teller-distorted octahedra by triple μ-N1,N2-1,2,4-triazole bridges, the geometric disposition of the ligands becomes such that important deviations from the ideal threefold axis running through the Cu^{II} ions are required. Also in the present compound, the N1,N2 bridging mode of all btre ligands involve unequal Cu−N distances, as well as Cu−N−N angles. The torsion angles Cu−N−N−Cu involving ligands 1, 2, 3, 4, 5, and 6 are 9.7(7)°, 20.7(7)°, 7.9(7)°, 4.9(8)°, −0.1(7)°, and 7.3(7)°, respectively.

The coordination octahedra around Cu1 and Cu3 are completed by two N-donating btre ligands and a coordinating water molecule, yielding an N_5O chromophore. For both terminal Cu^{II} ions, the axial coordination is formed by a water molecule and an N-donating btre ligand. The coordination plane of Cu2 [N201, N302, N401, N501] makes an angle of 68.3(2)° with the coordination plane of Cu1 [N101, N301, N511 $(-1 + x, y, z)$, N111 $(1 - x, 1 - y, 2 - z)$], whereas the angle with the least-squares plane through the equatorial coordination sphere of Cu3 [N402, N602, N211 $(1 + x, y, z)$, N611 $(2 - x, -y, 1 - z)$] is 61.4(2)°.

All 1,2,4-triazole rings are fairly planar: The maximum deviation of an atom from the least-squares plane through the ring atoms is 0.011(7) Å. The three-dimensional structure consists of three chains of trinuclear Cu units running in directions (1 −1 1), (1 0 0) and (1 1 −1). Each chain is formed by two ligands: 3 and 4, 2 and 5, and 1 and 6, respectively.

The btre ligands which are located on a crystallographic inversion center have N4−C1−C2−N4′ torsion angles of 180° and act as tetradentate ligands, linking two pairs of Cu^{II} ions originating from two different trinuclear units. Ligand 3 uses its N1 and N2 to link Cu1 and Cu2, and N1′ and N2′ to establish a bridge between Cu1 (symmetry operation: $1 - x, 1 - y, 1 - z$) and Cu2 $(1 - x, 1 - y, 1 - z)$. Ligand 4 bridges Cu2 and Cu3 and links Cu2 $(2 - x, -y, 2 - z)$ and Cu3 $(2 - x, -y, 2 - z)$ by its symmetry-related counterpart. The resulting Cu−Cu distances are in the range 10.742(2)−11.460(2) Å. In this way, a chain of trinuclear units running along the $x, -y, z$ direction is formed (see Figure 2a). In fact, this doubly bridging coordination mode of btre involves an inversion lying on the middle of the ethylene bridge. Consequently, it may be more correct to describe this as a twisted chain of trinuclear entities.

The four other btre molecules are tridentate ligands, which have a bent conformation, as is illustrated by the values for the N4−C1−C2−N4′ torsion angles involving the N4,N4′ ethylene linkage. These angles are −79.5(7)°, −86.1(7)°, 75.5(7)° and 63.0(7)° for the ligands marked 1, 2, 5 and 6, respectively. The tridentate coordination is established by forming both a long and a rather short Cu−N bond length within the N1,N2 bridging triazole, together with a short Cu−N distance involving the second triazole ring. Ligand 2 and ligand 5 establish an N1,N2 bridge between two Cu^{II} ions within the asymmetric unit, and they coordinate with N1 of the second 1,2,4-triazole ring to a terminal Cu^{II} of a symmetry-related trinuclear entity. Ligand 2 establishes an N1,N2 bridge between Cu1 and Cu2, while coordinating with its triazole counterpart to Cu3 $(-1 + x, y, z)$; while ligand 5 links Cu2 and Cu3 via its μ-N1,N2 coordination mode, and binds to Cu1 $(1 + x, y, z)$. The resulting Cu−Cu distances are: Cu1−Cu3 $(-1 + x, y, z)$ = 9.053(2) Å, Cu2−Cu3 $(-1 + x, y, z)$ = 10.243(2) Å and Cu2−Cu1 $(1 + x, y, z)$ = 10.136(2) Å. This yields a chain running along the x direction (Figure 2b).

A chain of trinuclear Cu^{II} entities along the $x, -y, -z$ direction is formed through the tridendate coordination of ligand 1 and ligand 6. Like ligands 2 and 5, these ligands also form a μ-N1,N2-1,2,4-triazole bridge between Cu^{II} ions within the asymmetric unit, together with the coordination of a nitrogen atom of the second 1,2,4-triazole ring to a symmetry-related Cu^{II} ion of another trinuclear unit. Ligand 1 links Cu1 and Cu2 via the N1,N2 bridging mode, and coordinates with N1′ to Cu1 $(1 - x, 1 - y, 2 - z)$. Ligand 6, which establishes an N1,N2 bridge between Cu2 and Cu3, binds to Cu3 $(2 - x, -y, 1 - z)$. The shortest Cu−Cu distances resulting from this coordination pathway are Cu1−Cu1 $(1 - x, 1 - y, 2 - z)$ = 9.262(2) Å and Cu3−Cu3 $(2 - x, -y, 1 - z)$ = 8.595(1) Å (Figure 2c).

The difference between the chains formed by ligands 2 and 5 and that formed by ligands 1 and 6 is that in the former chain, the link between each pair of adjacent tricopper units is formed by one ligand 2 and one ligand 5. In the latter chain, the links between adjacent tricopper units are formed by either two molecules of ligand 1 or two molecules of ligand 6.

In the present compound, the perchlorate anions are noncoordinating and some are involved in hydrogen bonding interactions with the btre ligands, as well as with the lattice water molecules. The noncoordinated nitrogen atoms of the tridentate ligands 1 and 2 are involved in hydrogen bonding. N112 $(2 - x, -y, 2 - z)$ is hydrogen-bonded to water oxygen atom O2, which is in turn coordinated to Cu3. N212 accepts an (intermolecular) hydrogen bond from the noncoordinated water molecule O3. Details of the hydrogen bonds are listed in Table 3. The shortest "intermolecular" Cu−Cu distance is formed through hydrogen bond links. Cu1−O1−H···O2 $(-1 + x, 1 + y, z)$ − Cu3 $(-1 + x, 1 + y, z)$ gives a Cu−Cu distance of 6.784(1) Å.

Table 3. Selected interatomic distances [Å] and angles [°] for the hydrogen bonding interactions in $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$; estimated standard deviations in parentheses

D−H···A	D−H	H···A	D···A	D−H···A
O1−H1A···O2[a]	0.81(5)	1.99(6)	2.729(7)	151(7)
O1−H1B···O21[b]	0.81(7)	2.15(7)	2.900(9)	154(7)
O2−H2A···N112[c]	0.81(4)	2.23(7)	2.931(8)	146(7)
O2−H2B···O31[d]	0.80(9)	2.02(9)	2.828(9)	178(8)
O2−H2B···O33[d]	0.80(9)	2.59(8)	3.057(9)	119(7)
O3−H3A···O13[b]	0.82(6)	2.29(6)	3.060(8)	157(7)
O3−H3A···O14[b]	0.82(6)	2.36(7)	3.046(8)	142(6)
O3−H3B···N212	0.81(7)	2.11(7)	2.913(8)	168(7)

Marked atoms are generated by symmetry operations: [a] $-1 + x, 1 + y, z$. − [b] $1 - x, 1 - y, 1 - z$. − [c] $2 - x, -y, 2 - z$. − [d] $1 - x, -y, 1 - z$.

Spectroscopic Properties

The UV/Vis spectrum shows a broad asymmetric band with a maximum situated at 11.6×10^3 cm^{-1} and a shoulder at 9.3×10^3 cm^{-1}, which is in agreement with the presence of both CuN_6 and CuN_5O chromophores, as well as with the tetragonal distortion of the Cu^{II} octahedra.[45]

There is no evidence for a strong deviation from T_d symmetry for the noncoordinating perchlorate anions, as is indicated by the strong ν_3 absorption at 1102 cm^{-1} and the ν_4 at 623 cm^{-1} observed in the infrared spectrum.[46]

Magnetic Measurements

The magnetic behavior of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$ is shown in Figure 3 in the form of a $\chi_M T$ vs. T plot, χ_M being the molar magnetic susceptibility and T the temperature. At 296 K the $\chi_M T$ value is 1.278 cm^3 mol^{-1} K, which is about the value expected for three uncoupled copper(II) ions. The value of $\chi_M T$ decreases upon cooling, reaching a value of 0.732 cm^3 mol^{-1} K at 2 K. This behavior is characteristic for compounds with an overall antiferromagnetic interaction between the metal(II) ions. The structure indicates the presence of interconnected linear trinuclear Cu^{II} units, these trinuclear entities being magnetically isolated. Therefore, the magnetic data have been interpreted using the expression for the molar magnetic susceptibility of a linear trinuclear system with S = 1/2.[11a,47]

$$\chi_M T = (N\beta^2 g^2/4k)[(1 + e^x + 10e^{3x/2})/(1 + e^x + 2e^{3x/2})] \qquad (1)$$

in which x = J/kT. J is the energy gap defined by the phenomenological spin Hamiltonian with quantum spin operators $\mathbf{S}_{Cu1}$, $\mathbf{S}_{Cu2}$, and $\mathbf{S}_{Cu3}$ where Cu1, Cu2 and Cu3 refer to nearest neighbor ions:

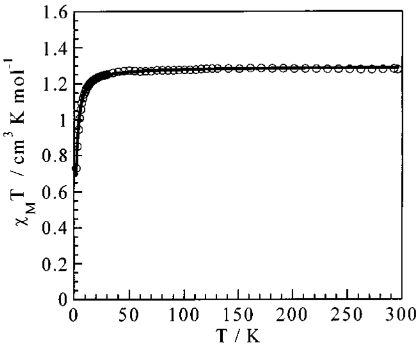

Figure 3. Observed (o) and calculated [—; $J = -1.01(2)$ cm^{-1}, g = 2.14(1)] $\chi_M T$ vs. T curves for $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$

$$\mathbf{H} = -J[S_{Cu1} \cdot S_{Cu2} + S_{Cu2} \cdot S_{Cu3}] \qquad (2)$$

The assumption of negligible magnetic exchange between second neighbor copper(II) ions is justified in view of the study of the triply N1,N2-1,2,4-triazole bridged $Fe^{II}-Fe^{II}-Fe^{II}$[30] and $Co^{II}-Co^{II}-Co^{II}$[48] trinuclear clusters, where the central metal ion is diamagnetic, and no magnetic interactions could be detected between the paramagnetic terminal metal ions. In Equation 1, N, g, β, k, and T have their usual meanings. The g factor must be considered as an average value of the local Zeeman factors, and intercluster exchange interactions were supposed to be negligible. A good fit has been obtained for the parameters g = 2.14(1) and $J = -1.01(2)$ cm^{-1} (see Figure 3).

The spectrum of the (S,S′) low-lying spin states, where S and S′ are the quantum numbers associated with the **S** and **S′** operators:

$$\mathbf{S} = \mathbf{S}_{Cu1} + \mathbf{S}_{Cu2} + \mathbf{S}_{Cu3}$$

$$\mathbf{S}' = \mathbf{S}_{Cu1} + \mathbf{S}_{Cu3}$$

consists of a ground doublet (1/2, 1), an excited doublet (1/2, 0) at the energy $-J$, and an excited quartet at the energy $-3J/2$. This excited spin quartet state is further split into two Kramers doublets, which to a first approximation can be labeled as M_S = ± 1/2 and ± 3/2.

The X-band powder EPR spectra for $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$ have been recorded at 298 K and 4 K. The spectrum at 4 K is shown in Figure 4. It exhibits features around g = 2 that can be assigned to the envelop of the three resonances within the M_S = ± 1/2 Kramers doublets, as well as a smaller feature around g = 5.6 that may be assigned to the resonance within the M_S = ± 3/2 Kramers doublet. It should be noticed that, due to the low symmetry of the Cu^{II} triad, the M_S = ± 1/2 and M_S = ± 3/2 Kramers doublets states arising from the spin quartet are somewhat mixed.

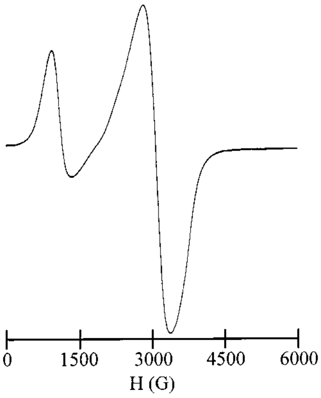

Figure 4. X-band powder EPR spectrum (ν = 9.46780 GHz) of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$ recorded at 4 K

Concluding Remarks

The btre ligand has been shown to be a powerful tool in preparing supramolecular architectures. The structure of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$ represents an unprecedented architecture of a three-dimensional compound. Recently, a polynuclear Cu^{II} compound of a bis(imidazole) ligand has been reported. $[Cu(bim)_{2.5}](ClO_4)_2 \cdot 2CH_3OH$ [bim = 1,2-bis(imidazole-1-yl)ethane][49] contains Cu^{II} ions in a distorted square-based pyramidal coordination environment. The neutral ligands in the *a*−*b* plane bind to four Cu^{II} ions in a *trans* mode, leading to a two-dimensional sheet arrangement. The resulting Cu−Cu distances are 7.05 Å and 11.43 Å in this *a*−*b* plane. Furthermore, the axially coordinating neutral bim ligand has a bent, *cis* conformation, and alternatively links the *a*−*b* plane to sheets above and below. The closest inter-sheet Cu−Cu separation is 12.55 Å.

Upon using the btre ligand, a larger versatility in coordination is anticipated due to the presence of the additional nitrogen atom within the 1,2,4-triazole ring compared to the imidazole. In fact, in $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6\cdot H_2O$ btre acts as a spacer between three and even four Cu^{II} ions. The tridentate ligands are bent, as is illustrated by the values for the N4−C1−C2−N4′ torsion angles involving the N4,N4′ ethylene linkage. These angles are −79.5(7)°, −86.1(7)°, 75.5(7)° and 63.0(7)° for the ligands marked 1, 2, 5 and 6, respectively. On the other hand, the N4−C1−C2−N4′ torsion angles of the tetradentate ligands 3 and 4 are restricted by crystallographic symmetry to a value of 180°.

Interestingly, the coordination mode of btre shows features already observed in coordination compounds of 3- or 4-substituted 1,2,4-triazoles where the well-known triply bidentate N1,N2 bridging of the 1,2,4-triazole ring has been found to result in linear trinuclear species.[21,30,31,35,50] In those cases, the chain growth is blocked by monodentately coordinated 1,2,4-triazole ligands and/or by water molecules. In fact, the trinuclear cation $[Cu_3(btre)_5(H_2O)_2]^{6+}$ can be regarded as a linear, trinuclear Cu^{II} compound of this type, in which the coordination environment about the terminal Cu^{II} ions is completed by two monodentate 1,2,4-triazole ligands and a water molecule. On the other hand, the btr ligand was originally designed in order to force a tetradentate coordination mode.[21] However, exclusively the N1,N1′ bidentate mode has been observed so far,[37−42] which may be due to charge distribution efficiency considerations, or more likely, may be ascribed to the fact that even in coordination compounds the btr ligand favors a conformation close to the one observed in the free ligand,[43] i.e. with fairly perpendicular 1,2,4-triazole nuclei. The more flexible nature of the ethylene linkage in the present btre ligand overcomes these problems, and indeed the tetradentate coordination has been achieved for some of the ligand molecules present. Furthermore, it could well be that this type of rigid tetradentate spacer allows a crystal packing of the trinuclear Cu^{II} units with distances close to those found in the compounds containing nonconnected trinuclear units of this type. Moreover, the bent, *cis*-btre ligands allows us to satisfactorily maintain these trinuclear entities, which are further stabilized by a network of hydrogen bonds.

In the present polynuclear Cu^{II} compound, a relatively small antiferromagnetic interaction [$J = -1.01(2)\ cm^{-1}$] has been found between adjacent metal(II) ions. It may be proposed that the linear trinuclear Cu^{II} cations represent the magnetic entities responsible for this magnetic interaction. Indeed, the magnetic data could satisfactorily be interpreted using the theoretical expression for linear trinuclear S = 1/2 units. The low *J* value can be explained on the basis of the superexchange pathway and the geometry around Cu^{II}. The unpaired electron for the d^9 ion clearly resides in the $d(x^2 - y^2)$ orbital, with hardly any density in the direction of the axially coordinating 1,2,4-triazole ligands. The magnitude of the antiferromagnetic interaction between Cu^{II} ions can therefore be explained by the superexchange pathway involving the σ orbitals of the N1,N2 diazine moiety of the bridging triazole network.[1−10] It should be noted that the magnetic orbitals located on the Cu^{II} ion are only favorably oriented to yield a considerable overlap on the 1,2,4-triazole ligand, linking the metal(II) ions with rather short Cu−N distances. Consequently, the main pathway for the superexchange only proceeds through one triazole ligand, i.e. ligand 3 between Cu1 and Cu2, and ligand 4 between Cu2 and Cu3. However, the bridging geometry of these ligands is slightly asymmetric, involving unequal Cu−N−N angles. Furthermore, the 1,2,4-triazole tends to twist slightly out of the equatorial plane formed by the two Cu^{II} ions involved, which is illustrated by the torsion angles of 7.9(7)° and 4.9(8)° involving ligands 3 and 4, respectively. These features lead to a rather inefficient propagation of the superexchange via this bridging network, which explains the rather low isotropic interaction parameter. This compares very well to the $J = -1.18(2)\ cm^{-1}$ (based on the Hamiltonian: $\mathbf{H} = -J\,[\,\Sigma_i\, S_i\cdot S_{i+1}]$) observed for the linear chain compound $[Cu(hyetrz)_3](ClO_4)_2\cdot 3H_2O$, having triple N1,N2-1,2,4-triazole bridges of comparable geometry.[8]

Only one linear trinuclear Cu^{II} compound containing triple N1,N2-1,2,4-triazole bridges has so far been structurally characterized. A detailed comparison with the magnetic data of $[Cu_3(metz)_6(H_2O)_4](CF_3SO_3)_6(H_2O)_4$ is not possible, since no accurate data are available as yet.[42][44]

We have shown that this first member of a new class of *N*,*N*′-bis(1,2,4-triazol-4-yl)alkane ligands leads to the creation of a unique new supramolecular Cu^{II} compound. Preliminary studies have already indicated that polynuclear Fe^{II} spin-crossover materials could be obtained using ligands of this family.

Experimental Section

Physical Measurements: Elemental analyses were performed by the Service Central d'Analyse (CNRS) in Vernaison, France. − Infrared spectra were carried out with a Perkin−Elmer Paragon 1000 FTIR spectrophotometer using KBr pellets. − UV/Vis spectra were recorded with a CARRY 5E spectrophotometer using the diffuse reflectance technique, with polytetrafluoroethylene as a reference. − X-band powder EPR spectra were obtained with a Bruker ESP 300 E electron spin resonance spectrometer. − Magnetic susceptibilities were carried out in the temperature range 300−2 K with a quantum design MPMS-5S SQUID magnetometer. − Magnetic data were corrected for diamagnetic contributions, which were estimated from the Pascal constants and were fitted to theoretical expressions by means of a Simplex routine. All parameters (*J*, *g*) were varied independently during the fitting procedure. This routine minimizes the function $R = |\Sigma|\chi_{obs} - \chi_{calc}|^2/|\Sigma|\chi_{obs}|^2|^{1.2}$.

Starting Materials: Commercially available solvents, monoformylhydrazine, triethyl orthoformate, ethylenediamine, and copper(II) perchlorate hexahydrate were used without further purification.

Synthesis of 1,2-Bis(1,2,4-triazol-4-yl)ethane (btre): The ligand btre was prepared from monoformylhydrazine, triethyl orthoformate, and ethylenediamine according to the general method described by Bayer et al.[51] Yield: 30%. M.p. > 260°C. − ^{1}H NMR (200 MHz, D_2O): δ = 2.67 (s, CH_2), 6.40 (s, trz−H), − IR: ṽ = 675 and 642 cm^{-1} (out-of-plane ring torsion vibrations of the 1,2,4-triazole), 887 cm^{-1} [C−H out of plane vibration (γ_{C-H})]. − $C_6H_8N_6$: calcd. C 43.90, H 4.91 N 51.19; found C 44.07, H 4.39, N 50.00.

Synthesis of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$: $Cu(ClO_4)_2 \cdot 6H_2O$ (0.48 mmol, 0.18 g), dissolved in 20 mL of water, was added to btre (1.52 mmol, 0.25 g), dissolved in 20 mL of water. The reaction mixture was diluted to 100 mL with water, and heated to give a clear solution. The compound precipitated upon cooling. The precipitate formed was left in the solution. Then, after a couple of days, well-shaped single crystals could be collected after slow evaporation of a part of the solvent at room temperature. Crystals were washed with water, and air-dried. Yield: 12.4%. − $C_{30}H_{46}Cl_6Cu_3N_{30}O_{27}$: calcd. C 21.68, H 2.79, Cl 12.80, Cu 11.47, N 25.28, O 25.99; found C 22.22, H 2.60, Cl 12.80, Cu 11.35, N 25.09, O 25.55.

Crystal Structure Determination of $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$: A blue, needle-shaped crystal of approximate dimensions 0.05 × 0.1 × 0.4 mm was mounted in a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf−Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 24 well-centered reflections (SET4[52]) in the range 10.0° < θ < 13.9°. The unit-cell parameters were checked for the presence of higher lattice symmetry.[53] Crystal data and details on data collection are presented in Table 4. Data were collected in ω scan mode with scan angle $\Delta\omega = 0.73 + 0.35\tan\theta$. Intensity data were collected up to θ = 26.5°. Intensity data of 11106 reflections were measured, 10579 of which were independent ($R_{int} = 0.0665$). Data were corrected for Lp effects and for 2% linear instability of the three periodically measured reference reflections during 50 h of X-ray exposure time, but not for absorption. The structure was solved by automated direct methods (SHELXS86[54]). Refinement on F^2 was carried out using full-matrix least-squares techniques (SHELXL-97[55]). Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms, except for the water hydrogen atoms, which were located in a difference Fourier map. Their coordinates were included as parameters in the refinement. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the water hydrogen atoms and 1.2 for the other hydrogen atoms. Final refinement included 318 parameters and final weights were $w^{-1} = \sigma^2(F_o^2) + (0.0365P)^2 + 2.98P$, where $P = [(F_o^2, 0)_{max} + 2F_c^2]/3$. No residual density was found outside −0.66 and 0.95 e Å^{-3}. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[56] Geometrical calculations and illustrations were performed with PLATON.[57] Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-124884. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat) + 44-1223/336-033; E-mail: deposit@ccdc.cam.uk].

Table 4. Crystallographic data for $[Cu_3(btre)_5(H_2O)_2](ClO_4)_6 \cdot H_2O$

Empirical formula	$C_{30}H_{44}Cu_3N_{30}O_2 \cdot 6(ClO_4) \cdot H_2O$
Molecular mass	1662.23
T [K]	150
Space group	P1bar (No. 2)
Crystal system	triclinic
a [Å]	12.488(1)
b [Å]	13.195(1)
c [Å]	19.756(2)
α [°]	78.959(8)
β [°]	84.553(8)
γ [°]	63.869(7)
V [Å^3]	2868.4(5)
Z	2
$\rho_{calcd.}$ [g/cm^3]	1.925
μ (Mo-K_α) [cm^{-1}]	15.0
Radiation [Å]	0.71073 (Mo-K_α, graphite monochromator)
$R(F)$[a]	0.058 [for 6484 $F_o > 4\sigma(F_o)$]
wR_2[b]	0.1214
GoF	1.012

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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