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Article

Use of a Reduced Schiff-Base Ligand to Prepare Novel Chloro-Bridged Chains of Rare Cu(II) Trinuclear Complexes with Mixed Azido/Oxo and Chloro/Oxo Bridges

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Two mixed bridged one-dimensional (1D) polynuclear complexes, $[Cu_3L_2(\mu_{1,1}\text{-}N_3)_2(\mu\text{-}Cl)Cl]_n$ (**1**) and $\{[Cu_3L_2(\mu\text{-}Cl)_3Cl]\cdot 0.46CH_3OH\}_n$ (**2**), have been synthesized using the tridentate reduced Schiff-base ligand HL (2-[(2-dimethylamino-ethylamino)-methyl]-phenol). The complexes have been characterized by X-ray structural analyses and variable-temperature magnetic susceptibility measurements. In both complexes the basic trinuclear angular units are joined together by weak chloro bridges to form a 1D chain. The trinuclear structure of **1** is composed of two terminal square planar $[Cu(L)(\mu_{1,1}\text{-}N_3)]$ units connected by a central Cu(II) atom through bridging nitrogen atoms of end-on azido ligands and the phenoxo oxygen atom of the tridentate ligand. These four coordinating atoms along with a chloride ion form a distorted trigonal bipyramidal geometry around the central Cu(II). The structure of **2** is similar; the only difference being a Cl bridge replacing the $\mu_{1,1}\text{-}N_3$ bridge in the trinuclear unit. The magnetic properties of both trinuclear complexes can be very well reproduced with a simple linear symmetrical trimer model ($H = -JS_iS_{i+1}$) with only one intracluster exchange coupling (J) including a weak intertrimer interaction (j) reproduced with the molecular field approximation. This model provides very satisfactory fits for both complexes in the whole temperature range with the following parameters: $g = 2.136(3)$, $J = -93.9(3)$ cm^{-1} and $zj = -0.90(3)$ cm^{-1} ($z = 2$) for **1** and $g = 2.073(7)$, $J = -44.9(4)$ cm^{-1} and $zJ = -1.26(6)$ cm^{-1} ($z = 2$) for **2**.

Introduction

The chemistry of multinuclear copper complexes has aroused considerable interest for their possible utility in modeling the multimetal active sites of metalloproteins[1,2] and understanding the fundamental science of magnetic interactions and magneto-structural correlations in molecular systems.[3] A good degree of success has been obtained in providing the exchange coupling between the azido, hydroxo, alkoxo, phenoxo, or chloro bridged copper centers by analyzing the results of numerous homodibridged compounds $\{Cu(\mu\text{-}X)_2Cu\}$,[4] also substantiated by theoretical calculations.[4d,5] The simplicity of these dimeric molecules makes them very popular as a subject of exhaustive studies for magnetic interactions, and the derived magneto-structural correlations can be extended easily to relatively complicated polymeric systems to explain their magnetic properties. For the situation where the bridging species that mediate the magnetic coupling are different, hardly any attempt has been made to correlate coupling with geometric parameters, largely because of a lack of suitable comparative structures containing the $\{Cu(\mu\text{-}X)(\mu\text{-}Y)Cu\}$ motif. There are some examples where mixed bridges link two

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copper(II) ions to result in a dinuclear entity,[6−22] and most of them contain binucleating ligands derived from 2-formyl salicylaldehyde.[7−14,16,17,19,23]

The degree of magnetic coupling between two Cu(II) centers is related to a number of parameters which can be determined using single crystal X-ray analysis. The pathway for coupling is the available orbital interactions between copper centers provided by the way in which the bridging species arrange the local copper geometries. The most usually encountered situations are penta-coordination with the extremes of trigonal bipyramidal and square-based pyramidal geometry that can be derived from octahedral geometry. In the square-pyramidal geometry, one of the ligands along the z-axis is removed, and the $d_{x^2−y^2}$ orbital is singly occupied. On the contrary in a trigonal bipyramidal environment, one ligand in the xy plane is removed and the d_{z^2} orbital is the "magnetic orbital".

Examples of trinuclear Cu(II) complexes, especially those containing the mixed bridged entitiy {Cu(μ-X)(μ-Y)Cu(μ-X)(μ-Y)Cu} are very limited.[14] The tri- or tetradentate Schiff bases are found to be very useful for the construction of phenoxo bridged trinuclear species. Such species can be linear or bent. The literature shows that in most of the reported compounds an additional bridging group (e.g., carboxylate, nitrate, halide, etc.) between the copper ions is also present in such trinuclear species, and the resulting tribridged molecules are linear.[24,25] There is an increasing demand for mixed-bridged angular trinuclear copper(II) systems to obtain a better understanding of the fundamental chemistry as well as the magnetic properties of biomolecules. The studies of such systems may be helpful to develop basic knowledge about the

exchange interactions between the paramagnetic centers of such systems.[26] Among the variety of mixed-bridging complexes, those containing phenoxo- and azido-/chloro- are of special interest because they represent valuable model compounds for the active site of a number of metalloenzymes and also possess interesting magnetic properties.[25c,d,27]

In this paper we report the syntheses, crystal structures, and magnetic properties of two novel one-dimensional (1D) polynuclear mixed bridged copper(II) complexes, $[Cu_3L_2(\mu_{1,1}-N_3)_2(\mu-Cl)Cl]_n$ (1) and $\{[Cu_3L_2(\mu-Cl)_3Cl]\cdot0.46CH_3OH\}_n$ (2), obtained from the reduced Schiff base ligand 2-[(2-dimethylamino-ethylamino)-methyl]-phenol (HL). In both compounds, the basic trinuclear angular units are joined together by a weak chloro bridge to form 1D chains. To our knowledge, such mixed-bridged trinuclear species are very rare, and bridging of such species by the chloride ion is unprecedented although there are numerous examples of various types of chloro bridged Cu(II) complexes.[28] The presence of an additional hydrogen atom on the N-atom in the reduced Schiff base facilitates the formation of an interesting H-bonding network which has also been analyzed.

Experimental Section

Materials. The reagents and solvents used were of commercially available reagent quality.

Caution! Azide complexes are potentially explosive; and caution should be exercised when dealing with such derivatives.

Synthesis of the Reduced Schiff Base Ligand (HL) 2-[(2-Dimethylamino-ethylamino)-methyl]-phenol. The Schiff base ligand was synthesized by refluxing a solution of salicylaldehyde (0.52 mL, 5 mmol) and N,N-dimethylethylenediamine (0.54 mL, 5 mmol) in methanol (30 mL) for 1 h. The solution was cooled to 0 °C, and solid sodium borohydride (210 mg, 6 mmol) was added slowly to this methanolic solution with stirring. After completion of the addition, the resulting solution was acidified with concentrated HCl (5 mL) and then evaporated to dryness.[29] The reduced Schiff base ligand HL was extracted from the solid mass with methanol, and this methanol solution (ca. 20 mL) was used for preparation of the complexes.

Synthesis of the Complex $[Cu_3L_2(\mu_{1,1}-N_3)_2(\mu-Cl)Cl]_n$ (1). An extracted methanol solution of HL as prepared above was added to a solution of $CuCl_2\cdot2H_2O$ (1.275 g, 7.5 mmol) in methanol (20 mL), and an aqueous solution (1 mL) of NaN_3 (0.325 g, 5.00 mmol) was added to this mixture with stirring. The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. Brown crystals of 1 suitable for X-ray diffraction were obtained after several days on slow evaporation of the solvent. Yield: (1.390 g, 76%), Anal. Calcd for $C_{22}H_{34}Cl_2Cu_3N_{10}O_2$: C, 36.09; H, 4.68; N, 19.13; Cu, 26.04%. found: C, 36.13; H, 4.59; N, 19.01; Cu, 25.92%. IR (KBr): ν(N−H),

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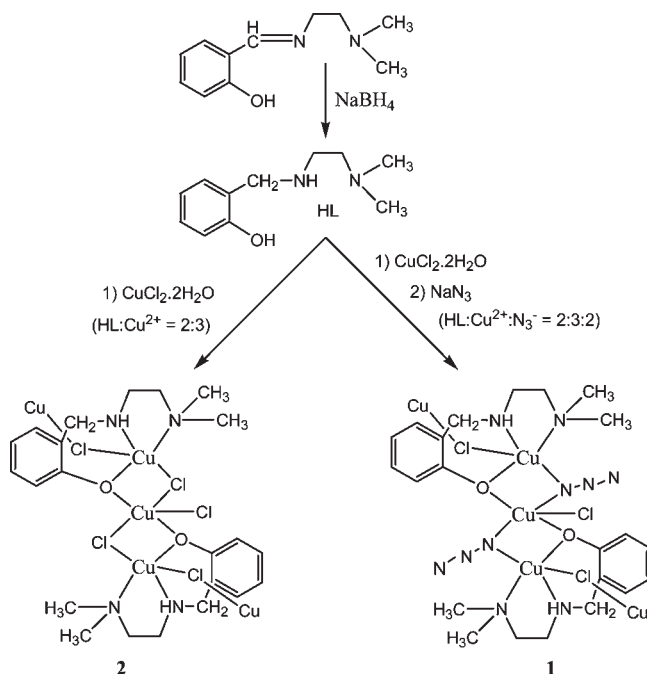**Table 1.** Crystal Data and Structure Refinement of Complexes **1** and **2**

	1	**2**
formula	$C_{22}H_{34}Cl_2Cu_3N_{10}O_2$	$C_{22.46}H_{35.84}Cl_4Cu_3N_4O_{2.46}$
M	732.11	733.69
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
$a/Å$	11.5818(6)	19.897(3)
$b/Å$	16.2364(9)	13.8715(8)
$c/Å$	16.2417(9)	14.3812(12)
β/deg	110.392(6)	104.487(5)
$V/Å^3$	2862.8(3)	2907.8(2)
Z	4	4
$D_c/g\ cm^{-3}$	1.699	1.676
μ/mm^{-1}	2.436	2.571
$F(000)$	1492	1493
$R(int)$	0.059	0.054
total reflections	19017	19998
unique reflections	8292	8419
$I > 2\sigma(I)$	4705	5690
R1, wR2	0.0418, 0.0760	0.0939, 0.1821
temp (K)	150	150

3235 cm^{-1}, ν(C−N), 1595 cm^{-1}; λmax (nm), [ε_{max} (dm^3 mol^{-1} cm^{-1})] (methanol), 612 (212).

Synthesis of the Complex $\{[Cu_3L_2(\mu\text{-}Cl)_3Cl]\cdot0.46CH_3OH\}_n$ **(2).** Another extracted methanol solution of HL (20 mL), prepared using the same quantity of reactants as stated above, was added to a solution of CuCl$_2$·2H$_2$O (1.275 g, 7.5 mmol) in methanol (20 mL). The mixture was stirred for 1 h and filtered. Deep green crystals of **2** suitable for X-ray diffraction were obtained on keeping the filtrate at room temperature for 24 h. Yield: (1.500 g, 82%). Anal. Calcd for [Cu$_3$L$_2$(μ-Cl)$_3$Cl],0.46-CH$_3$OH, C$_{22.46}$H$_{35.84}$Cl$_4$Cu$_3$N$_4$O$_{2.46}$, : C, 36.77; H, 4.92; N, 7.64; Cu, 25.98%. found: C, 36.70; H, 4.98; N, 7.54; Cu, 25.86%. IR (KBr): ν(N−H), 3208 cm^{-1}, ν(C−N), 1596 cm^{-1}; λmax (nm), [ε_{max} (dm^3 mol^{-1} cm^{-1})] (methanol), 608 (201).

Physical Measurements. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr pellets (4500−500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1200−350 nm) were recorded in a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurements were carried out in the temperature range 2−300 K with an applied magnetic field of 0.5 T on polycrystalline samples of compounds **1** and **2** (with masses of 42.27 and 46.68 mg, respectively) with a Quantum Design MPMS-XL-5 SQUID susceptometer. Isothermal magnetizations were performed on the same samples at 2 K with magnetic fields up to 5 T. Susceptibility data were corrected for the sample holders previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables.

Crystal Data Collection and Refinement. Crystal data for the two crystals are given in Table 1. 8292, 8419 independent data respectively were collected with Mo Kα radiation at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the CrysAlis program.[30] The structures were solved using direct methods with the Shelxs97 program.[31] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to

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Scheme 1. Formation of the Complexes

1.2 times (or 1.5 times for methyl hydrogen atoms) those of the atom to which they were attached. Absorption corrections were carried out using the ABSPACK program.[32] In **2**, two positions were located for a terminal chlorine atom attached to Cu(3), named Cl(3a) and Cl(3b), and these were given occupancy factors, x and $1 - x$. A solvent methanol molecule hydrogen bonded to Cl(3b) was given an equivalent occupancy of $1 - x$. x was refined to 0.54(1). The structures were refined on F^2 using Shelxl97[31] to R1 0.0418 and 0.0939 and wR2 0.0760 and 0.1821 for 4705, 5690 reflections with $I > 2\sigma(I)$ for **1** and **2**, respectively.

Results and Discussion

Synthesis of the Complexes. The condensation of *N,N*-dimethylethylenediamine in 1:1 molar ratio with salicylaldehyde afforded the Schiff base, 2-[(2-dimethylamino-ethylimino)-methyl]-phenol, which on reduction with sodium borohydride readily produced the reduced Schiff base, HL. HL on reaction with copper(II) chloride in a 2:3 molar ratio yielded compound **2**. Compound **1** was produced when sodium azide (equimolar to ligand) was also present in the reaction mixture (Scheme 1). The deprotonated ligand reacts readily with Cu(II) to occupy three of the four equatorial coordination sites and the azide (in **1**) or chloride (in **2**) ions coordinate to the remaining one. The coordinated azide (or chloride) and the phenoxo oxygen of two such mononuclear units coordinate to a free Cu(II) ion, which is present in excess to yield the mixed bridged trinuclear species. Connecting the two mononuclear units via Cu(II) is not surprising as the bridging abilities of both phenoxo oxygen and azide (or chloride) groups are well documented. Of the two chloride ions which are required to maintain the electroneutrality of such trinuclear complexes, one coordinates terminally to the central Cu(II) and the other bridges the trinuclear units to form the 1D chains (Scheme 1)

IR and Electronic Spectra. A moderately strong, sharp peak due to N−H stretching vibration at 3235 and 3208 cm^{-1} for complexes **1** and **2**, respectively, shows that the imine group of the Schiff base is reduced. The reduction of

the imine group is also very clearly indicated by the absence of the strong band due to imine vibration which appears in the region 1620−1650 cm^{-1} for the complexes of the corresponding unreduced Schiff bases.[33a] The sharp peak at 2076 cm^{-1} for complex **1** is due to $\nu(N_3)$ suggesting the end-on ($\mu_{1,1}$) bridging mode of the azide ion.[33b]

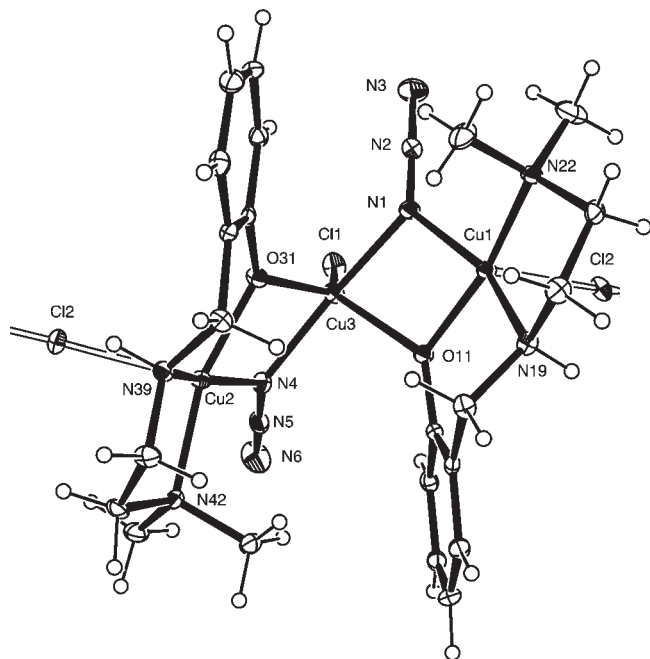The electronic spectra of these two compounds were recorded in methanol solution. The electronic spectra

Figure 1. Trinuclear structure of **1** with ellipsoids at 30% probability. The open bonds show the weak Cu···Cl interactions.

show a single absorption band at 612 and 608 nm for compounds **1** and **2**, respectively. The positions of these bands are typical of d−d transitions in Cu(II) ions with a square-pyramidal geometry.[34]

Crystal Structures of the Complexes. Structure of [Cu$_3$L$_2$($\mu_{1,1}$-N$_3$)$_2$(μ-Cl)Cl]$_n$ (1). The structure of **1** is shown in Figure 1 together with the atomic numbering scheme.

The structure consists of trinuclear Cu(II) units which are bridged by weak Cu···Cl interactions to form a 1D polymer (Figure 2a) by sharing the vertex of the trinuclear units (Figure 2b). The two outer copper atoms Cu(1) and Cu(2) have equivalent environments having four strong bonds in a equatorial plane being bonded to three atoms of the ligand together with an azide nitrogen atom. Bond lengths from Cu(1) are 1.914(2) Å to O(11), 2.014(2) Å to N(19), 2.031(2) Å to N(22) in the terdentate ligand, and 2.031(3) Å to the azide N(1). Equivalent distances from Cu(2) are 1.946(2) Å to O(31), 1.998(2) Å to N(39), 2.042(3) Å to N(42), and 2.000(3) Å to the azide N(4) (Table 2). The four donor atoms in the equatorial planes of Cu(1) and Cu(2) are almost planar with root mean square (rms) deviations of 0.038 and 0.052 Å, respectively, with the copper atoms 0.306(1) and 0.270(1) Å from the plane in the direction of a weakly bound chlorine atom in an axial position, namely, Cl(2) at 2.647(1) Å from Cu(2) and Cl(2^a) (^{a} = 0.5−x,−0.5+y, 1.5−z) at 2.539(1) Å from Cu(1). This Cl(2) atom thus forms a bridge between adjacent trinuclear units with a Cu(1^c)−Cl(2)−Cu(2) (^{c} = 0.5−x, 0.5+y, 1.5−z) angle of 140.6(1)°.

In the trinuclear unit, the central copper atom Cu(3) has a five-coordinate trigonal prismatic environment being bonded to two azide nitrogen atoms N(1) and N(4) which bridge to Cu(1) and Cu(2), respectively, and two oxygen atoms O(11) and O(31) which also bridge to
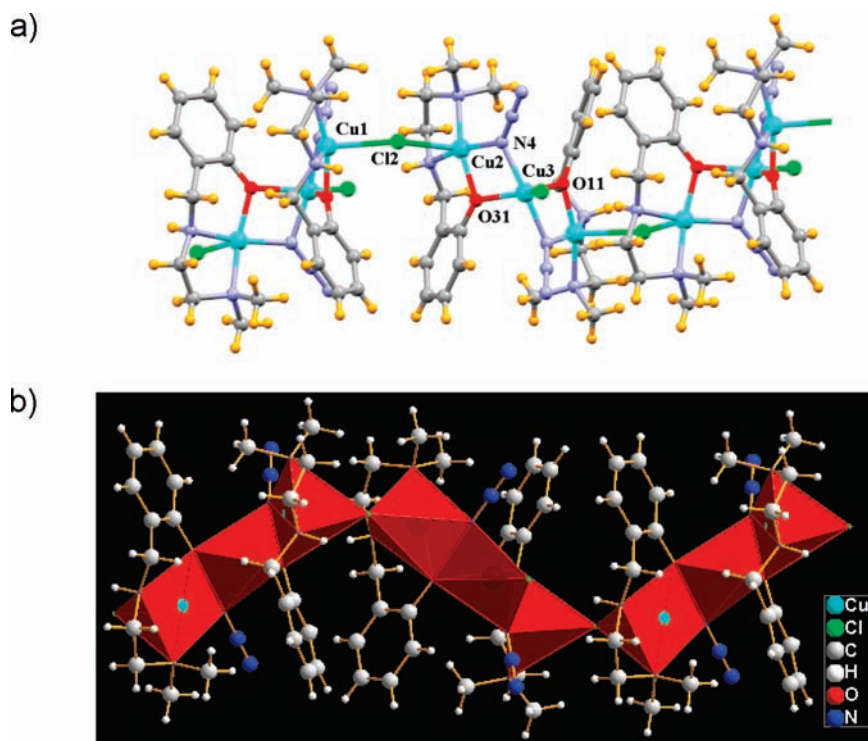

Figure 2. (a) 1D polymer formed by weak Cu···Cl interactions between the trinuclear units in compound **1**. (b) The vertex sharing 1D polymer formed by weak Cu···Cl interactions between the trinuclear units in compound **1**.

Table 2. Bond Distances (Å) and Angles (deg) for Complexes **1** and **2**

complex **1**		complex **2**	
Cu(1)−O(11)	1.914(2)	Cu(1)−N(19)	1.999(7)
Cu(1)−N(19)	2.014(2)	Cu(1)−N(22)	2.054(8)
Cu(1)−N(22)	2.031(2)	Cu(1)−O(11)	1.981(6)
Cu(1)−N(1)	2.031(3)	Cu(1)−Cl(1)	2.310(2)
Cu(1)−Cl(2)[a]	2.539(1)	Cu(1)−Cl(4)	2.624(2)
Cu(2)−O(31)	1.946(2)	Cu(2)−N(39)	2.000(6)
Cu(2)−N(39)	1.998(2)	Cu(2)−N(42)	2.070(8)
Cu(2)−N(4)	2.000(3)	Cu(2)−O(31)	1.982(6)
Cu(2)−N(42)	2.042(3)	Cu(2)−Cl(2)	2.315(2)
Cu(2)−Cl(2)	2.647(1)	Cu(2)−Cl(4)[b]	2.547(2)
Cu(3)−N(4)	1.993(3)	Cu(3)−O(11)	1.951(5)
Cu(3)−N(1)	2.002(3)	Cu(3)−O(31)	1.942(5)
Cu(3)−O(11	2.080(2)	Cu(3)−Cl(3b)	2.187(5)
Cu(3)−O(31)	2.091(2)	Cu(3)−Cl(3a)	2.296(4)
Cu(3)−Cl(1)	2.222(1)	Cu(3)−Cl(1)	2.480(2)
		Cu(3)−Cl(2)	2.500(2)
O(11)−Cu(1)−N(19)	91.38(9)	O(11)−Cu(1)−N(19)	92.4(3)
O(11)−Cu(1)−N(22)	165.16(10)	O(11)−Cu(1)−N(22)	163.8(3)
N(19)−Cu(1)−N(22)	85.95(10)	N(19)−Cu(1)−N(22)	85.8(3)
O(11)−Cu(1)−N(1)	78.73(9)	O(11)−Cu(1)−Cl(1)	82.6(2)
N(19)−Cu(1)−N(1)	158.34(11)	N(19)−Cu(1)−Cl(1)	165.6(2)
N(22)−Cu(1)−N(1)	98.66(10)	N(22)−Cu(1)−Cl(1)	95.3(2)
O(11)−Cu(1)−Cl(2)[a]	96.52(7)	O(11)−Cu(1)−Cl(4)	101.1(2)
N(19)−Cu(1)−Cl(2)[a]	97.27(8)	N(19)−Cu(1)−Cl(4)	90.5(2)
N(22)−Cu(1)−Cl(2)[a]	98.29(8)	N(22)−Cu(1)−Cl(4)	95.0(2)
N(1)−Cu(1)−Cl(2)[a]	102.93(8)	Cl(1)−Cu(1)−Cl(4)	103.7(1)
O(31)−Cu(2)−N(39)	93.07(9)	O(31)−Cu(2)−N(39)	93.0(3)
O(31)−Cu(2)−N(4)	78.31(9)	O(31)−Cu(2)−N(42)	165.2(3)
N(39)−Cu(2)−N(4)	165.16(10)	N(39)−Cu(2)−N(42)	85.0(3)
O(31)−Cu(2)−N(42)	162.21(9)	O(31)−Cu(2)−Cl(2)	83.3(2)
N(39)−Cu(2)−N(42)	85.52(10)	N(39)−Cu(2)−Cl(2)	161.9(2)
N(4)−Cu(2)−N(42)	98.97(11)	N(42)−Cu(2)−Cl(2)	94.1(2)
O(31)−Cu(2)−Cl(2)	104.15(7)	O(31)−Cu(2)−Cl(4)[b]	97.4(2)
N(39)−Cu(2)−Cl(2)	89.28(8)	N(39)−Cu(2)− Cl(4)[b]	94.3(2)
N(4)−Cu(2)−Cl(2)	104.45(7)	N(42)−Cu(2)−Cl(4)[b]	97.4(3)
N(42)−Cu(2)−Cl(2)	93.57(7)	Cl(2)−Cu(2)−Cl(4)[b]	103.7(2)
N(4)−Cu(3)−N(1)	166.57(11)	O(31)−Cu(3)−O(11)	172.2(3)
N(4)−Cu(3)−O(11)	95.60(9)	O(31)−Cu(3)−Cl(3b)	94.8(2)
N(1)−Cu(3)−O(11)	75.63(9)	O(11)−Cu(3)−Cl(3b)	92.7(2)
N(4) −Cu(3)−O(31)	75.13(9)	O(31)−Cu(3)−Cl(3a)	93.2(2)
N(1)−Cu(3)−O(31)	95.93(10)	O(11)−Cu(3)−Cl(3a)	93.9(2)
O(11)−Cu(3)−O(31)	98.99(8)	O(31)−Cu(3)−Cl(1)	97.2(2)
N(4) −Cu(3)−Cl(1)	97.63(8)	O(11)−Cu(3)−Cl(1)	78.8(2)
N(1) −Cu(3)−Cl(1)	95.73(8)	Cl(3b)−Cu(3)−Cl(1)	104.9(2)
O(11)−Cu(3)−Cl(1)	124.00(7)	Cl(3a)−Cu(3)−Cl(1)	144.2(1)
O(31)−Cu(3)−Cl(1)	136.99(6)	O(31)−Cu(3)−Cl(2)	79.3(2)
		O(11)−Cu(3)−Cl(2)	95.8(2)
		Cl(3b)−Cu(3)−Cl(2)	143.4(2)
		Cl(3a)−Cu(3)−Cl(2)	103.8(1)
		Cl(1)−Cu(3)−Cl(2)	111.7(1)

[a] Symmetry operation: 0.5−x, y−0.5, 1.5−z for complex **1**. [b] Symmetry operation: 0.5+x, 0.5−y, 0.5+z for complex **2**.

Cu(1) and Cu(2), respectively, and a terminal chlorine atom Cl(1). O(11), O(31), and Cl(1) make up the equatorial plane which together with Cu(3) provide a rms deviation of 0.006 Å. The two axial atoms are the azide nitrogen atoms N(1) and N(4). Bond lengths from Cu(3) are 2.002(3) and 1.993(3) Å to azide nitrogen atoms and 2.080(2) and 2.091(2) Å to ligand oxygen atoms and 2.222(1) Å to Cl(1). The distortions of the coordination polyhedra from the square pyramid to the trigonal bipyr-

(34) (a) Costes, J.-P.; Dahan, F.; Laurent, J.-P. *Inorg. Chem.* **1986**, *25*, 413. (b) Kwiatkowski, M.; Kwiatkowski, E.; Olechnowicz, A.; Ho, D. M.; Deutsch, E. *Inorg. Chim. Acta* **1988**, *150*, 65. (c) Bian, H.-D.; Xu, J.-Y.; Gu, W.; Yan, S.-P.; Cheng, P.; Liao, D.-Z.; Jiang, Z.-H. *Polyhedron* **2003**, *22*, 2927. (d) Ray, M. S.; Chattopadhyay, S.; Drew, M. G. B.; Figuerola, A.; Ribas, J.; Diaz, C.; Ghosh, A. *Eur. J. Inorg. Chem.* **2005**, 4562. (e) Sarkar, B.; Ray, M. S.; Drew, M. G.; Figuerola, A.; Diaz, C.; Ghosh, A. *Polyhedron* **2006**, *25*, 3084.

amid have been calculated by the Addison parameter (τ)[35] as an index of the degree of trigonality. The value of τ is defined as the difference between the two largest donor−metal−donor angles divided by 60, a value that is 0 for the ideal square pyramid and 1 for the trigonal bipyramid. The τ values are 0.11 and 0.05 for Cu(1) and Cu(2), respectively, indicating that the geometry around these two copper ions is nearly square pyramidal. However, the τ value (0.49) for Cu(3) shows that the geometry of the central Cu(II) ion is intermediate between the two ideal geometries.

Structure of $\{[Cu_3L_2(\mu\text{-}Cl)_3Cl]\cdot 0.46CH_3OH\}_n$ **(2).** The trinuclear structure of **2** is shown in Figure 3. As in **1**, the trinuclear units are bridged by chlorine atoms to form a vertex sharing 1D polymer (Figure 4).

The formula of this structure is similar to that in **1** but with chloride ions replacing azides. However, while the geometry of the outer atoms Cu(1) and Cu(2) is similar to that found in **1**, that of the central Cu(3) is very different. Cu(1) and Cu(2) show equivalent square planar geometries being bonded to the three donor atoms of the tridentate ligand together with a chlorine atom. Bond lengths from Cu(1) are 1.981(6) Å to O(11), 1.999(7) Å to N(19), and 2.054(8) Å to N(22) in the terdentate ligand and 2.310(2) Å to Cl(1) and from Cu(2) are 1.982(6) Å to O(31), 2.000(6) Å to N(39), 2.070(8) Å to N(42), and 2.315(2) Å to Cl(2) (Table 2). The four donor atoms form an equatorial plane with rms deviations of 0.038 and 0.010 Å, respectively, around Cu(1) and Cu(2) with the metal atoms 0.298(3) and 0.273(3) Å from the plane in the direction of an axial chloride ion, namely, Cl(4) which is 2.624(2) Å from Cu(1) and Cl(4[b]) ([b] = x+0.5, 0.5−y, z+0.5) which is 2.547(2) Å from Cu(2). As in **1**, the bridging chlorine atom forms a 1D polymer in which the Cu(1)−Cl(4)−Cu(2[d]) ([d] = x−0.5, 0.5−y, z−0.5) angle is 126.3(1)°, significantly smaller than the corresponding bridging angle of 140.6(1)° in **1**.

Just as in **1**, the central copper atom Cu(3) has a five-coordinate trigonal bipyramidal coordination sphere. Cu(3) is bonded to two bridging oxygen atoms from the ligand, two bridging chloride anions and a terminal chloride anion. However while in **1**, the bridging azides are in axial positions, in **2**, by contrast, it is the bridging oxygens O(11) and O(31) that are in axial positions with bond lengths of 1.951(5), 1.942(5) Å, significantly shorter than the distances of 2.080(2), 2.091(2) Å found in **1** where the oxygen atoms are in equatorial positions. This difference seems to be responsible for the considerable bent structure of **1** with a Cu(1)−Cu(3)−Cu(2) angle of 110.2(1)° compared to a quasi-linear structure of **2** where this angle is 171.3(1)°. In the equatorial plane there are two bridging chloride anions at 2.480(2) and 2.500(2) Å and a third chloride Cl(3) which is disordered over 2 sites, named Cl(3a) and Cl(3b). These two alternative positions are close to the equatorial plane being 0.063(5), 0.163(5) Å from the plane of Cu(3), Cl(1), and Cl(2). The two positions of Cl(3) are approximately equivalent as the angles subtended at the metal by Cl(3a) with Cl(1) and Cl(2) are 144.2(1)° and 104.9(2)° and by Cl(3b) are 103.8(2)° and 143.4(2)°, respectively. There is a methanol

(35) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
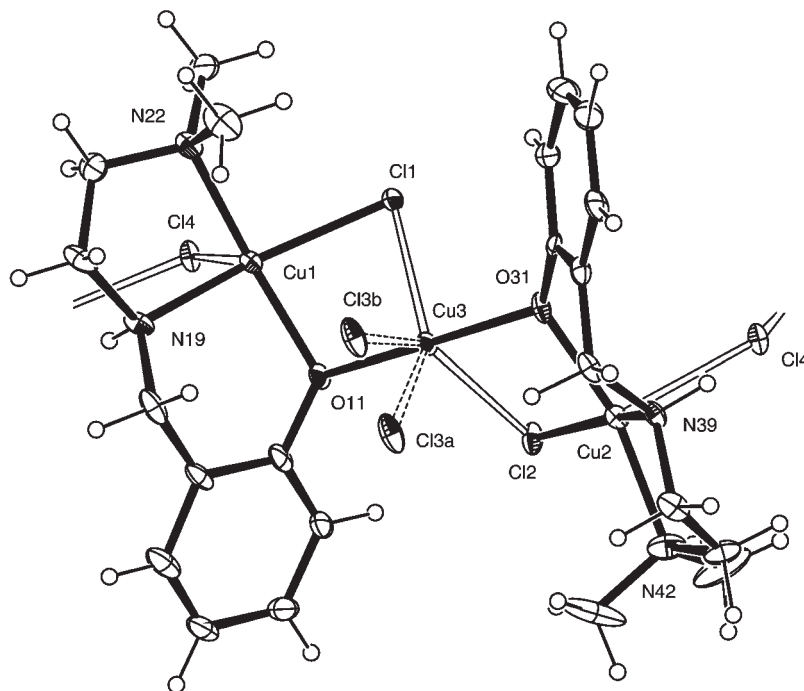
Figure 3. Trinuclear structure of **2** with ellipsoids at 30% probability. Atoms Cl(3a) and Cl(3b) are alternative positions with occupancies of 0.54(1) and 0.46(1), respectively, and bonds to the metal are shown as dotted lines. The weak Cu···Cl interactions are shown as open bonds.
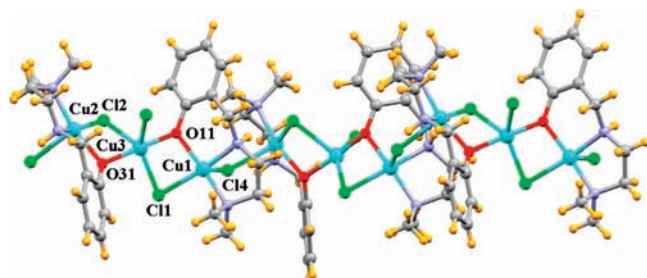

Figure 4. 1D polymer formed by weak Cu···Cl(4) interactions between the trinuclear units in compound **2**.

Table 3. Hydrogen Bonding Distances (Å) and Angles (deg) for the Complexes **1**–**2**

complex	D–H···A	D–H (Å)	A···H (Å)	D···A (Å)	∠D–H–A (deg)
1	N(19)–H···Cl(2)[a]	0.91	2.78	3.345(3)	121
2	N(19)–H···Cl(2)[b]	0.91	2.40	3.232(7)	152
	N(39)–H···Cl(4)[c]	0.91	2.62	3.298(6)	132

[a] Symmetry operation: $(0.5+x, 1.5-y, 0.5+z)$. [b] Symmetry operation: $(-0.5+x, 0.5-y, z-0.5)$. [c] Symmetry operation: $(1.5-x, -0.5+y, 2.5-z)$.

molecule hydrogen bonded to Cl(3b) with dimensions O−H···Cl 129°, O···Cl 3.23(3) Å, and H···Cl 2.62 Å. The solvent molecule was refined with an equivalent occupancy to the chloride to which it was attached. As in **1**, the τ values (0.03 and 0.05 for Cu(1) and Cu(2), respectively) indicate a nearly regular square pyramidal geometry for the two terminal Cu(II) ions but a consider-able distortion ($\tau = 0.47$(av.)) toward trigonal bipyramid for Cu(3). The Cu1···Cu3 and Cu2···Cu3 distances in **1** are 3.117 Å and 3.128 Å, respectively. The same distances in **2** are 3.053 Å and 3.083 Å. The distances between the two terminal copper atoms are 5.12 Å and 6.12 Å for the complexes **1** and **2**, respectively.

Hydrogen Bonding. In the extended structures of **1** and **2**, a self-assembled two-dimensional (2D) framework is formed by hydrogen-bonding interactions (Table 3). In complex **1**, the amine hydrogen atom N(19)−H forms a hydrogen bond with chloride ion Cl(2) (0.5+x, 1.5−y, 0.5+z) of a neighboring chain with dimensions 3.345(3) Å, 2.78 Å, 121° for N···Cl, H···Cl, and N−H···Cl, respectively (Figure 5). These hydrogen-bonding intera-ctions lead to the formation of a honeycomb-like 2D network with macrocyclic cavities involving six trinuclear
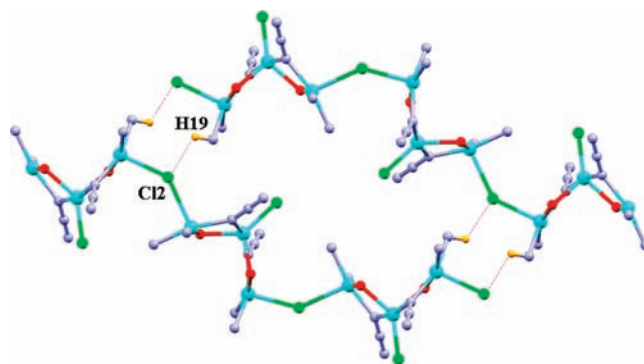

Figure 5. Hexameric macrocycle of **1**; carbon and hydrogen atoms except H19 have been excluded for clarity. Color code: Cu = light blue, N = dark blue, O = red, Cl = green.

molecules as shown in Figure 6. In complex **2**, the amine hydrogen atom N(19)−H forms an intrachain H-bond with chloride ion Cl(2) (−0.5+x, 0.5−y, z−0.5) whereas N(39)−H involves interchain H-bonding with Cl(4) (1.5−x, −0.5+y, 2.5−z) with dimensions 3.298(7) Å, 2.62 Å and 132° and 3.228(8) Å, 2.62 Å and 129° for N···Cl, H···Cl and N−H···Cl, respectively, (Figures S1 and S2).

Magnetic Properties. The thermal variation of the molar magnetic susceptibility per copper trinuclear unit
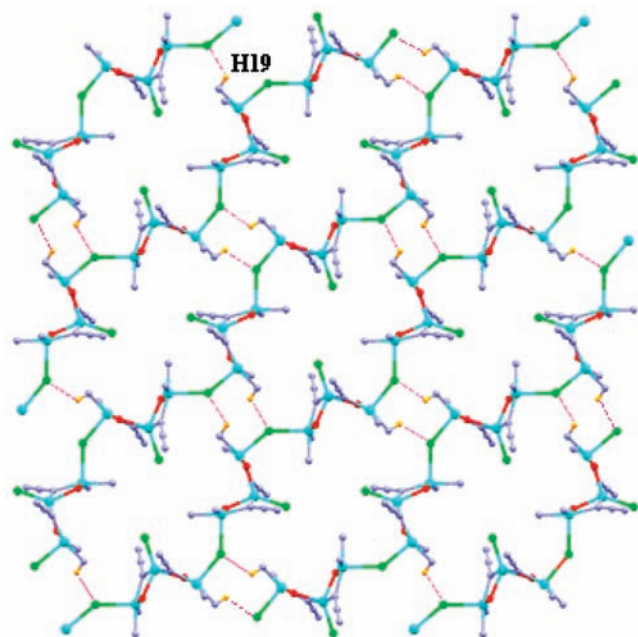
Figure 6. Supramolecular network in the lattice of **1**; carbon and hydrogen atoms except H19 have been excluded for clarity. Color code: Cu = light blue, N = dark blue, O = red, Cl = green.
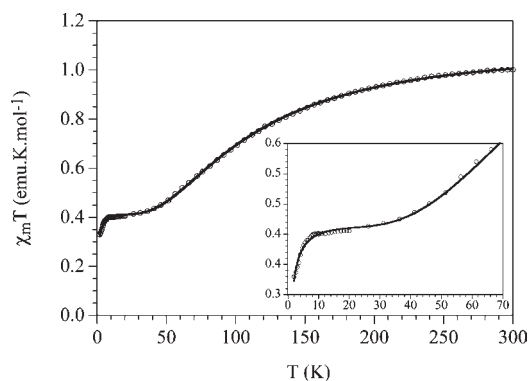

Figure 7. Thermal variation of the $\chi_m T$ product for compound **1**. Inset shows the low temperature region. Solid lines represent the best fit to the model (see text).

times the temperature ($\chi_m T$) for compound **1** shows at room temperature a value of about 1.0 emu K mol^{-1} (Figure 7). This value is slightly lower than expected for three isolated Cu(II) $S = 1/2$ ions (1.125 emu K mol^{-1} for $g = 2.0$). When cooling down the sample, the $\chi_m T$ product decreases to reach a value of about 0.4 emu K mol^{-1} below about 30 K that remains constant down to about 5 K and decreases again below this temperature (inset in Figure 7). This behavior indicates the presence of predominant antiferromagnetic interactions between the Cu(II) ions. In fact, the presence of a plateau with a value of about 0.4 emu K mol^{-1} is expected for an antiferromagnetically coupled Cu(II) linear trinuclear complex where the central spin is coupled with the two terminal ones, but there is no coupling between the terminal ones. As a result of the odd number of Cu(II) ions, the resulting spin ground state corresponds to an $S = 1/2$ ion, as clearly shown by the plateau that can be observed at low temperatures. The decrease observed at very low temperatures indicates that there in an additional intertrimer
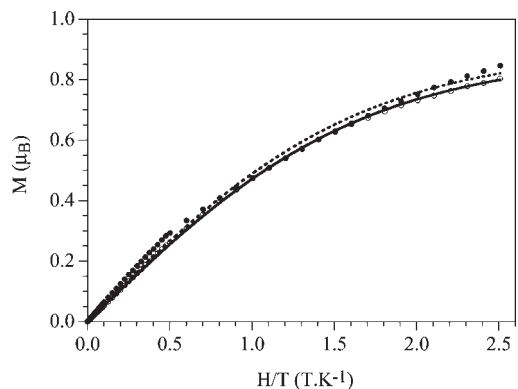

Figure 8. Isothermal magnetization of compounds **1** (solid circles) and **2** (empty circles) at 2 K. Solid and dashed lines are the fit to a Brillouin function for an $S = 1/2$ ion for **1** and **2**, respectively.

coupling, only effective at very low temperatures, that connects the $S = 1/2$ spin ground state of each Cu(II) trimer resulting in a further decrease of the magnetic moment at very low temperatures.

From these data and the molecular structure of compound **1** which contains chains of trimers with weak Cu−Cl−Cu intertrimer interactions, we have fitted the magnetic properties to a simple symmetrical Cu(II) $S = 1/2$ linear trimer model (the Hamiltonian is written as $H = -JS_iS_{i+1}$):[3]

$$\chi_{trim} = \frac{Ng^2\beta^2}{4kT} \frac{1 + \exp(x) + 10\exp(3x/2)}{1 + \exp(x) + 2\exp(3x/2)}$$

$$\text{with} \quad x = J/kT$$

where J is the intratrimer coupling constant. The weak intertrimer coupling arising from the long Cu−Cl−Cu intertrimer bridges is reproduced with the molecular field approximation:[36]

$$\chi = \frac{\chi_{trim}}{1 - (2zj/Ng^2\beta^2)\chi_{trim}},$$

where χ_{trim} is the susceptibility expression for the symmetrical trinuclear unit (see above) and zj is the product of the number of neighboring trinuclear units (z) times the intertrimer coupling constant (j).

This simple model reproduces very satisfactorily the magnetic properties of compound **1** in the whole temperature range (solid line in Figure 7) with the following set of parameters: $g = 2.136(3)$, $J = -93.9(3)$ cm^{-1}, and $zj = -0.90(3)$ cm^{-1} ($z = 2$ in this case, since each trimer is connected to only two neighboring trimers). Note that although the two intratrimer bridges are not identical, they are very similar and, to reduce the number of adjustable parameters, they have been assumed to be equivalent. The very satisfactory fit obtained with the model confirms that this assumption is acceptable.

A further confirmation of the antiferromagnetic coupling present in this compound can be obtained from the isothermal magnetization at 2 K that shows a saturation value of about 1.0 μ_B and a behavior that can be very well reproduced with a Brillouin function for an isolated $S = 1/2$ ion although with a reduced g value given the intertrimer antiferromagnetic interactions present at 2 K (Figure 8).

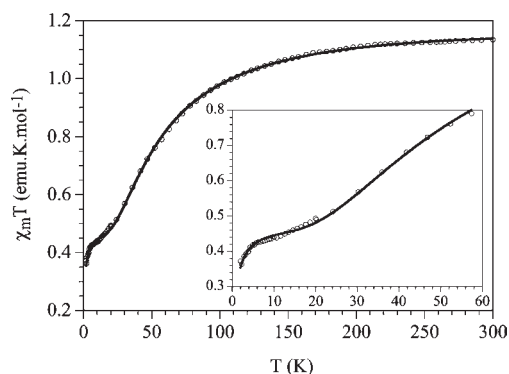(36) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

Figure 9. Thermal variation of the $\chi_m T$ product for compound **2**. Inset shows the low temperature region. Solid lines represent the best fit to the model (see text).

Table 4. Magnetic and Structural Parameters of Compound **1** and of All the Known Cu(II) Dimers Presenting a Mixed-Double $\mu_{1,1}$-N$_3$ and Oxo Bridge

CCDC code	J (cm^{-1})	Cu−O−Cu	−OR	Cu−N−Cu	ref.
CAWFEL	−200	102.5	OH	95.7	6
FAMKAF	−86.5	98.7	OPh	100.0	7
FIFWEW	−161	100.5	OPh	99.7	8
GIPVEG	−388	106.0	OPh	100.7	9
HONKAX	−119	102.1	OPh	102.9	10
JOGBUC	−482	98.4	OPh	104.6	11
LIBPAO	−188.6	101.3	OPh	98.3	22
ROGPOS	−132.4	99.2	OPh	99.9	12
SATYOB	−278	99.4	OPh	106.1	13
SATZES	−408	100.4	OPh	102.8	13
COMPOUND 1	−93.9	102.5	OPh	101.2	this work
	−93.9	101.5	OPh	103.2	

The thermal variation of the molar magnetic susceptibility per Cu(II) trinuclear unit times the temperature ($\chi_m T$) for compound **2** shows at room temperature a value of about 1.1 emu K mol^{-1}, very close to expected for three $S = 1/2$ Cu(II) non-interacting ions (1.125 emu K mol^{-1} for $g = 2$). When the temperature is lowered, the $\chi_m T$ value decreases to reach a value of about 0.45 emu K mol^{-1} at about 15 K. Below about 15 K, $\chi_m T$ remains constant down to about 5 K, and then it shows an additional decrease to reach a value of 0.36 emu K mol^{-1} at 2 K (Figure 9). This behavior is very similar to that shown by compound **1** and, as confirmed by the structural data, also indicates the presence of antiferromagnetically coupled Cu(II) linear trimers where the central spin is coupled with the two terminal ones, but there is no coupling between the terminal ones. As in compound **1**, the odd number of Cu(II) ions in the trimer results in a ground spin state $S = 1/2$ that is responsible of the plateau observed at low temperatures. The decrease of $\chi_m T$ at very low temperatures also indicates that there is an additional intertrimer coupling.

As already mentioned, the structure of compound **2** is very similar to that of compound **1** both containing chains of Cu(II) trimers connected through long Cu−Cl−Cu bridges. The only difference involves the intratrimer bridges: a $\mu_{1,1}$-N$_3$ and a O atom in **1** versus a Cl and an O atom in **2**. Since both kinds of intratrimer bridges are expected to generate antiferromagnetic couplings (see below), we have fitted the magnetic properties of compound **2** to the same simple symmetrical Cu(II) $S = 1/2$ linear trimer model used for compound **1** (see above). This simple model reproduces very satisfactorily the magnetic properties of compound **2** in the whole temperature range (solid line in Figure 9) with the following set of parameters: $g = 2.073(7)$, $J = -44.9(4)$ cm^{-1}, and $zJ' = -1.26(6)$ cm^{-1}, with z the number of nearest neighbors of each trimer ($z = 2$, as in **1**). The Hamiltonian is also written as $H = -JS_iS_{i+1}$. Note that, as observed in compound **1**, although the two intratrimer bridges are not identical, they are very similar and have been assumed to be equivalent.

As expected, the isothermal magnetization of compound **2** at 2 K shows very similar behavior to that of compound **1** with a saturation value of about 1.0 μ_B (Figure 8). As in compound **1**, the isothermal magnetization can be well reproduced with a Brillouin function for

an isolated $S = 1/2$ ion although with a reduced g value given the intertrimer antiferromagnetic interactions present at 2 K.

Compound **1** is the first example of a chloro bridged 1D chain of Cu(II) trimers containing mixed $\mu_{1,1}$-N$_3$ and oxo bridges, and, therefore, its magnetic properties cannot be compared with other similar complexes. Nevertheless, there are some Cu(II) dimers containing these kind of mixed double bridges. Thus, the CCDC database (updated Nov. 2009) shows up to 14 structurally characterized copper dimers presenting mixed $\mu_{1,1}$-N$_3$ and oxo bridges although only 10 have been also magnetically characterized (see Table 4). All these compounds show quite strong antiferromagnetic couplings with J values (normalized for a spin Hamiltonian $H = -JS_1S_2$) in the range −86 to −482 cm^{-1} (see Table 4). Unfortunately, there is no direct relationship between the J values and the Cu−O−Cu nor the Cu−N−Cu bond angles in these compounds. This fact can be easily explained from previous magneto structural correlations[4a,37−40] and theoretical calculations[4d,5] for oxo-bridged complexes (either hydroxo, alkoxo, or phenoxo) showing that, although the main parameter governing the magnetic coupling is the Cu−O−Cu angle, there are some others that need to be considered.[22] These correlations establish that for the phenoxo bridges present in compound **1** with Cu−O−Cu bond angles of 102.53(10)° and 101.54(9)° the magnetic coupling should be about 400 cm^{-1}, well above the experimental value (ca. −94 cm^{-1}). There are two explanations for the lower experimental values. On the one hand, although the geometry of the terminal Cu(II) ions is close to the square pyramid (the Addison parameters, τ, are 0.11 and 0.05 for Cu(1) and Cu(2), respectively, see above),[35] the geometry of the central Cu(II) ion is intermediate between the trigonal bipyramid and the square pyramid ($\tau = 0.49$ for Cu(3), see above). This fact reduces significantly the orbital overlap between the central and the terminal Cu(II) ions and, therefore, the magnetic coupling. On the other hand, the $\mu_{1,1}$-N$_3$ bridge is well-known to give rise to ferromagnetic coupling for low Cu−N−Cu angles and antiferromagnetic coupling for large angles, with a crossing angle of about 104°.[33,41] In compound

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Table 5. Magnetic and Structural Parameters of Compound **2** and of All the Known Cu(II) Dimers and Trimers Presenting a Mixed-Double Chlorine and Oxo Bridge

CCDC code	J (cm^{-1})	Cu−O−Cu	−OR	Cu−Cl−Cu	ref.
PETSOX	−291	103.5	OPh	85.6	14
	−162	106.5	OPh	78.2	
FESJIW	−335	111.4	OPh	89.6	15
FOGGIR	−443	113.4	OPh	86.1	9
IBUJOF	−85	117.3	OPh	78.1	17
JEDFUU	−348	112.8	OR	87.7	18
OBOWUY	−374	116.2	OPh	84.8	19
UFATEB	−104	109.5	OPh	82.7	21
WAHSOO	−177	112.4	OPh	81.8	21
COMPOUND 2	−44.9	103.6	OPh	79.5	
	−44.9	101.8	OPh	79.1	this work

1 the Cu−N−Cu bond angles are 101.25(12)° and 103.18(11)° and, therefore, they are expected to originate moderate to strong ferromagnetic couplings of about 100 cm^{-1} that should partially cancel the antiferromagnetic coupling expected for the phenoxo bridge, resulting in a reduction of the antiferromagnetic coupling, as experimentally observed.

For compound **2** the situation is quite similar since there is only one known example of trimeric Cu(II) complex with double-mixed chloride and oxo bridges[14] and, therefore, we cannot establish any magneto-structural correlation. Nevertheless, a search in the CCDC database (updated Nov 2009) shows up to 20 Cu(II) dimers presenting similar double-mixed chloride and oxo bridges. Among these, only seven have been structurally and magnetically characterized (see Table 5). In all these complexes the magnetic coupling is antiferromagnetic and quite strong, with J values ranging from −85 to −443 cm^{-1} (normalized for a spin Hamiltonian $H = -JS_1S_2$, Table 5). Although compound **2** presents the lowest antiferromagnetic coupling in this table, this fact can also be explained by two reasons: (1) The central Cu(II) ion presents a trigonal bipyramidal geometry whereas the two external Cu(II) ions present quite regular square pyramidal geometries. Thus, the Addison parameters are 0.03 and 0.05 for Cu(1) and Cu(2), respectively whereas $\tau = 0.47$(av.) for the central Cu(3). (2) A second fact is the acute Cu−Cl−Cu angle observed in compound **2** (both angles are below 80°). Although we cannot establish a direct magneto-structural correlation between the Cu−Cl−Cu angle and the magnetic coupling in these Cu(II) dimers, the clear trend is that as this angle decreases, the magnetic coupling becomes smaller. This fact is further supported by compound IBUJOF, that presents

the lowest Cu−Cl−Cu angle and also the lowest J value and by compound **2** that also presents very low Cu−Cl−Cu angles, in agreement with the low J value found in this compound.

Conclusions

The use of the tridentate reduced Schiff-base ligand HL (2-[(2-dimethylamino-ethylamino)-methyl]-phenol) with Cu(II) and potentitally bridging ligands as chloride or azide anions has afforded two related trinuclear Cu(II) complexes. These two complexes confirm once again the ability of tridentate Schiff base ligands to chelate and bridge Cu(II) ions while leaving some coordination positions vacant that can be easily occupied by diverse bridging or terminal ligands. In the title compounds the use of azide and chloride anions has led to the formation of two novel chloro-bridged 1D chains of trinuclear units presenting double mixed-bridges ($\mu_{1,1}$-N$_3$ and O in **1** and Cl and O in **2**). The originality of both complexes is clearly evidenced by the fact that such angular trinuclear Cu(II) complexes with mixed-double μ-$_{1,1}$N$_3$ and oxo or chloro and oxo bridges is very rare, and joining of such trinuclear units with chloride ion to result in 1D chains is unprecedented. The magnetic properties of both compounds are very similar: both complexes present moderate antiferromagnetic couplings that can be very well rationalized from the structural parameters of the mixed-double bridges. The use of similar Schiff base or reduced Schiff base ligands combined with different halide and pseudo halide ligands is expected to lead to novel mixed bridged compounds with original structures. The magnetic properties of a series of such complexes would help to draw a magneto-structural correlation. This work is underway.