FULL PAPER

Trinuclear Cu^{II} Complexes Containing Peripheral Ketonic Oxygen Bridges and a μ$_3$-OH Core: Syntheses, Crystal Structures, Spectroscopic and Magnetic Properties

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Four new trinuclear copper(II) complexes, [(CuL^1)$_3$(μ$_3$-OH)](ClO$_4$)$_2$·H$_2$O (**1**), [(CuL^2)$_3$(μ$_3$-OH)](ClO$_4$)$_2$ (**2**), [(CuL^3)$_3$-(μ$_3$-OH)](ClO$_4$)$_2$·H$_2$O (**3**), and [(CuL^4)$_3$(μ$_3$-OH)](ClO$_4$)$_2$·H$_2$O (**4**), where HL^1 = 8-amino-4,7,7-trimethyl-5-azaoct-3-en-2-one, HL^2 = 7-amino-4-methyl-5-azaoct-3-en-2-one, HL^3 = 7-(ethylamino)-4-methyl-5-azahept-3-en-2-one, and HL^4 = 4-methyl-7-(methylamino)-5-azahept-3-en-2-one, have been derived from the four tridentate Schiff bases (HL^1, HL^2, HL^3, and HL^4) and structurally characterized by X-ray crystallography. For all compounds, the cationic part is trinuclear with a Cu$_3$OH core held by three carbonyl oxygen bridges between each pair of copper(II) atoms. The copper atoms are five-coordinate with a distorted square-pyramidal geometry; the equatorial plane consists of the bridging oxygen atom of the central OH group together with three atoms (N, N, O) from one ligand whereas an oxygen atom of a second ligand

occupies the axial position. Magnetic measurements have been performed in the 2–300 K temperature range. The experimental data could be satisfactorily reproduced by using an isotropic exchange model, $H = -J(S_1S_2+S_2S_3+S_1S_3)$ yielding as best-fit parameters: $J = -66.7$ and $g = 2.19$ for **1**, $J = -36.6$ and $g = 2.20$ for **2**, $J = -24.5$ and $g = 2.20$ for **3**, and $J = -14.9$ and $g = 2.05$ for **4**. EPR spectra at low temperature show the existence of spin frustration in complexes **3** and **4**, but it has not been possible to carry out calculations of the antisymmetric exchange parameter, G, from magnetic data. In frozen methanolic solution, at 4 K, hyperfine splitting in all complexes and spin frustration in complex **4** seem to be confirmed.

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Introduction

Cyclic trinuclear metal complexes[1] are of interest because these systems can be regarded as geometrically spin-frustrated and offer the opportunity to test magnetic exchange models.[2] In fact, geometrically frustrated antiferromagnetic compounds have attracted much attention over the past few years because of their propensity to adopt unusual, even exotic magnetic ground states, which remain poorly understood.[3]

μ-Hydroxo or μ-oxo ions have generally been observed as central bridging ligands in cyclic trinuclear compounds. The existence of the M$_3$O core held by the peripheral bridging ligands is well documented in the chemistry of iron(II/III) and chromium(III).[4] There are only a few reports with

a Cu$_3$O(H) core of which the majority contain oxime-oximate-,[5] N,N-pyrazole-,[6] or N,N-triazole[7]-type peripheral ligands. Examples of cyclic trinuclear complexes with ketonic oxygen bridges are, however, very rare. To the best of our knowledge, in the literature only three such complexes containing Schiff-base ligands, for example, 7-amino-4-methyl-5-azahept-3-en-2-one (AMAH),[8] 8-amino-4-methyl-5-azaoct-3-en-2-one (AMAO),[9] and 7-(dimethylamino)-4-methyl-5-azahept-3-en-2-one (AE)[10] are known. The first complex having an AMAH ligand was isolated accidentally during the preparation of the ternary complex, having pyridine as the other ligand. All three complexes were synthesized conveniently by adding triethylamine to the respective reaction mixtures. In order to investigate if the existence of these complexes is an exception or the formation of such trinuclear Cu^{II} complexes is a general phenomenon for this type of ligand, we synthesized four very similar tridentate N,N,O donor Schiff-base ligands derived from C- or N-substituted diamines and 2,4-pentanedione (Scheme 1, HL^1–HL^4) to obtain the desired complexes. Another objective of the synthesis of these compounds is to study their magnetic properties, especially the existence of spin frustration, which has not been detected in the other three reported complexes.[8–10] This paper re-

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

ports the synthesis, crystal structure, and magnetic properties of the four cyclic trinuclear compounds. The structural and magnetic properties of the complexes will be compared with the data of the other three similar compounds reported in the literature.
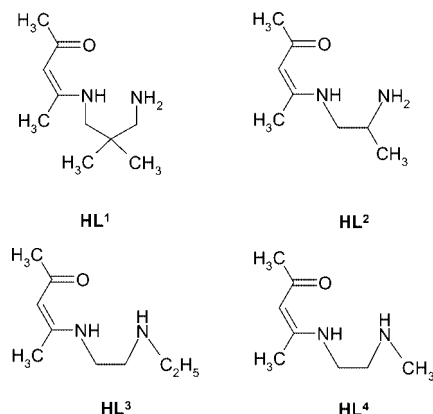
Scheme 1.

Results and Discussion

The four tridentate ligands HL^1, HL^2, HL^3, and HL^4, on treatment with a methanol solution of copper perchlorate hexahydrate and triethylamine in a 2:2:3 ratio, yielded the trinuclear complexes **1**–**4**, respectively (Scheme 2). Complexes **2** and **3** were obtained readily on mixing the constituents; no hydrolysis of the product occurred during synthesis. On the other hand, ligands HL^1 and HL^4 are rather susceptible to hydrolysis and for higher yields of **1** and **4** dry methanol was used as the reaction medium. All the complexes, however, can easily be purified by recrystallization from methanol. The formation and stability of these self-assembled cyclic trinuclear complexes may be visualized in the following way:
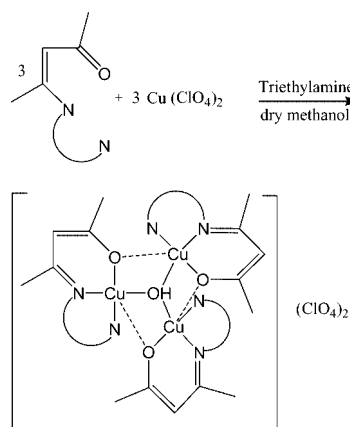
Scheme 2.

The chelating tridentate ligand coordinates to the Cu^{II} centers as usual to occupy the three coordination sites. In a slightly alkaline medium, the hydroxy ion, which is well known for its bridging ability, can be coordinated to the

fourth coordination site to bridge two metal centers. However, coordination of the hydroxy ion to the three metal centers is not very common, as steric crowding may destabilize the resulting tetrahedral arrangement until and unless it gains some additional stability by other means. In the present systems, the three mononuclear units are assembled around the hydroxy ion in such a way that the ketonic oxygen atom of one unit is coordinated to the apical position of the Cu^{II} ion of the neighboring unit to result in a cyclic peripheral bridging that provides the required stability for the trinuclear structure (Scheme 2). As a requirement of the basal–apical bridging, the mononuclear units need to be perpendicular to each other which, fortuitously, seems to be the preferred arrangement to minimize steric contacts.

Description of the Structure of Complexes 1–4

The crystal structures of all four compounds (**1**–**4**) are built up from discrete trinuclear cations [Cu$_3$L$_3$(μ$_3$-OH)]$^{2+}$ and noncoordinated perchlorate anions in a ratio of two anions per cation. In each of the complexes **1**, **3**, and **4** there is, in addition, one lattice water molecule. The trinuclear structure of **2** is shown in Figure 1 together with the common numbering scheme [complexes **1**, **3**, and **4** have very similar molecular structures, see Figures S1, S2, and S3, respectively in the Supporting Information (see also the footnote on the first page of this article)]. Selected bond lengths and bond angles are summarized in Tables 1 and 2, respectively.
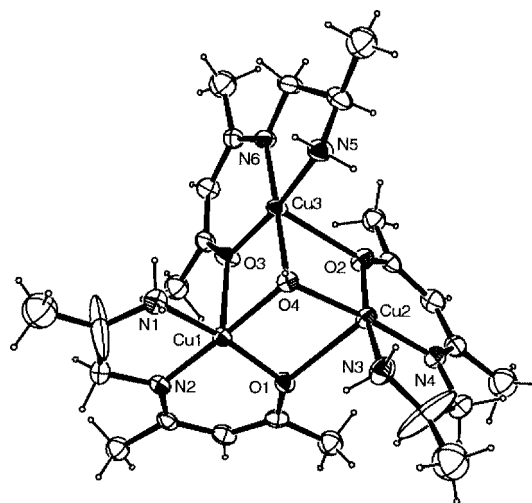

Figure 1. ORTEP-3 view of the [(CuL^2)$_3$(OH)]$^{2+}$ cation of complex **2** (30% thermal ellipsoids) including the atom numbering scheme.

The trinuclear cationic part is comprised of three CuL subunits in which each copper(II) ion is coordinated to a deprotonated tridentate monoanionic ligand L. The subunits are held together by two distinct bridging systems: (i) the oxygen atom (O4) of a single, triply bridging hydroxo group, which is coordinated to each of the three copper centers, and (ii) the three bridging carbonyl oxygen atoms, each of them from a different ligand molecule. The resulting trinuclear species do not contain any threefold symmetry

Table 1. Selected bond lengths [Å] of complexes **1–4**.

	1	2	3	4
Cu1–O1	1.918(6)	1.914(5)	1.911(6)	1.912(8)
Cu1–O3	2.475(6)	2.375(6)	2.370(7)	2.318(9)
Cu1–O4	2.058(5)	2.020(5)	2.032(7)	2.016(6)
Cu1–N1	1.999(8)	1.996(6)	2.029(8)	2.054(14)
Cu1–N2	1.947(8)	1.932(6)	1.939(10)	1.970(10)
Cu2–O1	2.508(8)	2.496(5)	2.306(7)	2.359(7)
Cu2–O2	1.916(5)	1.902(6)	1.916(6)	1.915(8)
Cu2–O4	2.033(5)	2.001(5)	2.018(6)	2.024(7)
Cu2–N3	2.029(7)	1.985(8)	2.025(8)	1.985(11)
Cu2–N4	1.984(6)	1.931(6)	1.917(8)	1.921(11)
Cu3–O2	2.418(7)	2.406(5)	2.326(6)	2.290(8)
Cu3–O3	1.953(6)	1.912(5)	1.907(8)	1.909(9)
Cu3–O4	2.014(5)	2.025(5)	2.003(5)	2.033(7)
Cu3–N5	2.023(8)	1.993(6)	2.026(9)	2.038(10)
Cu3–N6	1.980(7)	1.944(7)	1.936(8)	1.932(11)
Cu1–Cu2	3.329(3)	3.238(2)	3.172(4)	3.182(3)
Cu2–Cu3	3.241(4)	3.211(4)	3.165(3)	3.164(4)
Cu1–Cu3	3.303(3)	3.165(3)	3.205(3)	3.173(3)

Table 2. Selected bond angles [°] for complexes **1–4**.

	1	2	3	4
O1–Cu1–O3	95.1(2)	97.2(2)	94.9(2)	95.6(3)
O1–Cu1–O4	82.9(2)	86.4(2)	83.6(3)	85.6(3)
O1–Cu1–N1	165.6(3)	166.1(2)	168.6(3)	168.6(5)
O1–Cu1–N2	94.3(3)	94.5(2)	93.4(3)	91.8(4)
O3–Cu1–O4	71.1(2)	74.6(2)	73.4(2)	74.8(3)
O3–Cu1–N1	91.5(3)	96.4(2)	96.4(3)	95.5(5)
O3–Cu1–N2	107.5(3)	102.7(2)	108.7(3)	111.2(4)
O4–Cu1–N1	87.1(2)	94.3(2)	98.6(3)	94.9(4)
O4–Cu1–N2	176.7(3)	177.2(2)	176.6(3)	173.8(4)
N1–Cu1–N2	95.9(3)	85.5(2)	84.0(4)	86.5(5)
O1–Cu2–O2	92.9(2)	97.7(2)	90.9(3)	97.3(3)
O1–Cu2–O4	70.0(2)	72.7(2)	74.6(2)	74.6(2)
O1–Cu2–N3	85.4(2)	93.3(2)	96.3(3)	94.4(3)
O1–Cu2–N4	112.4(2)	101.3(2)	110.4(3)	108.0(4)
O2–Cu2–O4	83.4(2)	85.1(2)	84.4(2)	84.4(2)
O2–Cu2–N3	172.1(3)	168.8(3)	172.6(3)	168.1(4)
O2–Cu2–N4	94.7(2)	94.7(2)	93.6(3)	93.1(4)
O4–Cu2–N3	88.8(2)	96.6(2)	96.0(2)	96.8(4)
O4–Cu2–N4	177.1(2)	173.9(2)	174.7(3)	176.7(4)
N3–Cu2–N4	93.0(3)	84.7(3)	85.4(3)	85.2(4)
O2–Cu3–O3	96.9(2)	91.1(2)	98.2(2)	91.8(3)
O2–Cu3–O4	72.1(2)	72.6(2)	74.9(2)	75.3(3)
O2–Cu3–N5	108.6(2)	96.9(2)	93.8(3)	94.2(3)
O2–Cu3–N6	100.2(3)	109.5(2)	104.9(3)	113.0(3)
O3–Cu3–O4	84.1(2)	85.6(2)	85.0(3)	84.1(3)
O3–Cu3–N5	149.3(3)	171.7(2)	167.8(3)	173.4(3)
O3–Cu3–N6	94.9(3)	94.8(2)	93.2(4)	94.3(4)
O4–Cu3–N5	87.6(3)	94.8(3)	96.0(3)	94.8(4)
O4–Cu3–N6	172.0(3)	177.9(2)	178.1(4)	171.6(3)
N5–Cu3–N6	97.1(3)	84.5(3)	85.9(4)	85.8(5)
Cu1–O4–Cu2	108.9(2)	107.3(2)	103.1(3)	103.9(3)
Cu1–O4–Cu3	108.4(2)	102.9(2)	105.2(3)	103.2(3)
Cu2–O4–Cu3	106.4(2)	105.8(2)	103.8(2)	102.5(3)

axis. In all four compounds no specific chirality for the propeller arrangements around the hydroxide ion is found. The three copper(II) ions and the bridging hydroxo group form a flattened trigonal pyramid, with the copper atoms falling at the corners of approximately equilateral sides and angles: 3.329(4), 3.241(4), 3.303(3) Å and 60.3(1), 61.2(1), 58.5(1)° for complex **1**; 3.238(2), 3.211(4), 3.165(3) Å and 58.8(1), 61.0(1), 60.2(1)° for complex **2**; 3.172(4), 3.165(3), 3.205(3) Å and 60.8(4), 59.7(4), 59.5(4)° for complex **3**; and 3.182(3), 3.164(4), 3.173(3) Å and 60.0(5), 60.3(5), 59.7(5)° for complex **4**. The face-capping oxygen atom (O4) is located at 0.728(5), 0.797(4), 0.836(6), and 0.861(6) Å above the plane defined by the Cu$_3$ triangle for complexes **1–4**, respectively. The presence of Cu$_3$OH is confirmed 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,[6c,7b,8–10] agree well with a roughly tetrahedral or pseudotetrahedral sphere of Cu, Cu, Cu, H ligands around the oxygen atom.

As for the copper environment, in all four structures the three copper atoms of the trinuclear entity are five-coordinate, with a (4+1) square-pyramidal (NNOO and O) geometry. The four coordinating atoms making up the basal plane are the carbonyl oxygen atom, one imine nitrogen atom, and one amino nitrogen atom from the tridentate Schiff-base ligand (L), and the hydroxo group OH⁻, while the apical site is occupied by one oxygen atom of another tridentate Schiff-base ligand, which, in turn, is basal to a second copper atom. As expected, the axial Cu–O bond is much longer than the equatorial one. It may be emphasized that the oxygen atom involved in this basal–apical bridge pertains to a carbonyl function, which is generally considered as a nonbridging group. Within each mononuclear unit the copper atom does not lie in the basal plane. As usual, each copper ion is displaced from the least-squares plane through the basal atoms towards the apical oxygen atom by 0.071(1), 0.085(1), 0.112(1), and 0.137(2) Å for Cu(1); 0.031(1), 0.023(1), 0.105(2), and 0.118(2) Å for Cu(2); and 0.159(1), 0.079(1), 0.099(1), and 0.130(2) Å for Cu(3) in complexes **1–4** respectively. The lengths of the bonds between the copper atoms and the donor sites (O, N, N) of the tridentate ligand are within the range of values normally found for such bonds.[8–11] They show only small variations in going from one unit to the other. The six-membered chelate ring formed by the acetylacetone moiety is essentially planar and the interatomic distances and angles of the ring are roughly identical in the three mononuclear units of **2** and **3**. However, in **1** and **4** the same rings deviate considerably from planarity and the deviation is different in the three subunits. The highest deviation is observed in the subunit with Cu1 for both **1** and **4** in which the six-membered ring assumes almost a boat and twist-boat conformation, respectively, with puckering parameters φ = 195(2) and 199(4)°, θ = 124.0(17) and 120.7(33)° and Q = 0.269(6) and 0.206(9) Å.[12] The trimethylene fragment in complex **1** and dimethylene fragments in the other three complexes from the starting diamines constitute the other chelate ring in the complexes. In all three subunits these six-membered chelate rings of complex **1** and five-membered chelate rings of complex **2** assume half-boat and envelope conformations, respectively. However, considerable differences have been found in the bond angles of the chelate rings among the subunits in both the complexes (7.0° for **1** and 11.7° for **2**).

Table 3. Selected structural parameters for complexes **1**–**4** and three reported complexes **A**, **B**, and **C** related to their magnetic properties.

	1	2	3	4	A	B	C
Cu(1)–O(H)–Cu(2) [°]	108.9(3)	107.3(2)	103.1(3)	103.9(3)	104.8(1)	105.4(2)	102.9(1)
Cu(1)–O(H)–Cu(3) [°]	108.4(2)	102.9(2)	105.2(3)	103.2(3)	104.9(1)	106.5(2)	102.9(1)
Cu(2)–O(H)–Cu(3) [°]	106.4(2)	105.8(2)	103.8(2)	102.5(3)	105.5(1)	108.3(2)	102.9(1)
Cu–O(H)–Cu′ [°] (av)	107.9	105.3	104.0	103.2	105.1(1)	106.7(2)	102.9
O(H)···Cu3 plane [Å][a]	0.728(5)	0.797(4)	0.836(6)	0.861(6)	0.804(2)	0.796(5)	0.881(6)
Cu/Cu′ [°] (av)[b]	89.7	85.8	94.6	92.5	82.9(1)	83.7(3)	92.3
τ	0.19,	0.19,	0.13,	0.09,	0.01,	0.26,	0.04,
	0.08,	0.08,	0.04,	0.14,	0.11,	0.09,	0.05,
	0.39	0.10	0.17	0.03	0.09	0.20	0.03
–J [cm^{-1}][c]	–66	–36	–24	–15	–24	–30	–2.4
Ref.	this work	this work	this work	this work	[8]	[9]	[10]

[a] Deviation of the oxygen atom of the triply bridging hydroxy group above the plane of the three copper atoms. [b] Coplanarity between the least-squares planes defined by [O(H), N, N, O]; average value calculated from the Cu1/Cu2, Cu1/Cu3, Cu2/Cu3 dihedral angles. [c] The J values from the literature have been modified according to the Hamiltonian used in this paper.

Conformational analysis shows different conformations for the five-membered chelate rings in complexes **3** and **4**. In complex **3**, the ring with Cu2 is in envelope conformation on C12, whereas the rings with Cu1 and Cu3 have half-chair conformation twisted on N1···C3 and N5···C21, respectively. But for complex **4**, both the five-membered chelate rings with Cu1 and Cu2 assume half-chair conformation twisted on N1···C3 and N3···C12, respectively, whereas the ring with Cu3 is in envelope conformation on C21. However, among the subunits in each complex a considerable difference in the bond angles of the chelate rings has been found in complex **4** only (14.1°), whereas in complex **3** the difference is negligible (2.5°).

The distortions of the coordination polyhedron from the square pyramid to the trigonal bipyramid have been calculated by the Addison parameter (τ)[13] 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 0.19, 0.19, 0.13, and 0.09 for Cu(1); 0.08, 0.08, 0.04, and 0.14 for Cu(2); and 0.39, 0.10, 0.17, and 0.03 for Cu(3) in complexes **1**–**4**, respectively. The values clearly indicate that in **1** the distortion towards a trigonal bipyramid is significantly different in the three mononuclear units and that in Cu(3) it is considerably high. The τ values of the other three reported complexes[8–10] are also shown in Table 3 for comparison.

The perchlorate anions in the complexes show some disorder. In **1**, one of the perchlorate ions is disordered such that the oxygen atoms are distributed over two sets of tetrahedral sites around the same chlorine atom, while the other shows the complete anion distributed over two separate sites. By contrast, the perchlorate ions in **2** and **3** are ordered. In **4** the oxygen atoms show very high thermal motion but no discernible disorder pattern could be refined successfully. In complex **3**, one perchlorate oxygen atom,

Table 4. Hydrogen bonding distances [Å] and angles [°] for complexes **1**–**4**.

Compound	D–H···A[a]	D–H	D···A	H···A	D–H···A
1	N1−H1a···Ow	0.90	3.223(13)	2.36	161
	N5–H5b···O5	0.90	3.132(11)	2.29	156
	N3–H3a···O8	0.90	3.331(15)	2.47	160
	N3–H3b···O10	0.90	2.92(2)	2.06	160
	O4–H4···Ow	0.98	2.848(10)	1.87	175
2	N1–H1a···O7	0.90	3.201(13)	2.31	168
	N1–H1b···O9	0.90	3.389(15)	2.59	148
	N1–H1b···O12	0.90	3.07(2)	2.22	158
	N5–H5a···O9	0.90	2.991(15)	2.30	133
	N3–H3b···O8	0.90	3.018(14)	2.34	132
	O4–H4···O5	0.90	2.972(11)	2.03	161
	N5–H5b···O6^i	0.90	3.354(12)	2.47	167
	N3–H3a···O5^i	0.90	3.302(11)	2.43	162
3	N1–H1···O5	0.90	3.319(13)	2.51	148
	N1–H1···O8	0.90	3.475(14)	2.70	143
	N3–H3···O12	0.90	3.43(3)	2.54	165
	N5–H5···O10	0.90	3.144(15)	2.24	170
	O4–H4···Ow	0.98	2.820(11)	1.86	166
4	N3–H3···O9	0.90	3.415(17)	2.61	147
	N3–H3···O10	0.90	3.263(16)	2.43	151
	N5–H5···O5	0.90	3.124(17)	2.38	139
	N5–H5···O6^j	0.90	3.683(30)	2.90	145
	O4–H4···Ow	0.98	2.762(13)	1.80	164

[a] Symmetry equivalent: i) 1 – x, –y, 1 – z; j) 1 – x, 1 – y, 2 – z.

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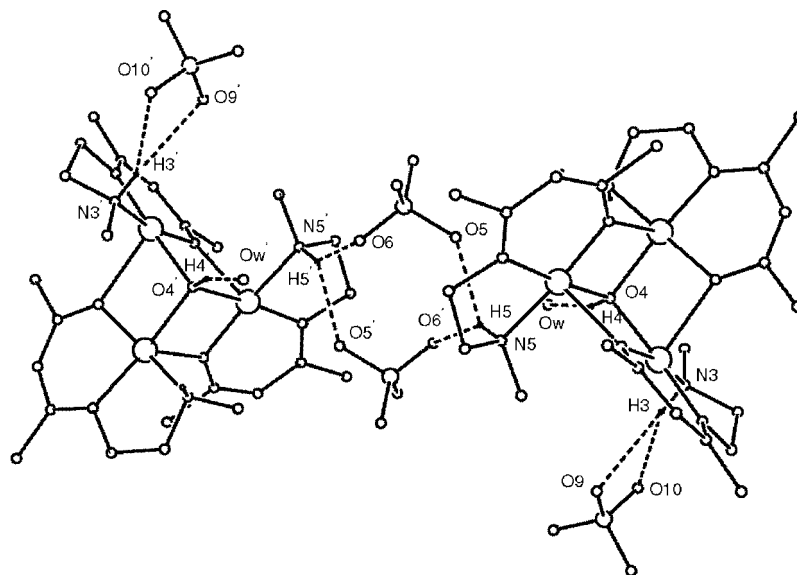
Figure 2. Illustration of the aggregation of the isolated trimeric unit by hydrogen-bonding interactions between the $[(CuL^4)_3(OH)]^{2+}$ cation and perchlorate anions in the solid state of complex **4**. Atoms marked with a prime are transformed by symmetry element $1 - x$, $1 - y$, $2 - z$.

O10, forms a weak association with the Cu2 ion at a distance of 2.961(13) Å, whereas all other Cu–O(perchlorate) distances are about 4 Å. The perchlorate ions play a significant role in the H-bonding network in all complexes.

In all four complexes hydrogen-bonding interactions are observed among the isolated trimeric units, the perchlorate anions, and the water of crystallization (Table 4). A detailed discussion of these interactions for complexes **1**–**3** along with diagrams is presented in the Supporting Information. H bonding of complex **4** is only discussed here as an example. In complex **4** two centrosymmetrically related trinuclear units are linked by an N–H⋯O hydrogen bond involving hydrogen atom H5(N5) and oxygen atom O6 of the two centrosymmetrically related perchlorate ions (Figure 2, Table 4). The hydrogen atom H5(N5), through which two trimers are linked, is also involved in another N–H⋯O contact with O5 of one of two perchlorate anions showing bifurcated hydrogen-bond formation. H3(N3) also forms strong bifurcated hydrogen bonds with two oxygen atoms, O9 and O10, of another perchlorate ion. One of the three hydrogen atoms, H1(N1), does not participate in hydrogen bonding. The water of crystallization (Ow) is stabilized, contributing to the hydrogen-bonding network, with H4 of the triply bridging hydroxo group by an O–H⋯O contact.

IR and Electronic Spectra

Compounds **1**, **3**, and **4** contain a noncoordinating water molecule, which makes the assignment of O–H stretching somewhat ambiguous. However, the well-defined bands at 3520, 3505, 3556, and 3550 cm^{-1} for complexes **1**–**4**, respectively, appear within the typical range for O–H stretching vibrations in monohydroxo-bridged copper complexes.[14] Therefore these bands can be attributed to ν(O–H) of the triply bridging hydroxo group. The additional broad but

well-defined bands with the maximum at 3430 cm^{-1} for complex **1**, 3425, 3390 cm^{-1} for complex **3** and 3420, 3377 cm^{-1} for complex **4** are attributable to the presence of a noncoordinating water molecule with a strong hydrogen-bonding network (vide crystal structure). The remaining bands for the complexes above 3000 cm^{-1} may be assigned to ν(N–H) stretching vibrations. Concerning the ClO$_4^-$ anions, the ν_3 mode at 1091, 1100, 1102, and 1097 cm^{-1} for **1**–**4**, respectively, is somewhat broadened, but the ν_4 band at 623, 620, 623, and 622 cm^{-1}, respectively, is devoid of any splitting and consistent with the IR-active normal modes for T_d symmetry, suggesting that these anions are not coordinated to the copper atoms as substantiated by the crystal structures.

The electronic spectra in the solid state and in methanol solution have been recorded for the four complexes. The observed ligand-field band is in agreement with the fact that the trinuclear structure is retained in methanol, as similar visible absorption bands are observed in the solid state and in methanol solution for all complexes. The reflectance electronic spectra of all four complexes display a single absorption band at 595, 593, 601, and 586 nm in the solid state and 612, 615, 587, and 595 nm in methanol. The positions of these bands are consistent with the observed square-based geometry around the copper centers.[15]

Magnetic Properties

Magnetic susceptibilities were determined for complexes **1**–**4** over the temperature range 2–300 K in an applied field of 0.1 T. The temperature dependence of $\chi_M T$ (χ_M being the magnetic susceptibility per Cu$_3$ entity) for complex **1** is shown in Figure 3 (complexes **2**, **3**, and **4** have very similar temperature dependences of $\chi_M T$: see Figures S7, S8, and S9, respectively, in the Supporting Information). At room

temperature the $\chi_M T$ values for all four complexes are close to 1.2 cm^{3}mol^{-1}K, as expected for the three independent Cu^{II} ions. As T is lowered, $\chi_M T$ decreases, reaching values close to 0.40 cm^{3}mol^{-1}K at 2 K. Complexes **1**–**3** show a plateau before reaching the final value, while **4** does not show this plateau. This value (0.4 cm^{3}mol^{-1}K) is close to the spin-only value for a system with one unpaired electron with $g > 2.00$. This behavior indicates an antiferromagnetic interaction between the Cu^{II} ions, with an unpaired electron per Cu$_3$ unit in the ground state. The formation of this plateau ($S = 1/2$) is dependent upon the corresponding existence of noticeable intermolecular (intertrimer) exchange interactions. This situation has also been observed in other similar compounds.[8–10]
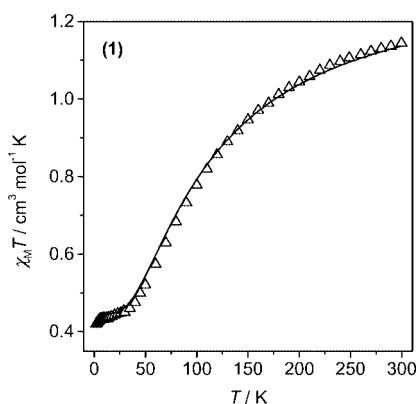

Figure 3. Plot of the $\chi_M T$ [cm^{3}mol^{-1}K] vs T [K] in the range 2–300 K for **1**. The solid line is generated from the best-fit magnetic parameters.

The magnetic-exchange interaction in a triangular arrangement of three $S = 1/2$ ions results in three electronic states, that is, a quartet state ($S = 3/2$; ^{4}A$_2$) and two doublet states ($S = 1/2$; ^{2}E) (Scheme 3). Within the simple model of an isotropic exchange interaction for an equilateral triangle, both of the doublet states have the same energy, which differs $3J$ from the energy of the quartet state. From the known structures of **1**–**4**, and considering that the three
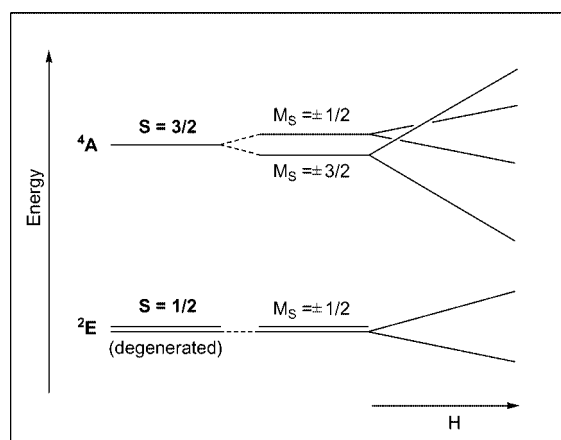
copper atoms of the Cu$_3$O(H) unit are structurally almost equivalent, and so that $J_{12} = J_{13} = J_{23} = J$, the isotropic Heisenberg–Dirac–van Vleck (HDVV) Hamiltonian formalism [Equation (1)] was used to describe the interactions of the spins.

$$H_{HDVV} = -J_{12}S_1S_2 - J_{13}S_1S_3 - J_{23}S_2S_3 \qquad (1)$$

From this Hamiltonian, a solution of the magnetic susceptibility may be derived as follows [Equation (2)]:[7a,7b,16]

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

where N, g, β, k, and T have their usual meanings. Because of the above-mentioned experimental variation of $\chi_M T$ at low temperatures, the inclusion of an additional Weiss-like parameter θ [so that T is replaced by $T - \theta$ in Equation (2)], which would account for possible, low-temperature, intertrimer magnetic interaction mainly due to the hydrogen bonds among trinuclear entities, was deemed appropriate.

Experimental data for **1**–**4**, corrected for diamagnetic contributions and TIP (0.3×10^{-3} cm^{3}mol^{-1}), were analyzed with the theoretical expression, which results from the modified Equation (2). Fitting was performed on $\chi_M T$. The best-fitted curves are plotted in Figure 3 and Figures S7, S8, and S9, along with the experimental data. The best-fit parameters obtained are $J = -66.7$ cm^{-1}, $g = 2.19$, and $\theta = -0.13$ with $R = 2×10^{-4}$ for **1**; $J = -36.6$ cm^{-1}, $g = 2.2$, and $\theta = -0.22$ with $R = 1.9×10^{-4}$ for **2**; $J = -24.5$ cm^{-1}, $g = 2.2$, and $\theta = -0.24$ with $R = 2.1×10^{-4}$ for **3** and $J = -14.9$ cm^{-1}, $g = 2.05$, and $\theta = -0.13$ with $R = 2.2×10^{-4}$ for **4** (where R is the agreement factor defined as $\Sigma_i[(\chi_M T)_i^{exp} - (\chi_M T)_i^{calc}]^2/\Sigma_i[(\chi_M T)_i^{exp}]^2$. The θ values are consistent with the intertrimer interactions, mainly the hydrogen bonds that link the trinuclear entities. All J values are gathered in Table 3 together with the most important structural parameters: Cu–O–Cu angles, Cu–O distances, distance from the O(H) atom to the mean Cu3 plane and the τ distortion parameter of each copper(II) ion. Considering that we have used only one J value, angles and distances given in Table 3 correspond to the average values of the triangles. However, it is clear that these values agree with those reported in the literature for similar triangular complexes.[8–10]

The most interesting feature concerning these triangular complexes is the possibility to show the spin frustration when the geometry is almost equilateral. Indeed, as indicated by Haasnoot et al.,[7a] the canonical example of spin frustration in any lattice is based on an equilateral triangular plaquette. With the typical isotropic spin Hamiltonian $-\Sigma_{ij}J_{ij}S_iS_j$, if J_{ij} is negative, which favors the antiparallel correlation, and J_{ij} is equal for all nearest neighbor pairs, then only two of the three spin constraints can be satisfied simultaneously, that is the system is geometrically frustrated. In order to interpret the magnetic properties of these frustrated systems it is necessary to go beyond the framework of the above isotropic exchange model and to introduce *antisymmetric exchange interactions*.[7a]

The spin frustration requires a highly symmetrical (equilateral) triangle. Complexes **1**–**4** are not fully equilateral,

Scheme 3.

thus spin-frustration behavior might not be expected. From magnetic data it is very difficult − mostly impossible − to calculate the antisymmetric exchange term G_{AB}. In most cases, the possibilities of intertrimeric exchange − such as in **1**–**4** because of the hydrogen bonds − preclude any exact calculation of this parameter. However, some very interesting calculations have been recently reported on singular cases:[7a] for example, Solomon et al. have reported an exhaustive study on a symmetric hydroxo-bridged trinuclear Cu[II] complex (such as **1**–**4**) by means of nonconventional techniques, such as variable-temperature variable-field magnetic circular dichroism combined with powder/single-crystal EPR.[17] From all literature data it seems more appropriate to utilize EPR measurements for the study of the spin frustration. Obviously, in this study it is important to investigate EPR behavior at a very low temperature, when only the degenerate $S = 1/2$ states are populated. In this case, one of the signatures of spin frustration is the appearance of some g values lower than 2.00.[18]

EPR Spectra

The X-band EPR spectra of complexes **1**–**4** were recorded on powder samples varying the temperature between 4 and 295 K (Figure 4). The EPR spectra of trinuclear $S = 1/2$ compounds have been analyzed in terms of three active states (one quartet and two doublets), with temperature-dependent population.[18–22] In the light of the superexchange parameter from the magnetic measurements, at low temperatures only the doublets should be populated, whereas at room temperature signals due to the transitions inside the quartet may also be observed. This transition may show noticeable zero-field splitting (ZFS) ($S = 3/2$). Complexes **1**–**3** show a broad band (mainly complex **2**) at low fields, due undoubtedly to the presence of ZFS of the $S = 3/2$ state. Complex **4** does not show any mark of the ZFS (D parameter). Only one quasi-isotropic band is observed at this temperature. The possible spin frustration can only be observed at low temperatures. From Figure 4 it can be seen that complexes **1** and **2** do not have any signal that could be attributed to spin frustration. However, complexes **3** and **4** show unequivocally a band at high field that corresponds to $g = 1.98$, which cannot be explained as g_x, g_y, g_z for an $S = 1/2$ state without the introduction of spin frustration.[18] The antisymmetric exchange in spin-frustrated systems can give $g_\perp$ values close to 1.5.[18]

We have also carried out the EPR measurements in frozen methanol solution (Figures 5 and S10). The X-band spectra at low temperatures (60 K to 4 K) clearly show the hyperfine splitting in the $g_\parallel$ approximately of 190 Gauss for all four triangles. In $g_\perp$ there is also a significant partial splitting, mainly in complex **4** (Figure 5). In this case the splitting can be masked by the band at $g \approx 1.98$, as already shown in the solid state. Thus, the EPR data in solution seem to confirm, at least in complex **4**, the existence of the spin frustration together with the hyperfine splitting.
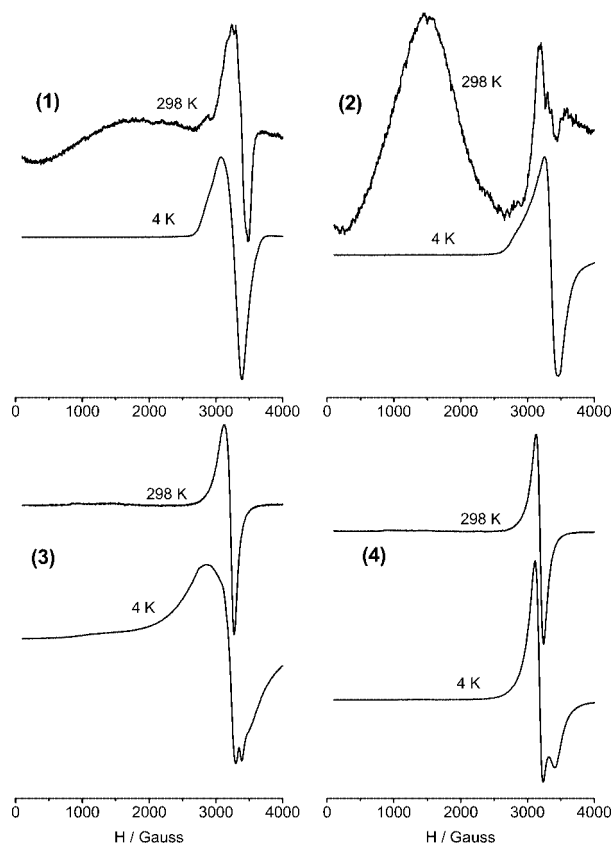

Figure 4. Polycrystalline X-band EPR spectra for complexes **1**–**4** at room temperature and 4 K.
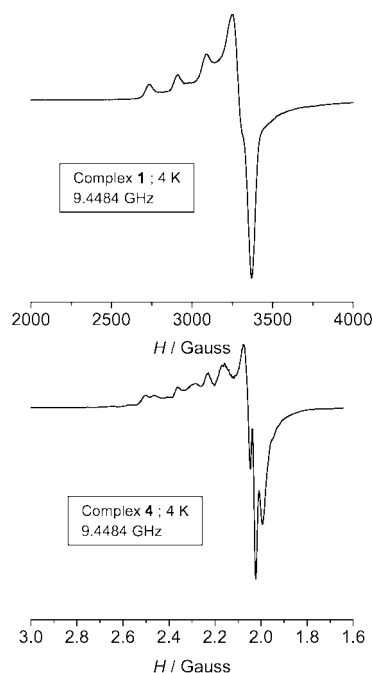

Figure 5. X-band EPR spectra for **1** and **4** in frozen methanolic solution at 4 K. For **1** the abscissa is given in Gauss to see the hyperfine splitting; for **4** the abscissa is given in g values to see the low values of $g_\perp$ attributed to the spin frustration already shown in solid state.

Discussion

Previous work has established relationships between magnetic coupling and certain structural features.[5c,6c,7a] Most of the trinuclear compounds containing a pyramidal Cu$_3$O(H) core described in the literature can be systematized in four groups depending on the type of peripheral bridge: those with an N,O (mainly from an oxime-oximate ligand bridge),[5] those with an *N,N*-pyrazole bridge,[6] those with an *N,N*-triazole bridge,[7] and those with Schiff bases that act as tridentate N$_2$O ligands with only three compounds reported,[8–10] which have arisen from the condensation of the carbonyl function with only one end of the diamine. Because the electronic factors related to the nature of the ligands that afford the bridge are decisive,[7a] we were prevented from correlating the magnitude of the magnetic coupling within the above four classes of Cu$_3$O clusters.[8,9] From Table 3 it can be seen that the main structural differences for complexes **1**–**4** lie in the difference in the distance of the oxygen atom above the plane of the copper atoms (the maximum difference is 0.13 Å) and in the average of the Cu–O(H)–Cu′ angles (the maximum difference is 4.7°). The maximum variation in the –*J* values is 51 cm^{-1}. These features indicate that the shortest distance of the O(H) group above the plane formed by the three copper ions in the trinuclear Cu^{II} complexes and the greatest Cu–O–Cu′ angle provide the strongest antiferromagnetic coupling.

In triangular arrangements of symmetric antiferromagnetically coupled metal ions, the magnetic properties at low temperatures can become complicated by the possible presence of spin-frustration effects, because of the presence of the antisymmetric exchange interaction (ASE) term.[7a,7b] The experimental EPR data for **3** and **4** indicate that this term is non-zero and the phenomenon of spin frustration occurs. For **1** and **2** all data seem to indicate that there is no spin frustration.

Concluding Remarks

The carbonyl functional group is generally considered as a nonbridging group but the facile synthesis of the four new trinuclear complexes **1**–**4** and the other three reported complexes suggests that the monocondensation products of various diamines and acetylacetone are a group of tridentate ligands that can readily be involved in *basal–apical*-type peripheral oxo bridging to result in the formation of trinuclear Cu^{II} complexes with a Cu$_3$OH core by self-assembly. All four complexes show antiferromagnetic coupling, as was also found in the three similar peripheral bridging complexes.[8–10] The magnetostructural correlation suggests that the greatest coplanarity of the three principal ligand planes, the shortest distance of the O(H) group above the Cu$_3$ plane, and the greatest Cu–O–Cu′ angles provide the strongest antiferromagnetic coupling.

Experimental Section

Materials: All the chemicals were of reagent grade and used without further purification. The four monocondensed ligands, HL^1, HL^2, HL^3, and HL^4, were synthesized in our laboratory by the methods described below. The ligand HL^1 was prepared for the first time. ***Caution!*** *Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.*

Physical Measurements: Elemental analyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer and the Cu contents in all the complexes were estimated spectrophotometrically.[23] IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FTIR spectrophotometer. Electronic spectra in methanol (1200–350 nm) were recorded with a Hitachi U-3501 spectrophotometer. The magnetic measurements were carried out in the "Servei de Magnetoquimica (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL magnetometer in the temperature range of 2–300 K and the magnetic field was 1 T. The diamagnetic corrections were evaluated from Pascal's constants. EPR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer, varying the temperature between 4 and 300 K.

Preparation of 8-Amino-4,7,7-trimethyl-5-azaoct-3-en-2-one (HL^1) and 7-Amino-4-methyl-5-azaoct-3-en-2-one (HL^2): These two ligands are the single-condensation products of 2,2-dimethyl-1,3-propanediamine and 1,2-propanediamine, respectively, with 2,4-pentanedione. They were prepared by applying a method similar to that adopted for the half condensation of 1,2-ethanediamine or 1,3-propanediamine with 2,4-pentanedione as reported earlier, that is by allowing the constituents to react in chloroform under high dilution.[8,9,24–27] A solution of 2,4-pentanedione (1.1 mL, 10 mmol) in chloroform (50 mL) was added dropwise to a solution of 2,2-dimethyl-1,3-propanediamine (1.03 mL, 10 mmol) or 1,2-propanediamine (0.80 mL, 10 mmol) in chloroform (50 mL) at room temperature. After addition, the solution was stirred for an additional 3 h and the chloroform was evaporated under reduced pressure. The resultant viscous oil was collected as the ligand and dissolved in methanol (30 mL).

Preparation of 7-(Ethylamino)-4-methyl-5-azahept-3-en-2-one (HL^3) and 4-Methyl-7-(methylamino)-5-azahept-3-en-2-one (HL^4): HL^3 and HL^4 were prepared by condensation of the NH$_2$ group of *N*-ethyl-1,2-ethanediamine (0.90 mL, 10 mmol) and *N*-methyl-1,2-ethanediamine (0.74 mL, 10 mmol) with 2,4-pentanedione (1.1 mL, 10 mmol), respectively, in methanol (30 mL) under reflux for 3 h. The Schiff-base ligands were not isolated and the yellow methanolic solutions were used directly for complex formation.

Synthesis of [(CuL^1)$_3$(μ$_3$-OH)](ClO$_4$)$_2$·H$_2$O (1), [(CuL^2)$_3$(μ$_3$-OH)](ClO$_4$)$_2$ (2), [(CuL^3)$_3$(μ$_3$-OH)](ClO$_4$)$_2$·H$_2$O (3), and [(CuL^4)$_3$-(μ$_3$OH)](ClO$_4$)$_2$·H$_2$O (4): A solution of Cu(ClO$_4$)$_2$·6H$_2$O (3.7 g, 10 mmol) in methanol (20 mL) was added to a stirred solution of each of the ligands, HL^1, HL^2, HL^3, and HL^4 (10 mmol), in methanol (10 mL). Triethylamine (2.1 mL, 15 mmol) was then added dropwise to this solution with constant stirring. In the case of **1** and **4**, an immediate separation of a small amount of green hydrolyzed product occurred during the addition of triethylamine, which was filtered off. If the methanol contained water, the amount of the hydrolyzed products for these two compounds increased. Therefore, the methanol was dried before using as solvent for the synthesis of **1** and **4**. The resulting green and blue filtrates of **1** and **4**, respectively, were set aside at room temperature. Overnight, single crystals appeared, as green prisms for **1** and blue hexagons for **4**. The resulting blue and green solutions for HL^2 and HL^3, respectively, upon stirring at room temperature slowly yield the desired compounds, complex **2** as a precipitate and complex **3** as a microcrys-

Table 5. Crystal data and refinement details of complexes **1–4**.

	1	2	3	4
Empirical formula	$C_{30}H_{60}Cl_2Cu_3N_6O_{13}$	$C_{24}H_{46}Cl_2Cu_3N_6O_{12}$	$C_{27}H_{52}Cl_2Cu_3N_6O_{13}$	$C_{24}H_{46}Cl_2Cu_3N_6O_{13}$
Formula mass	972.37	872.22	930.30	888.22
Space group	*Pbca*	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
Crystal system	orthorhombic	triclinic	triclinic	triclinic
a [Å]	17.450(19)	11.818(14)	12.342(15)	12.500(14)
b [Å]	14.586(19)	12.161(14)	12.352(15)	12.499(14)
c [Å]	34.30(4)	15.190(16)	15.136(18)	13.790(14)
α [°]	90	71.05(1)	79.55(1)	84.01(1)
β [°]	90	78.44(1)	81.97(1)	79.66(1)
γ [°]	90	62.72(1)	64.11(11)	63.64(1)
V [Å^3]	8730(18)	1832(4)	2037(4)	1898(4)
Z	8	2	2	2
$D_{calcd.}$ [g cm^{-3}]	1.480	1.581	1.517	1.554
μ [mm^{-1}]	1.63	1.9	1.746	1.869
R indices	$R_1 = 0.080$	$R_1 = 0.0697$	$R_1 = 0.0800$	$R_1 = 0.0840$
$[I > 2\sigma(I)]$	$wR_2 = 0.1257$	$wR_2 = 0.1465$	$wR_2 = 0.2251$	$wR_2 = 0.2579$

talline precipitate. Stirring was continued for 1 h for both complexes. The products were collected by filtration and were recrystallized from methanol. The filtrates were left to stand overnight in a refrigerator. Single crystals suitable for X-ray diffraction analysis were obtained as blue plates for complex **2** and as hexagonally shaped green single crystals for complex **3**.

Complex 1: Yield: 2.0 g (60%). $C_{30}H_{60}Cl_2Cu_3N_6O_{13}$ (972.37): calcd. C 36.94, H 6.16, Cu 19.55, N 8.62; found C 37.02, H 6.37, Cu 19.98, N 8.49. UV/Vis (methanol): λ_{max} (ε_{max}) = 593 (249 dm^3 mol^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3325, 3279, 3170 [ν(N–H)]; 1516 cm^{-1} [ν(C=N)]; 3520 [ν(O–H)] cm^{-1}.

Complex 2: Yield: 2.3 g (80%). $C_{24}H_{46}Cl_2Cu_3N_6O_{12}$ (872.22): calcd. C 33.02, H 5.27, Cu 21.84, N 9.63; found C 33.52, H 5.49, Cu 22.09, N 9.48. UV/Vis (methanol): λ_{max} (ε_{max}) = 615 (298 dm^3 mol^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3330, 3266, 3158 [ν(N–H)]; 1515 [ν(C=N)]; 3505 [ν(O–H)] cm^{-1}.

Complex 3: Yield: 2.0 g (65%). $C_{27}H_{52}Cl_2Cu_3N_6O_{13}$ (930.30): calcd. C 34.83, H 5.59, Cu 20.47, N 9.03; found C 35.03, H 5.92, Cu 20.01, N 9.37. UV/Vis (methanol): λ_{max} (ε_{max}) = 587 (282 dm^3 mol^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3390 3243 [ν(N–H)]; 1518 [ν(C=N)]; 3556 [ν(O–H)] cm^{-1}.

Complex 4: Yield: 1.3 g (45%). $C_{24}H_{46}Cl_2Cu_3N_6O_{13}$ (888.22): calcd. C 32.42, H 5.18, Cu 21.45, N 9.46; found C 32.83, H 5.03, Cu 20.97, N 9.98. UV/Vis (methanol): λ_{max} (ε_{max}) = 595 (249 dm^3 mol^{-1} cm^{-1}) nm. IR: $\tilde{\nu}$ = 3377, 3247 [ν(N–H)]; 1515 [ν(C=N)]; 3550 [ν(O–H)] cm^{-1}.

Crystallographic Studies: Suitable single crystals of all four complexes were positioned at 70 mm from the image plate. A total of 100 frames were measured at 2° intervals with a counting time of 2 min. 5786, 6505, 6526 and 6690 independent reflections for complexes **1–4**, respectively, were measured with Mo-K_α radiation using the MARresearch Image Plate System at 293 K. Data analyses were carried out with the XDS program.[28] The structures were solved by direct methods with the SHELX86 program.[29] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they are attached. Empirical absorption corrections were carried out using the DIFABS program.[30] The structures were refined on F^2 using SHELXL[31] for 3318, 5056, 3482, and 2303 reflections respectively, with $I > 2\sigma(I)$. The crystal structure illustrations were generated using ORTEP-3.[32] Selected crystallographic data are summarized in Table 5. CCDC-236467 (**1**), -236468 (**2**), -259938 (**3**), and -259939 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Discussion of H bonds of complexes **1–3**.

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