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A Very Rare Hydrogen-Bridged Hexanuclear Cu^{II} Complex Containing a Triangular Cu_3O Core Capped by an Unusual Triply Coordinated Perchlorate Anion

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An unusual hexanuclear Cu^{II} complex, $[\{[Cu(NHDEPO)]_3(\mu_3\text{-}O)(O_3ClO)\}_2(\mu\text{-}H)]\cdot 7ClO_4\cdot 4H_2O$ (**1**) was prepared starting from $Cu(ClO_4)_2\cdot 6H_2O$ and the oxime-based Schiff base ligand NHDEPO (= 3-[3-(diethylamino)propylimino]butan-2-one oxime). Structural characterization of the complex reveals that it consists of two triangular Cu_3O units, the copper ions being at the corners of an equilateral triangle, separated by an O···O distance of 2.447(5) Å, held together solely by a proton. In each triangle, the copper atoms are in square-pyramid environments. The equatorial plane consists of the bridging oxygen of the central OH^- (O^{2-}) group together with three atoms (N, N, O) of the Schiff base. An unusual triply coordinated perchlorate ion (μ_3-κO:κO′:κO′′) interacts in axial position with the three copper ions. Variable-temperature (2–300 K) magnetic susceptibility measurements show that complex **1** is antiferromagnetically coupled ($J = -148\ cm^{-1}$). The EPR data at low temperature clearly indicates the presence of spin frustration phenomenon in the complex.

Introduction

Polynuclear transition metal complexes continue to attract considerable attention because they act as useful tools for understanding size-dependent physical properties such as magnetic, optics, and electronics.[1] Much effort has centered on the synthesis and modification of such complexes with detailed examination of their structures and properties with a view to devising new synthetic routes to novel magnetic molecular materials. The study of polynuclear coordination complexes in particular has produced species with novel structures and interesting magnetic properties depending upon the choice of metal, ligand and also the auxiliary ligands and allowed the discussion of some of the structure–function correlations.[2] Perhaps the best understood examples are the bis-μ-hydroxo copper(II) complexes.[3] These complexes were some of the first to offer a clear correlation between structure and function with ferromagnetic or antiferromagnetic behaviour being dependent on structural factors. Among the different types of hydroxo-bridged Cu^{II} complexes, triangular copper(II) complexes are an important class where μ-hydroxo or μ-oxo ions have generally been observed as central bridging ligands and oxime, *N*,*N*-pyrazole-, *N*,*N*-triazole or Schiff-base-type ligands act as peripheral bridge.[4] The three unpaired electrons in the triangular Cu^{II} core interact magnetically via super exchange involving Cu^{2+}–O–Cu^{2+} pathways. The core could exist in either a spin-frustrated ($S_{total} = 1/2$, doubly degenerate) state or in a $S_{total} = 3/2$, quartet state. Spin frustration is one of the most interesting characteristic of this type of the μ_3-oxo-bridged triangular (equilateral) complexes. This phenomenon occurs when all the interactions between spin pairs cannot simultaneously have their optimal value and is generally observed in cases of odd-membered rings having antiferromagnetic coupled spins, especially in highly symmetrical triangular units. In order to interpret the magnetic properties of these frustrated systems it is necessary to go beyond the framework of the isotropic exchange model and to introduce *antisymmetric exchange interactions*.[5] However, from magnetic data it is very difficult to calculate the antisymmetric exchange term due to the simultaneous presence of intermolecular coupling at low temperatures. Generally it seems more appropriate to utilize EPR measurements for the study the presence of the spin frustration.[5]

Literature study shows that the triangular Cu_3O species may undergo "dimerization" through the formation of a bis(hydroxo) or bis(oxo) or oxo-hydroxo bridge resulting in hexanuclear Cu^{II} complexes. Among these, the oxo-hydroxo bridge is very rare.[6] We report here the crystal structure and magnetic study of a new oxo-hydroxo-bridged self-assembled hexanuclear Cu^{II} complex based on $Cu(ClO_4)_2$ and

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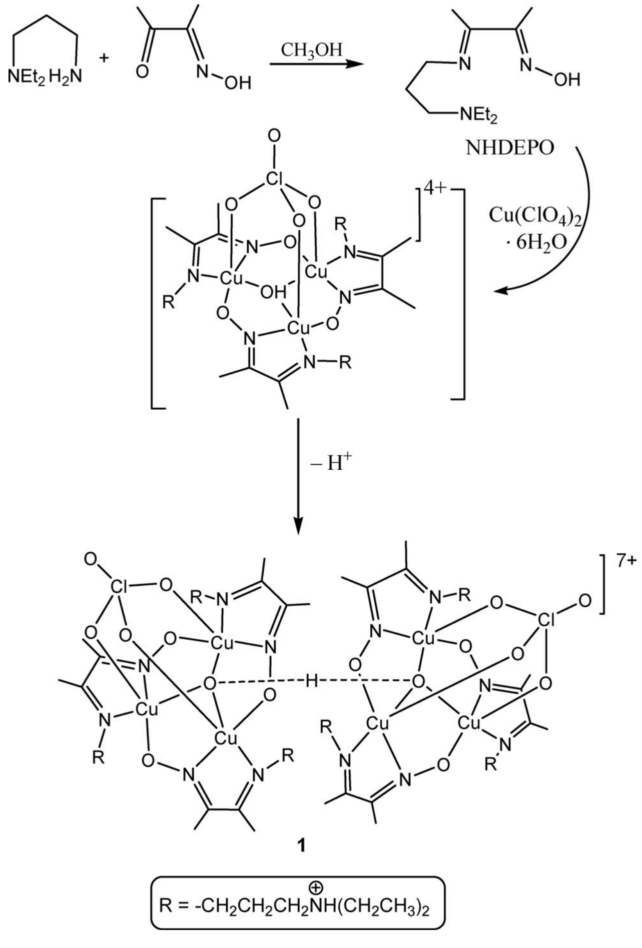
an oxime ligand (HL). The complex is the first report of a structure in which two Cu_3O triangles are connected solely by a single hydrogen bridge. Another interesting feature of the present complex is that the axial position of the Cu^{II} ions of each triangle is occupied by a very rare triply coordinating bridging mode (μ_3-perchlorato-O,O',O'') of the perchlorate anion.[5,7]

Results and Discussion

Synthesis of Complex 1

The mono-condensed ligand, 3-[3-(diethylamino)propylimino]butan-2-one oxime (NHDEPO) has been prepared by reacting diacetylmonoxime and 3-(diethylamino)propylamine in 1:1 molar ratio in methanol. NHDEPO reacts smoothly with $[Cu(ClO_4)_2]\cdot 6H_2O$ furnishing the hexanuclear Cu^{II} complex from methanol solution. It is to be noted that between the two trinuclear units that linked together by a proton to form the hexanuclear species, only one is deprotonated (Scheme 1). Interestingly, we did not use any base to synthesize the complex. The tertiary amine group of the Schiff base ligand acts as a base to generate the hydroxy ion in situ and deprotonate the OH group of oxime function. It remains uncoordinated as pendant arm (Scheme 1). We tried to isolate the trinuclear complex by adding one equivalent base (triethylamine) to the methanol solution of hexanuclear complex but got back the same complex on evaporation of the resulting solution. The UV/Vis spectra of the compound remains unaltered on adding the base (triethylamine, one equivalent) corroborating the stability of the hexanuclear complex even at higher pH.



Scheme 1.

IR and UV/Vis Spectra

The band for azomethine (C=N) group present in the compound is distinct and occurs within 1639–1603 cm^{-1}. Here the lowering of the position of the band reiterates their coordination to the metal centre. A strong and broad band, centered at 3417 cm^{-1}, is due to the presence of water molecules. The appearance of a strong band with slight splitting appears in the region 1100 cm^{-1} indicating the presence of ClO_4^- anion. The slight splitting may be due to the coordination of the ion to three metal centres in accordance with the observation in the crystal structure of the compound.

The electronic spectrum of compound **1** is recorded in methanol solution. The electronic spectrum shows a single absorption band at 612 nm. The positions of these bands are typical d-d bands in the square-pyramidal Cu^{II} surrounding.[8]

Description of the Structure of $[\{[Cu(NHDEPO)]_3(\mu_3\text{-}O)(O_3ClO)\}_2(\mu\text{-}H)]\cdot 7ClO_4\cdot 4H_2O$ (1)

The crystal structure of **1** comprises of discrete hexanuclear units of the cationic compound of $[\{[Cu(NHDEPO)]_3(\mu_3\text{-}O)(O_3ClO)\}_2(\mu\text{-}H)]^{7+}$, as shown in Figure 1, together with seven perchlorate anions and four water molecules. The hexanuclear unit is constructed from two crystallographically independent trinuclear units, **1-A** and **1-B**. The units **1-A** and **1-B** are very similar having only small differences in bond angles and distances (Table 1). A labeled diagram of the trinuclear unit **1-A** of complex **1** is shown in Figure 2. These two trinuclear units are connected via a hydrogen atom H1 which bridges O(1A) and O(1B) to produce the hexanuclear unit as shown in Figure 1. The O(1A)···O(1B) distance is 2.447(5) Å, which confirms that a hydrogen atom must be located between the two atoms. An analysis has been carried out from low temperature neutron diffraction studies of organic molecules[9] containing hydrogen bonds and the shortest O···O distance has been found to be 2.39 Å between oxygen atoms. The position of H(1) was not located in a difference Fourier map but this previous analysis[9] of neutron diffraction structures, where the position of the hydrogen atom was accurately determined, shows that for O···O distances up to 2.50 Å, it is most likely that the hydrogen is positioned equidistant between the two oxygen atoms and our refinement was carried out assuming this to be the case. A recent example of a symmetrical hydrogen bond with O···O distances of 2.406(3), 2.418(3) Å has been published[10] Additional evidence for the existence

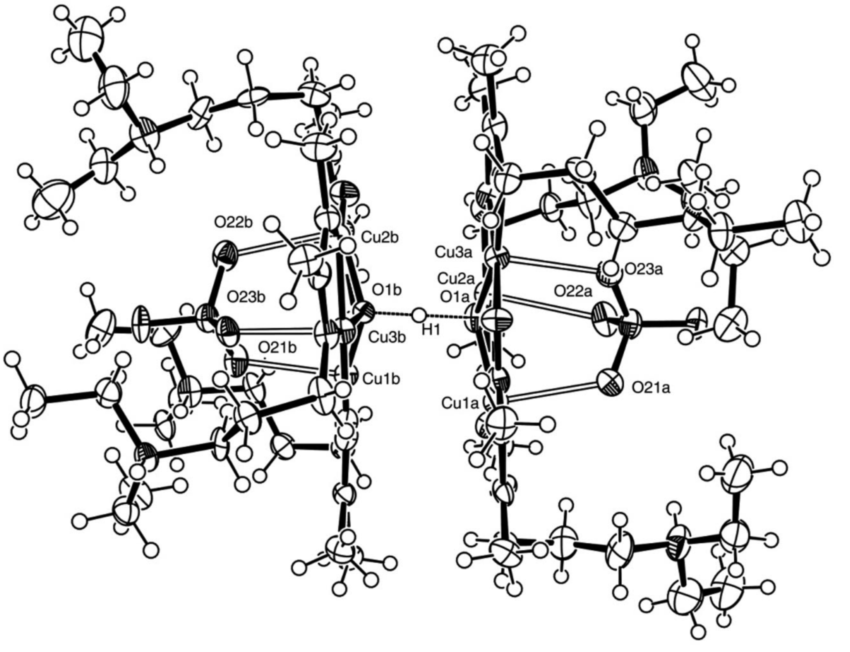


Figure 1. The structure of the $[\{[Cu(NHDEPO)]_3(\mu_3\text{-}O)(O_3ClO)\}_2(\mu\text{-}H)]^{7+}$ cation in **1** with ellipsoids at 50% probability. The weak Cu–O(perchlorate) bonds are shown as open lines.

Table 1. Dimensions in the metal coordination spheres (distances [Å], angles [°]).

	X = A			X = B		
	n = 1, *m* = 3 *p* = 1	*n* = 2, *m* = 5 *p* = 3	*n* = 3, *m* = 1 *p* = 5	*n* = 1, *m* = 3 *p* = 1	*n* = 2, *m* = 5 *p* = 3	*n* = 3, *m* = 1 *p* = 5
Cu(*n*X)–O(1X)	1.890(4)	1.903(3)	1.891(3)	1.902(3)	1.912(3)	1.900(3)
Cu(*n*X)–N(*p*2X)	1.964(4)	1.956(5)	1.965(4)	1.981(4)	1.959(4)	1.965(4)
Cu(*n*X)–N(*p*5X)	1.980(4)	1.977(4)	1.975(4)	1.953(4)	1.984(4)	1.975(4)
Cu(*n*X)–O(*m*1X)	1.938(4)	1.922(4)	1.931(3)	1.931(3)	1.919(4)	1.933(3)
Cu(*n*X)–O(2*n*X)	2.496(4)	2.719(3)	2.546(4)	2.436(4)	2.585(4)	2.526(3)
O(1X)–Cu(*n*X)–N(*p*2X)	87.0(2)	89.6(2)	88.3(2)	88.5(2)	87.3(2)	88.5(2)
O(1X)–Cu(*n*X)–N(*p*5X)	165.2(2)	170.2(2)	165.4(2)	166.3(2)	167.7(2)	168.7(2)
O(1X)–Cu(*n*X)–O(*m*1X)	94.3(2)	93.4(2)	92.2(2)	92.0(2)	93.7(1)	93.4(1)
N(*p*2X)–Cu(*n*X)–N(*p*5X)	81.5(2)	81.2(2)	81.1(2)	81.7(2)	81.4(2)	81.1(2)
N(*p*2X)–Cu(*n*X)–O(*m*1X)	176.0(2)	176.9(2)	174.2(2)	173.1(2)	173.9(2)	178.2(2)
N(*p*5X)–Cu(*n*X)–O(*m*1X)	96.5(2)	95.7(2)	97.3(2)	96.7(2)	97.0(2)	97.1(2)

of this bridging proton is the fact that there are seven discrete perchlorates in the asymmetric unit and so to achieve charge balance the hexanuclear unit must be 7+.

In each of the $Cu_3(NHDEPO)_3(ClO_4)O$ units, the three copper atoms (Cu1, Cu2, Cu3) adopt a (4+1) square pyramidal (NNOO and O) geometry. The four coordinating atoms making up the basal plane are – imine nitrogen atom and oxime nitrogen atom of the ligand (NHDEPO), oximato oxygen atom of the ligand associated with another copper(II) ion of the triangular unit and the central hydroxo group OH^-, while the apical site is occupied by one oxygen atom of perchlorate anion. The dimensions in the copper coordination spheres are listed in Table 1. Equivalent dimensions are listed in rows and the similarity between equivalent dimensions is apparent. Thus Cu-μ_3(O) distances range from 1.890(4)–1.912(3) Å and Cu–O(oxime) from 1.919(4)–1.938(4) Å while Cu–N(oxime) distances from 1.956(5)–1.981(4) Å and Cu–N(imine) from 1.919(4)–1.938(4) Å. Thus the r.m.s. deviations of the four donor atoms from the equatorial square plane are respectively 0.051, 0.026, 0.041, 0.026, 0.005, 0.038 Å with the copper atoms deviating from these planes by distances of 0.112, 0.032, 0.138, 0.143, 0.096, 0.037 Å. The two perchlorate anions are only weakly attached to the copper atoms with distances ranging from 2.436(4) to 2.719(3) Å. Least squares planes calculations on the three coordination spheres in each $[Cu_3(NHDEPO)_3(ClO_4)O]$ moiety but omitting O(1) are coplanar with r.m.s deviations of 0.082 and 0.132 Å, respectively. The bridging oxygen atoms O(1A) and O(1B) are displaced by 0.40 and 0.46 Å from these planes to become closer together. These two planes are approximately parallel, intersecting at 2.1(1)°. The three Cu···Cu distances in the planar moieties arrange from 3.198 to 3.221 Å. The closest distance between copper atoms from different moieties is 3.532 Å. The protonated secondary amine groups of the ligands do not coordinate the metal

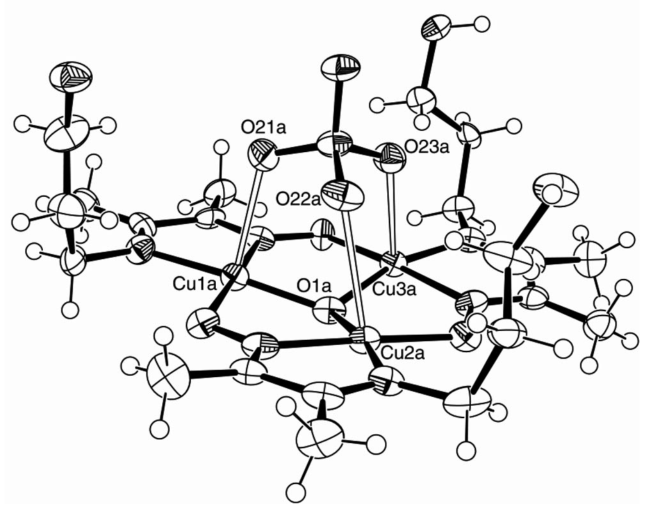


Figure 2. The $[Cu_3(NHDEPO)_3(ClO_4)O]$ moiety in **1** with ellipsoids at 30% probability. The weak Cu–O(perchlorate) bonds are shown as open lines.

center, instead they remain as pendant arms and are tilted away from the copper(II) triangle, on the side opposite to the central oxygen atom.

All six amino nitrogen N–H groups form hydrogen bonds as shown in Table 2 either to a perchlorate oxygen atom or to one of the solvent water molecules. These later also form hydrogen bonds to other water molecules or perchlorate oxygen atoms.

The structure of compound **1** is unique in the sense that until now no other hexa nuclear Cu^{II} complex is reported in which two trinuclear units are linked solely by a hydrogen bridge. In 2000, Curtis et al. reported a very similar complex[5] but in that complex, in addition to the O–H–O bridge, the two triangles are also linked by the weak coordination bonds formed by the oxygen (oxime) atoms of one triangle to the axial positions of the copper atoms of adjacent triangle with the bond length of 2.762 Å. The distances are long but should be considered as weak axial bonds for the Jahn–Teller distorted d^9 system (summation of van der Waals radii of copper and O is 2.92 Å). In complex **1**, the shortest distance between the copper atoms in one triangle to the oxygen atom of the other triangle is 3.036 Å, which is too long to be considered as a bond. Another interesting feature of the complex is that one of the perchlorates is acting as a μ_3-ligand, spanning Cu(1a), Cu(2a) and Cu(3a) of one triangle and another one spanning Cu(1b), Cu(1b) and Cu(3b) of the other triangle at relatively long Cu–O (ClO_4) distances (Table 2). Just as other multiply bridging perchlorate motifs, μ_3-κO,κO′,κO′′-bridging perchlorate anions (Scheme 1) are very rare, and in copper chemistry this has only been observed in a very few cases.[5,7]

Magnetic Properties

Variable-temperature dc magnetic susceptibility of complex **1** was measured in the temperature range 2–300 K in an applied field of 1 T. Figure 3 shows the $\chi_M T$ vs. T plot. The magnetic interaction within each triangle is mediated by Cu–O–N–Cu and Cu–O(H)–Cu bonding. The gradual decrease of $\chi_M T$ values, per Cu_3O unit, with decreasing T, clearly indicates the existence of an antiferromagnetic interaction. At room temperature $\chi_M T$ is very low ($0.603\ cm^3\,mol^{-1}\,K$) with respect to value expected for three independent Cu^{II} ions. The typical plateaus, at low temperatures, corresponding to the isolated trinuclear Cu^{II} complexes with antiferromagnetic coupling between the metal ions (spin doublet state, $\chi_M T = 0.375$, $g = 2.00$) do not appear due to the existence of spin frustration and the weaker interaction between the two Cu_3O units of the hexanuclear complex though the O–H–O bond. In order to investigate the magnetic behavior of complex **1**, an isotropic Heisenberg–Dirac–van Vleck (HDVV) Hamiltonian formalism was used in the approach [Equation (1)].

$$H = -J_{12}S_1S_2 - J_{23}S_2S_3 - J_{13}S_1S_3 \tag{1}$$

According to the structural data there are two crystallographically independent trimers, **1-A** and **1-B**, with different values of their geometrical parameters, taking into account this feature, a simple trimer model with only one coupling parameter J is taken to fit the magnetic susceptibility data. The expression of the magnetic susceptibility from the Hamiltonian in which Weiss-like parameter θ was considered to analyze the experimental variation of $\chi_M T$ at low temperatures is [Equation (2)].

Table 2. Hydrogen-bonding distances [Å] and angles [°] for the complex **1**.[a]

D–H	A [symmetry element]	d(D···A)	d(H···A)	∠D–H···A
N(21A)–H(21A)	OW(3) [$-x + 1, -y, -z + 1$]	2.764	1.87	169
N(41A)–H(41A)	O(54) [$-x + 1, -y, -z + 1$]	3.068	2.24	151
N(41A)–H(41A)	O(53) [$-x + 1, -y, -z + 1$]	3.098	2.29	147
N(61A)–H(61A)	OW(1) [$-x + 2, -y + 1, -z + 1$]	2.894	2.05	155
N(21B)–H(21B)	O(74) [$x, y, z + 1$]	3.019	2.17	156
N(41B)–H(41B)	O(11)	2.934	2.14	145
N(61B)–H(61B)	O(32) [$x + 1, y, z$]	2.880	1.98	169
O(42)	OW(1) [$x - 1, y, z$]	2.831		
O(73)	OW(4) [$1 - x, 1 - y, 1 - z$]	2.818		
OW(2)	OW(4)	2.715		
OW(3)	OW(2) [$1 - x, 1 - y, 1 - z$]	2.643		

[a] Hydrogen atoms of water molecules were not located.

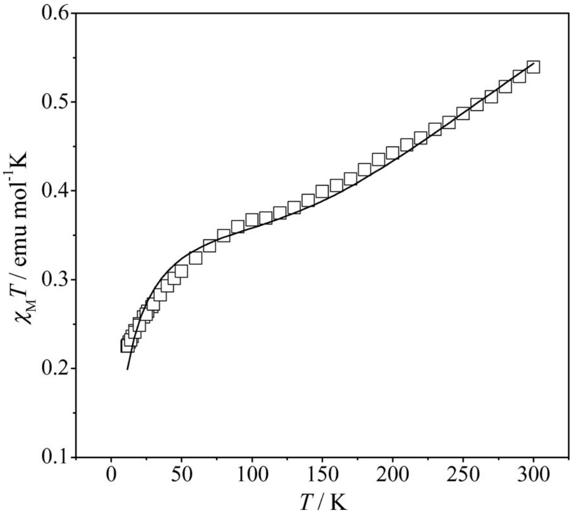


Figure 3. Plot of $\chi_M T$ [cm^{3}mol^{-1}K] vs. T [K] in the range 2–300 K for **1**. The black solid line represents the best-fitting results.

$$\chi_M = \frac{Ng^2\beta^2}{4k(T-\theta)}\,\frac{1+5\exp(3J/kT)}{\exp(3J/kT)+1} \qquad (2)$$

The experimental data for **1**, corrected for diamagnetic contributions and TIP (0.3×10^{-3} cm^{3}mol^{-1}) were analyzed by Equation (2) on $\chi_M T$. The results of the best fit, as shown in Figure 3 (solid line), are $J = -148$ cm^{-1}, $g = 2.05$, $\theta = -11$ K and $R = 1.3\times10^{-4}$ [$R = \Sigma_i|(\chi_M T_i)_{obs} - (\chi_M T_i)_{calcd}|^2/\Sigma_i(\chi_M T_i)_{obs}]^2$. At low temperatures the magnetic interaction through the bridging proton appears together with the intermolecular interactions and the antisymmetric exchange effects, so all this interactions are evaluated jointly in the θ parameter.

It is well known that in triangular complexes when the arrangement of the magnetic centers corresponds to equilateral triangles showing antiferromagnetic coupling, they give rise to spin frustration effects:[11,12] it is impossible for all possible pairings of spins to be simultaneously antiferromagnetic. The necessity to introduce an antisymmetric exchange (G) in the treatment of the magnetic data of highly symmetric spin clusters has long been known.[5] In complex **1** the presence of inter-trimeric magnetic exchange, mainly due to the O–H–O bridge between the trinuclear units giving hexanuclear units, that is observable at low temperatures as the antisimmetric exchange G, precludes any calculation of this term. From the literature data it seems more appropriate to study the possibility of the presence of spin frustration by means of EPR spectra, at very low temperatures, when only the degenerate $S = 1/2$ states are populated. One of the signatures of spin frustration is the appearance of g values lower than 2.00.[13–16]

The X-band EPR spectra of the hexanuclear complex **1** were recorded on power sample varying the temperature between 298 at 4 K (Figure 4), being anisotropic below 35 K. At 4 K signals are observed with $g_{\parallel} \approx 2.06$ and $g_{\perp} \approx 1.91$. The low g value of 1.91 shows the presence of the antisymmetric exchange in the trinuclear unit, assuming that the magnetic interaction between the two trinuclear units is almost negligible.

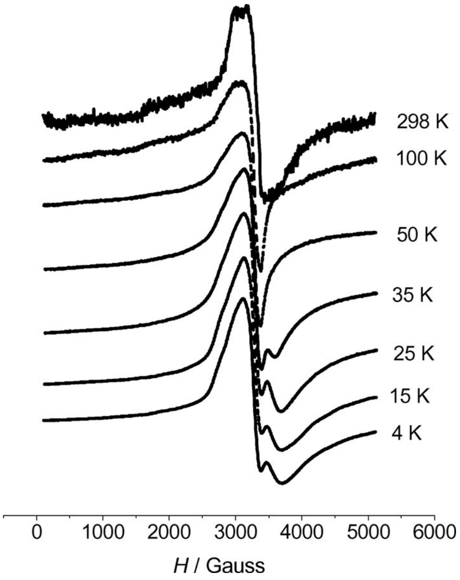


Figure 4. EPR powder spectra at several temperatures for complex **1**.

Discussion

Literature works have established relationships between the magnetic coupling and structural features for trinuclear Cu^{II} complexes with [Cu$_3$O(H)] core. The principal structural factors that influence the magnetic exchange are:

i) The Cu–O–Cu bridging angles that have an average value of 115° for the two independents trimers. This value would indicate noticeable antiferromagnetic coupling

ii) The O(H)···Cu$_3$ plane distance, with values of 0.389 Å for **1-A** and 0.435 Å for **1-B**, diminishing, thus, the antiferromagnetic coupling.

iii) The planarity of peripheral bridges planes defined by [O(H), N, N, O], with an average value of 13.58° for **1-A** and 17.45° for **1-B**. More coplanarity provide strongest antiferromagnetic coupling.

iv) The electronic factors of the peripheral ligands.

The quite strong antiferromagnetic interaction ($J = -148$ cm^{-1}) of complex **1** is in good agreement with literature data.[17–20]

Conclusions

We have shown here that a novel hydrogen-bridged hexanuclear species is formed by self-assembly when the Schiff base ligand (NHDEPO) is added to a methanolic solution of [Cu(ClO$_4$)$_2$]·6H$_2$O. The magnetic measurements show that the Cu^{II} ions are strong antiferromagnetically coupled within the trinuclear units through the oximato- and central oxo-groups. The hydrogen bridge that connects the trinuclear entity also mediates moderate antiferromagnetic coupling. The EPR spectra which become anisotropic below 35 K, show $g_{\perp} \approx 1.91$ at 4 K, this feature is a clear signature of the presence of spin-frustration in the complex.

Experimental Section

Starting Materials: All the chemicals were of reagent grade and were used without further purification.

Physical Measurements

General: Elemental analyses (C, H and N) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR 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 Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL susceptometer in the temperature range of 2–300 K and the magnetic field was 10.000 G. EPR spectra were recorded on powder samples at X-Band frequency with a Bruker 300E automatic spectrometer, varying the temperature between 4 and 298 K.

$[\{[Cu(NHDEPO)]_3(\mu_3\text{-}O)(O_3ClO)\}_2(\mu\text{-}H)]\cdot 7ClO_4\cdot 4H_2O$ (1): A mixture of diacetylmonoxime (10 mmol, 1.011 g) and 3-(diethylamino)-propylamine (5 mmol, 0.8 mL) in methanol (25 mL) was refluxed for about 3 h. It was then cooled and a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (5 mmol, 1.85 g) in methanol (20 mL) was added with continuous stirring. A green compound precipitated out immediately. It was filtered and washed with diethyl ether and then redissolved in CH_3OH. Green parallelepiped-shaped crystals of complex **1** suitable for X-ray diffraction were obtained by slow-evaporation of the solvent. Yield 70 %. $C_{66}H_{147}Cl_9Cu_6N_{18}O_{48}$ (2660.310): calcd. C 29.80, N 9.48, H 5.53, Cu 14.33; found C 29.88, N 9.34, H 5.48, Cu 14.52. $\lambda_{Max/nm}$ (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 608 (201). IR: $\tilde{\nu}$ = ν(C=N), 1635 , ν(OH), 3417 , ν(ClO_4^-), 1082 cm^{-1}.

Crystallographic Studies: Crystal data are given in Table 3. 28541 independent data were collected with Mo-K_α radiation at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analysis was carried out with the CrysAlis program.[21] The structure was solved by direct methods with the Shelxs97 program.[22] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atom bridging O(1A) and O(1B) was not located in a difference Fourier map but was positioned in between and refined with distance constraints as equidistant from both. The hydrogen atoms bonded to the water molecules were not located and not. included. An absorption correction was carried out using the ABSPACK program.[23] The structure was refined on F^2 using Shelxl97[22] to R_1 0.0645, wR_2 0.1308 for 12061 reflections with $I > 2\sigma(I)$.

Table 3. Crystal data and structure refinement of complex **1**.

Empirical formula	$C_{66}H_{146}Cl_9Cu_6N_{18}O_{48}$
Formula weight	2660.30
Space group	$P\bar{1}$
Crystal system	triclinic
a [Å]	13.8027(4)
b [Å]	19.0714(6)
c [Å]	22.8523(9)
α [°]	69.778(3)
β [°]	77.979(3)
v [°]	71.981(3)
V [Å^3]	5333.2(3)
Z, calculated density [g/cm^3]	2, 1.657
μ [mm^{-1}] (Mo-K_α)	1.498
F(000)	2758
Crystal size	0.05 × 0.05 × 0.30
Refinement method	SHELXL-97 on F^2
θ range for data collection [°]	2.2–30.0
R(int.)	0.043
Number of unique data	28541
Number of data with $I > 2\sigma(I)$	12061
R_1, wR_2 with $I > 2\sigma(I)$	0.0645, 0.1563
Goodness-of-fit on F^2	0.889

CCDC-746239 (for **1**) contains 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.

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[1] a) *Clusters and Colloids. From Theory to Applications* (Ed.: G. Schmid), VCH Verlagsgesellschaft, Weinheim (Germany), **1994**; b) *Physics and Chemistry of Metal Cluster Compounds* (Ed.: L. J. de Jongh), Kluwer, Dordrecht, The Netherlands, **1994**.

[2] a) *Magnetism: Molecules to Materials* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**; b) *Magneto-Structural Correlations in Exchange Coupled Systems* (Eds.: R. D. Willett, D. Gatteschi, O. Kahn), NATO ASI Series, Ser. C, Reidel, Dordrecht, **1985**, *140*; c) *Research Frontiers in Magnetochemistry* (Ed.: C. J. O'Connor), World Scientific, Singapore, **1993**.

[3] R. P. Doyle, M. Julve, F. Lloret, M. Nieuwenhuyzend, P. E. Kruger, *Dalton Trans.* **2006**, 2081–2088 and references cited therein.

[4] a) R. Beckett, B. F. Hoskins, *J. Chem. Soc., Dalton Trans.* **1972**, 291–295; b) S. Baral, A. Chakravorty, *Inorg. Chim. Acta* **1980**, *39*, 1–8; c) F. Akagi, Y. Michihiro, Y. Nakao, N. Matsumoto, T. Sato, W. Mori, *Inorg. Chim. Acta* **2004**, *357*, 684–688; d) F. B. Hulsbergen, R. W. M. ten Hoedt, J. Verschoor, J. Reedijk, A. L. Spek, *J. Chem. Soc., Dalton Trans.* **1983**, 539–545; e) K. Sakai, Y. Yamada, T. Tsubomura, M. Yabuki, M. Yamaguchi, *Inorg. Chem.* **1996**, *35*, 542–544; f) J. P. Costes, F. Dahan, J. P. Laurent, *Inorg. Chem.* **1986**, *25*, 413–416; g) M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz, D. M. Ho, E. Deutsch, *Inorg. Chim. Acta* **1988**, *150*, 65–73; h) H. D. Bian, J. Y. Xu, W. Gu, S. P. Yan, P. Cheng, D. Z. Liao, Z. H. Jiang, *Polyhedron* **2003**, *22*, 2927–2932; i) M. S. Ray, S. Chattopadhyay, M. G. B. Drew, A. Figuerola, J. Ribas, C. Diaz, A. Ghosh, *Eur. J. Inorg. Chem.* **2005**, 4562–4571; j) P. Mukherjee, M. G. B. Drew, M. Estrader, C. Diaz, A. Ghosh, *Inorg. Chim. Acta* **2008**, *361*, 161–172 and references cited therein.

[5] S. Ferrer, F. Lloret, I. Bertomeu, G. Alzuet, J. Borrás, S. García-Granada, M. Liu-González, J. G. Haasnoot, *Inorg. Chem.* **2002**, *41*, 5821–5830, and references cited therein.

[6] N. F. Curtis, O. P. Gladkikh, S. L. Heath, K. R. Morgan, *Aust. J. Chem.* **2000**, *53*, 577–582.

[7] a) Y. Agnus, R. Louis, B. Metz, C. Boudon, J. P. Gisselbrecht, M. Gross, *Inorg. Chem.* **1991**, *30*, 3155–3161; b) J. Ackermann, F. Meyer, H. Pritzkow, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2627–2631.

[8] a) P. A. Gale, *Coord. Chem. Rev.* **2003**, *240*, 191–221; b) L. Raehm, L. Mimassi, C. Guyard-Duhayon, H. Amouri, M. N. Rager, *Inorg. Chem.* **2003**, *42*, 5654–5659; c) M. Du, X.-H. Bu, Z. Huang, S.-T. Chen, Y.-M. Guo, C. Diaz, J. Ribas, *Inorg. Chem.* **2003**, *42*, 552–559; d) A. Bashall, A. D. Bond, E. L. Doyle, F. Garcia, S. Kidd, G. T. Lawson, M. C. Parry, M. McPartlin, A. D. Woods, D. S. Wright, *Chem. Eur. J.* **2002**, *8*, 3377–3385.

[9] Th. Steiner, W. Saenger, *Acta Crystallogr., Sect. B* **1994**, *50*, 348–357.

[10] B. H. Courtney, B. W. O. Juma, S. F. Watkins, F. R. Fronczek, G. G. Stanley, *Acta Crystallogr., Sect. C* **2006**, *62*, 268–270.

[11] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, **1993**.

[12] J. K. McCusker, E. A. Schmitt, D. N. Hendrickson, in: D. Gatteschi, O. Khan, J. S. Miller, F. Palacio (Eds.), *Magnetic Molecular Materials*, Kluwer, Dordrecht, **1991**, *297*.

[13] X. Liu, M. P. de Miranda, E. J. L. McInnes, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* **2004**, 59–64.

[14] B. Sarkar, M. S. Ray, M. G. B. Drew, A. Figuerola, C. Diaz, A. Ghosh, *Polyhedron* **2006**, *25*, 3084–3094.

[15] J. Padilla, D. Gatteschi, P. Chaudhuri, *Inorg. Chim. Acta* **1997**, *260*, 217–220.

[16] B. S. Tsukerblat, M. I. Brlinski, V. E. Fainzil'berg, *Sci. Rev. B: Chem.* **1987**, *9*, 288–336.

[17] R. J. Butcher, C. J. O. Connor, E. Sinn, *Inorg. Chem.* **1981**, *20*, 537–545.

[18] M. Angoroni, G. A. Ardizzoia, T. Berenghelli, G. La Monica, D. Gatteschi, N. Masciocchi, M. Moret, *J. Chem. Soc., Dalton Trans.* **1990**, 3305–3309.

[19] B. S. Tsukerblat, M. I. Belinskii, V. E. Fainzil'berg, *Sov. Sci. Rev. B (Engl. Trans.)* **1987**, *9*, 337–481.

[20] S. Ferrer, J. G. Haasnoot, J. Reedijk, E. Müller, M. B. Cingi, M. Lanfranchi, A. M. M. Lanfredi, J. Ribas, *Inorg. Chem.* **2000**, *39*, 1859–1867.

[21] *Crysalis* (v1), Oxford Diffraction Ltd., Oxford, UK, **2005**.

[22] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.

[23] *ABSPACK*, Oxford Diffraction Ltd., Oxford, UK, **2005**.

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